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

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HIGHLIGHTS

- Electrochemical intercalation of bis(trifluoromethanesulfonyl)imide (TFSI) anions into graphite for dual-ion cells.
- *Ex situ* and *in situ* X-ray diffraction of TFSI intercalation into graphite.
- Calculation of the periodic repeat distance, the intercalant guest gallery height and the gallery expansion for various stages.
- Conclusion of the maximum stoichiometry of the TFSI intercalated graphite at different cell conditions.

ARTICLE INFO

ABSTRACT

"Dual-graphite" cells use graphite as intercalation host at both electrodes, where the energy storage mechanism is based on the intercalation of lithium ions into the negative and the intercalation of electrolyte anions into the positive electrode. In this contribution, the electrochemical intercalation of bis(trifluoromethanesulfonyl)imide (TFSI) anions from an ionic liquid-based electrolyte (Pyr$_{14}$TFSI) into graphite was studied using *ex situ* and *in situ* X-ray diffraction. We prove that the TFSI intercalated graphite exists in a series of staged phases. As for this electrode material the discharge capacity can be strongly influenced by the cut-off potential and temperature, the stage transitions and compositions of the TFSI intercalated graphite were determined in dependency of different temperatures and cut-off potentials. From the experimental data, the periodic repeat distance of the graphite intercalation compound, the TFSI gallery height and the maximum stoichiometries of C_n^+TFSI$^-$ at these different conditions are calculated and discussed.

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1. Introduction

Graphite is a redox-amphoteric intercalation host and therefore able to yield so-called donor-type and acceptor-type graphite intercalation compounds (GICs) via electrochemical intercalation of cations and anions at different potentials [1,2]. The current predominantly used donor-type GIC redox couple LiC$_x$/C$_x$ is the major active compound for state-of-the-art negative electrodes in lithium ion batteries [3–6]. The anions capable to form acceptor-type GICs are mainly fluoro-, chloro-, or oxometalates such as PF$_6^-$, AsF$_6^-$, BF$_4^-$ [7–9], AlCl$_4^-$, SO$_4^-$ or NO$_3^-$ [10–12]. In addition, also larger carbon-based anions such as trifluoroacetate (CF$_3$COO$^-$) [13] and

bis(trifluoromethanesulfonyl)imide ((CF$_3$SO$_2$)$_2$N$^-$) [14,15] have been demonstrated to form acceptor-type GICs.

The hexagonal structure of graphitic carbon with ABAB stacking consists of graphene sheets, which means that the intercalated guests can be accommodated in the gaps between the layers. It is well known, that the process of guest species uptake does not occur in every layer simultaneously. During intercalation the intercalant must overcome the cohesive van-der-Waals energy between two adjacent graphene layers; the electrostatic repulsion between different intercalant layers as well as an intralayer attraction between intercalant atoms induces further intercalation within the same layer contrary to further intercalation into another unoccupied layer [16–19]. These effects are proposed to be responsible for the so-called "staging" mechanism.

The different stages of intercalation into graphite are labeled with respect to the number of carbon layers between each

intercalated molecule layer (Fig. 1). Therefore, the maximum stage of intercalation is stage 1, i.e. with only one carbon layer in between two intercalant guest layers. The GICs generally display well-defined stages (n) that can be related to the periodic repeat distance (I_c), the intercalant gallery height (d_i) and the gallery expansion (Δd) by using

$$I_C = d_i + 3.35 \text{ Å} \cdot (n - 1) = \Delta d + 3.35 \text{ Å} \cdot n = l \cdot d_{obs} \qquad [1]$$

where l is the index of (00l) planes oriented in the stacking direction and d_{obs} is the observed value of the spacing between two adjacent planes [20,21]. Therefore, a well suited technique to observe and determine the staging mechanism of intercalation processes into graphitic carbon is X-ray diffraction.

Recently, we reported that "dual-ion cells" [22,23] based on the intercalation of bis(trifluoromethanesulfonyl)imide (TFSI) anions into a graphite positive electrode from a well suited ionic liquid-based electrolyte with a high stability vs. oxidation, namely *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr$_{14}$TFSI) [24–30], delivered very promising electrochemical results. These dual-ion cells are superior to existing dual-ion cell systems [31–34] concerning their electrochemical performance in terms of discharge capacity (exceeding 100 mAh g^{-1} based on the graphite cathode weight), cycling stability and coulombic efficiency (99% after 500 cycles) depending on the applied cut-off potential and temperature [22,23].

In this contribution, we investigate the staging mechanism of the bis(trifluoromethanesulfonyl)imide (TFSI) anion intercalation into a graphite positive electrode using *ex situ* and *in situ* X-ray diffraction techniques in combination with cyclic voltammetry and constant current charge/discharge cycling. The dual-ion system investigated in this work is based on a graphite cathode, a metallic lithium anode and an ionic liquid electrolyte containing lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as electroactive salt in *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)

imide (Pyr$_{14}$TFSI), which offers the exceptional stability needed at higher electrode potentials [28].

