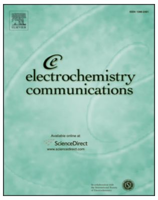
Electrochemistry Communications 71 (2016) 52–55

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom



New insights into the uptake/release of FTFSI$^-$ anions into graphite by means of *in situ* powder X-ray diffraction

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ARTICLE INFO

Article history:
Received 22 July 2016
Received in revised form 5 August 2016
Accepted 8 August 2016
Available online 10 August 2016

Keywords:
Anion intercalation
Dual-ion cell
In situ PXRD
Staging
Gallery height
FTFSI

ABSTRACT

The redox-amphoteric character of graphite enables its utilization as intercalation host for various types of cations and anions to form either donor-type or acceptor-type graphite intercalation compounds (GICs), respectively. While the donor-type GIC LiC_6 is commonly used in the field of lithium ion batteries, acceptor-type GICs were suggested for application in dual-ion cells. In this contribution, the electrochemical intercalation/de-intercalation of fluorosulfonyl-(trifluoromethanesulfonyl) imide (FTFSI$^-$) anions into graphite was studied for dual-ion cells during a cyclic voltammetry experiment using *in situ* powder X-ray diffraction. For the GICs, a series of most dominant stages could be assigned and the periodic repeat distance as well as the FTFSI$^-$ gallery height/gallery expansion were determined. The obtained dominant stage numbers of the formed GICs were correlated to cell voltage ranges. Upon charge, a transition of the different stages was observed, while upon discharge stage 1 was still preserved for a broad voltage range. These novel findings indicate different mechanisms for the uptake and release of the anions.

1. Introduction

Electrochemical energy storage systems using graphite as positive electrode have been proposed under the name dual-ion cells [1]. During charge (= increase of cathode potential), the cations from the electrolyte intercalate/insert/deposit into/on the negative electrode, while simultaneously the anions are intercalated into the positive electrode to form acceptor-type GICs. During discharge (= decrease of cathode potential), the reverse processes take place, hence, the ions are released back into the electrolyte [2]. Anion intercalation into carbon also needs to be regarded for high voltage lithium ion batteries, where the conductive carbon black additive may take up electrolyte salt anions like PF_6^-, which results in extra charge and discharge capacities [3].

A characteristic ordering property that is observed with regard to the structure of GICs is the so-called staging phenomenon, which is characterized by a periodic array of intercalate layers in a matrix of graphene layers commonly denoted as stage number n [4]. Consequently, a maximum stage of 1 can be obtained, where one graphene layer is located between two intercalant layers. To gain an insight into the structure of the GICs that are formed during the electrochemical intercalation of ions, powder X-ray diffraction (PXRD) is a powerful tool. The observed intensity pattern commonly follows the order I $(00n+1) >$ I $(00n+2) >$ I (all other reflections) [5,6]. Thus, the two most intense reflections that can be observed in the PXRD pattern of a stage n GIC can be assigned as $(00l)$ reflections with $l = n + 1$ or $n + 2$ [5,7]. By calculating the ratio of the $d_{(n+2)} / d_{(n+1)}$ reflections, the most dominant stage of the observed GIC can be designated [7]. Beside the stage number, also the periodic repeat distance I_c, the intercalant gallery height d_i and the gallery expansion Δd can be determined by following expression,

$$I_c = d_i + 3.35\,\text{Å} \cdot (n-1) = \Delta d + 3.35\,\text{Å} \cdot n = l \cdot d_{obs.}$$

where l is the index of $(00l)$ planes and d_{obs} is the observed value between two adjacent graphene planes [4,8–10].

In this contribution, the staging mechanism was studied in detail during the electrochemical intercalation and de-intercalation of fluorosulfonyl-(trifluoromethanesulfonyl) imide (FTFSI$^-$) anions into graphite by means of *in situ* PXRD in combination with a cyclic voltammetry (CV) experiment. Since the best electrochemical results with regard to a high Coulombic efficiency and high reversible capacity at 20 °C were obtained for dual-ion cells employing an electrolyte based on FTFSI$^-$ anions, we selected this electrolyte for this *in situ* PXRD study [11,12]. Based on our results, it was possible to deduce the most dominant stage number n, the periodic repeat distance I_c, the FTFSI$^-$ gallery height d_i and the FTFSI$^-$ gallery expansion Δd. Finally, the dominant stages of the GICs were correlated to certain voltage ranges in order to track the transitions of the GIC structure.

