

X-ray diffraction studies of the electrochemical intercalation of bis(trifluoromethanesulfonyl) imide anions into graphite

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Recently, electrochemical energy storage devices using graphitic carbons as positive electrode have been proposed as "dual-ion cells" in literature [1, 2].

In this type of electrochemical cell, the lithium ions from the electrolyte are inserted/deposited into/on the negative electrode (e. g. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /metallic lithium) and the corresponding electrolyte anions are intercalated into the positive graphite electrode during the charging process. During discharging, both anions and lithium ions are released back into the electrolyte. Therefore, the electrolyte in this type of cell does not only act as charge carrier, but also as active material [1, 2].

The study's main focus is on the intercalation of bis(trifluoromethanesulfonyl) imide anions (TFSI⁻) into a graphite cathode from an ionic liquid-based electrolyte, namely N-butyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl) imide ($\text{Pyr}_{14}\text{TFSI}$) [1, 2]. This type of ionic liquid exhibits several beneficial properties compared to the state-of-the-art organic solvent based electrolytes, such as a broad electrochemical stability window with a high stability vs. oxidation, low safety hazards (a very low volatility at ambient pressure and nonflammability), a broad liquid range, high thermal stability and an overall good compatibility with existing lithium ion battery electrodes [3, 4]. Overall, the dual-ion system displays an excellent cycling stability and a capacity retention of more than 99% after 500 charge/discharge cycles, outperforming reported organic solvent-based dual-graphite/dual-ion cells. Furthermore, it was pointed out that depending on the upper charging end potential and cycling temperature, coulombic efficiencies of more than 99% and specific discharge capacities exceeding 100 mAh g^{-1} (based on the graphite cathode active weight) can be obtained [1, 2].

During intercalation, the TFSI⁻ anion has to overcome the cohesive van-der-Waals energy between two adjacent graphene layers. Thus, the anion intercalation is associated with an increase in the gallery height of graphite [5].

The focus of this work is on the study of the reversible TFSI⁻ anion uptake and release into a graphite cathode by using an *in-situ* X-ray diffraction technique [5]. Here, it will be shown that the TFSI⁻ intercalated graphite exists in a series of staged phases (see *Figure 1*). From the experimental data, the periodic repeat distance of the graphite intercalation compound, the TFSI⁻ gallery height/volume expansion and the maximum stoichiometries of $\text{C}_n^+\text{TFSI}^-$ are calculated and discussed.

We will show that a gallery height of ca. 8 Å can be determined, which is associated with a volume increase of up to about 140% for the TFSI⁻ anion uptake. In addition, it will be demonstrated that the electrochemical TFSI⁻ anion uptake and therefore the maximum stage number as well as the $\text{C}_n^+\text{TFSI}^-$ stoichiometry depends on the electrochemical cycling

conditions, such as the cycling temperature or the upper charging end potential. Here, we will show that a maximum stoichiometry of ca. $\text{C}_{19}^+\text{TFSI}^-$ can be expected.

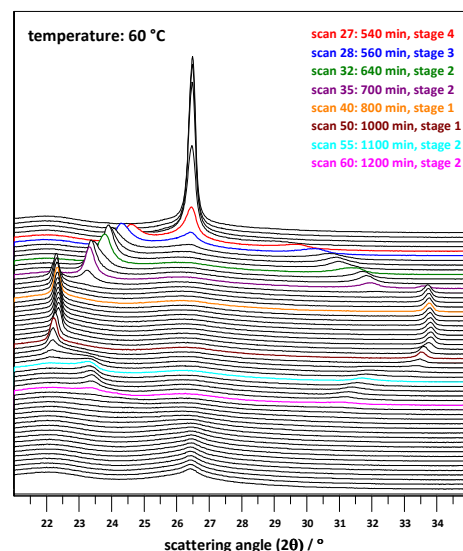


Figure 1. *In-situ* X-ray diffraction patterns of TFSI⁻ anion intercalation/de-intercalation into/from KS6L graphite (TIMCAL) for the metallic lithium/graphite dual-ion cell. The measurement was performed in a half cell setup (coin cell) with lithium metal as counter electrode. Electrolyte: $\text{Pyr}_{14}\text{TFSI}$, 1M LiTFSI . Measurement temperature: 60 °C.

References

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