As the discharge capacity for the dual-ion system can be tailored by either the cut-off potential or the temperature [23] a systematic investigation of the staging transitions and compositions of the staged phases is performed at different cut-off potentials and temperatures, namely at 20 °C and 60 °C. From our results we are able to deduce the periodic repeat distance (I_c) and TFSI gallery heights (d_i) for different stage-*n*-GICs. Moreover, TFSI intercalated structures and stoichiometries, C_n^+TFSI$^-$, providing different stages, are proposed by correlating the X-ray diffraction results and the TFSI dimensions to the obtained discharge capacity and the theoretical specific discharge capacities.

2. Experimental

Electrode films of the positive electrodes consisted of a composition of 90 wt. % of synthetic graphite TIMREX® KS6 (TIMCAL®, d_{50} = 3.2 μm/d_{90} = 6 μm), 5 wt. % of sodium carboxy-methylcellulose (CMC) as binder (Walocel CRT 2000 PPA 12, Dow Wolff Cellulosics®) and 5 wt. % of conductive carbon black agent C-nergy Super C65 (TIMCAL®). At first, the binder polymer was allowed to dissolve in de-ionized water to form a 2.5 wt. % solution. Adding the required amount of conductive agent Super C65 to the binder/water mixture was followed by magnetic stirring to obtain a homogenized slurry. Shortly after the addition of KS6 graphite, the slurry was dispersed using a T 25 Ultra Turrax® (1 h, 5000 rpm) to receive a well homogenized, non agglomerated paste. The paste was cast on a freshly etched aluminum foil (30 μm, purity >99.9%, etched with 5 wt. % KOH) applying a standard lab-scale doctor-blade equipment. The gap of the doctor blade was set to 120 μm wet film thickness, leading to an average graphite cathode mass loading of 2.5 mg cm^{-2}. After casting, the tapes were transferred into an atmospheric oven and dried for 12 h at 80 °C. Electrodes with a diameter of 12 mm were cut out and a further drying step was
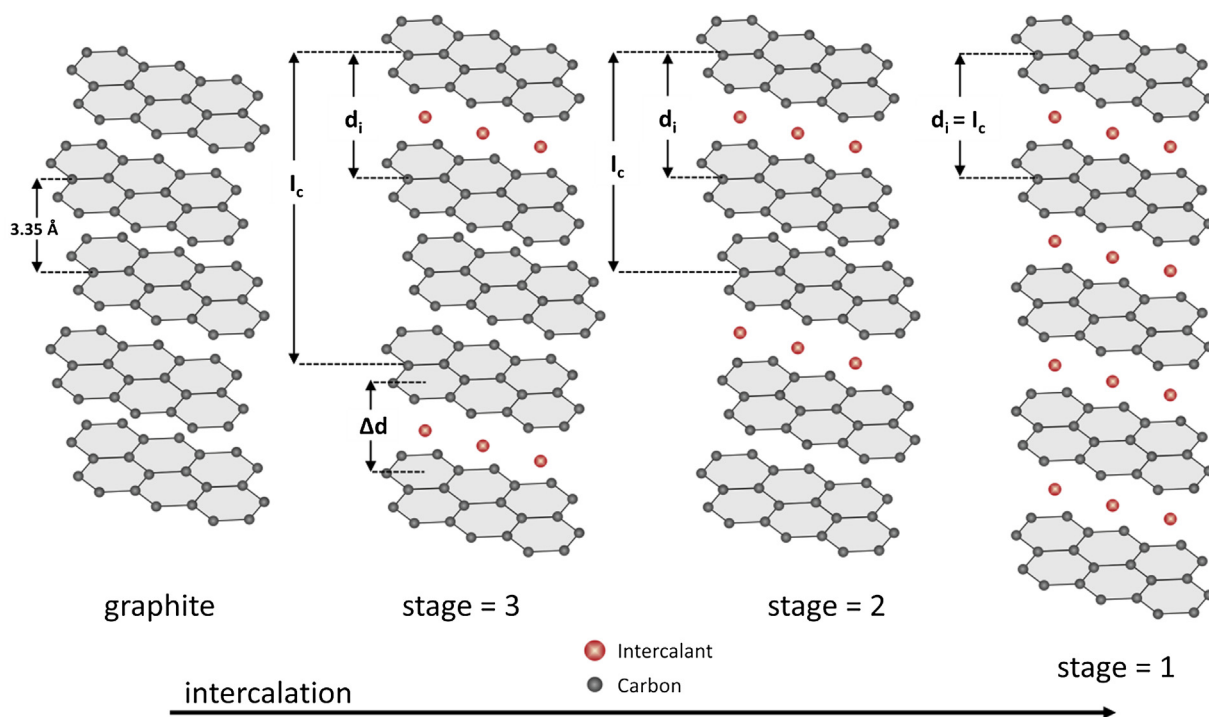

Fig. 1. Schematic illustration of the staging mechanism of intercalant guest species into graphite: I_c = periodic repeat distance; d_i = intercalant gallery height; Δd = gallery expansion. Stage 1 intercalated graphite depicted on the right side being the maximum possible intercalation stage.