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http://dx.doi.org/10.1016/j.elecom.2016.08.003

2. Experimental

The graphite positive electrode was composed of a ratio of 90:5:5 wt.% of synthetic graphite KS6L (*Imerys*), sodium-carboxymethylcellulose as binder (*Walocel CRT 2000 PPA 12, Dow Wolff Cellulosics*) and conductive carbon black C-nergy Super C65 (*Imerys*). The details for electrode preparation have been described previously [12].

In situ PXRD measurements were performed in a modified two-electrode coin cell, where an X-ray transparent window was introduced in a commercial *CR2016* coin cell (*Hohsen Corp.*). The details for the cell assembly have been described previously [8]. A mixture of *N*-butyl-*N*-methylpyrrolidinium fluorosulfonyl-(trifluoromethanesulfonyl) imide ($Pyr_{14}FTFSI$, *Proviscο CS.*, purity 98%) with 1 M LiFTFSI (*Proviscο CS.*, purity 97%) was used as electrolyte. After cell assembly, the cell rested for 24 h to enhance the wetting of the electrode by the viscous electrolyte.

PXRD measurements were performed during a CV experiment with a *Bruker D8 Advance* X-ray diffractometer in Bragg-Brentano geometry, equipped with Ni filtered Cu Kα (1.54 Å) radiation. The measurements were conducted in a range between 20° and 35° 2θ using a Lynxeye detector in continuous mode, applying an accelerating voltage of 40 kV and a current of 40 mA. The total scan time was adjusted to 20 min to deliver a sufficient resolution while being as short as possible at the same time. The CV measurement was conducted using a multi-channel potentiostat/galvanostat (*VMP, Biologic Science Instruments*) with a low scan rate of 20 μV s^{-1} in order to avoid rapid structural changes. Prior to charging to 5.20 V, the cell rested under open circuit voltage (OCV) conditions for 20 min, followed by a constant voltage step at the upper voltage limit for 3 h. Subsequently, the cell was discharged to 3.40 V, followed by constant voltage step at the lower cut-off voltage for 1 h. In this context, the background was defined as combination of two measurements, where no reflections were present in a certain range. The PXRD pattern of neat graphite should only exhibit the (002) reflection at 26.55° 2θ in the measured region. Hence, this measurement was defined as background in the range between 20 – 24.5° and 31–35° 2θ. To complement the gap between these 2θ ranges, the scan 100 was used, where a maximum reflection-to-reflection distance was found without any reflections in the range between 24.5° to 31° 2θ. The fitting of the reflections was conducted using a Voigt function.

3. Results and discussion

The cell voltage and specific current *versus* time plots of the 1st cycle of the CV measurement are illustrated in Fig. 1a, while the corresponding PXRD patterns (with background correction) are shown in Fig. 1b.

For the sake of clarity the first 39 scans in Fig. 1b, which exhibit no apparent differences, are not depicted in the waterfall plot of the PXRD patterns since up to 800 min of experiment time no or only a negligible current flow is detected. Consequently, one can assume that also no or only a very low amount of $FTFSI^-$ anions is embedded into graphite. The color-coded data points of Fig. 1a can be directly correlated to the respective PXRD scans in Fig. 1b, which are highlighted in the same color as the circles. A summary of the different parameters of the colored scans and data points is given in Table 1, including notably the dominant stage n, the periodic repeat distance I_c, the gallery height d_i and gallery expansion Δd. However, these parameters exhibit slightly different values than in our previous publication [12], which is most likely attributed to the different electrochemical techniques (*in situ* data in the first cycle *vs. ex situ* data after 50 charge/discharge cycles) that were used for the charge/discharge of the cells. Some structural changes might also have been proceeded between cell disassembly and the PXRD measurements.

The first observable dominant stage is 5, which is found at a cell voltage of 4.54 V. Already at a lower cell voltage the formation of a GIC, represented by the appearance of two additional reflections as well as by the current flow, is visible. However, the $(00n+2)$ reflection is only indicated, thus, the determination of the scattering angle of this reflection is not possible. Therefore, the determination of the stage number of scan 59 cannot be conducted. Starting at 4.59 V (scan 62), the PXRD measurements point at the formation of a stage 4 GIC, which is maintained until scan 64. By further increasing the cell voltage, stage 3 was detected at 4.69 V (scan 66) and stage 2 (scan 71) at 4.81 V. A structure of mainly stage 2 and partially stage 1 was attained at 5.07 V (scan 82). After charging to 5.20 V and applying a constant voltage step at this value for around 114 min (scan 93), the ratio of stage 2 to stage 1 was reversed. Hence, mainly stage 1 and partially stage 2 were observed. A pure stage 1 structure was obtained by maintaining at 5.20 V for additional 40 min (scan 95). Although most of the subsequent diffraction patterns were measured during discharge, a stage 1 GIC was still preserved. The first stage change upon discharge took place at 4.70 V (scan 117), where a stage mix containing primarily stage 2 and to certain extent stage 1 was detected. During further discharge, a transition to a stage 2 GIC took place at 4.61 V (scan 121). This stage was

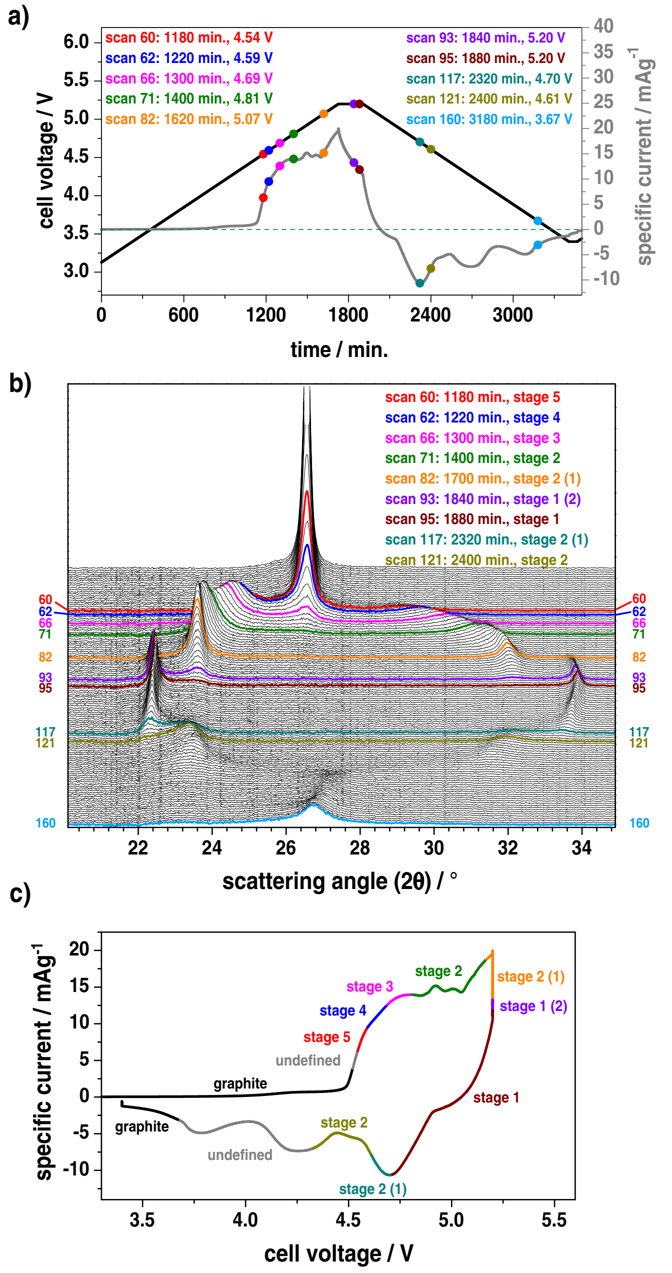

Fig. 1. a) Cell voltage and specific current *versus* time plots of the 1st cycle of the CV experiment, b) the corresponding *in situ* X-ray diffraction patterns of $FTFSI^-$ intercalated graphite and c) assignment of the most dominant stages to the voltage regions.