In-Situ Raman Study of the Intercalation of Bis(trifluoromethylsulfonyl) imid Ions into Graphite inside a Dual-Ion Cell

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Anion intercalation into graphite is a central process for energy storage in dual-ion battery cells. Electrochemical investigations show a strong kinetic hindrance of the intercalation process in the first charging cycle and less kinetic hindrance in subsequent cycles. In order to obtain information about the structure and properties of the graphite electrode during cycling and about the origin of the kinetic hindrance, we carried out an in-situ Raman spectroscopy study during the first and second charging/discharging cycle of a dual-ion cell. This cell consisted of a metallic lithium anode, a graphite cathode and a Pyr1,4TFSI/LiTFSI mixture as electrolyte. We show that the TFSI⁻ anion intercalation is not fully reversible, implying that TFSI⁻ anions remain inside the graphite matrix after completion of the first charging/discharging cycle. This is in contrast to the reversible intercalation/deintercalation of cations, like Li⁺ ions. Remarkably, the TFSI⁻ intercalation leads to enhanced Raman signals, also in stark contrast to Li⁺ intercalation. We discuss the in-situ Raman spectra in terms of staging phenomena, mechanical strain formation, electronic charge densities, and defects. Furthermore, we show that intercalation-induced defects are self-healing over time. Our results suggest that there is an anti-correlation between the kinetic barrier for TFSI⁻ intercalation in graphite and the number of defects.

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1. Introduction

Nowadays, one of the major challenges in energy storage research is the development of secondary batteries with higher energy densities, higher power densities, longer life times, and reduced production costs. The most wide spread secondary batteries for many modern applications are lithium-ion batteries (LIBs). However, there are various alternative types of batteries, which are subject to intensive research, such as lithium-air batteries [1–4], lithium–sulfur batteries [5–7], sodium-ion batteries [8–11] and dual-ion cells [12–23]. Dual-ion cells make use of the intercalation of anions into graphite cathode. Major advantages of this type of cell are: (i) The cells are free of heavy metals and thus environment-friendly. (ii) They often exhibit a very long cycle life [14,15,18,19].

Intercalation into graphite is a phenomenon that has been used for decades in energy storage systems. The most prominent example is the electrochemical intercalation of Li⁺ ions into graphite [24–30]. This process has been investigated by means of various characterization techniques, such as in-situ XRD [31,32], X-ray photoelectron spectroscopy [33], dilatometry [34–36], computational simulations [37–39], and in-situ Raman spectroscopy [40–42]. In comparison to this donor-type graphite intercalation compound (GIC), anion intercalation into graphite is much less widespread due to the absence of an important technological application of acceptor-type GICs. However, electrochemical intercalation of anions into graphite resulting in acceptor-type GICs has already been known since the 1930s [43]. It was also investigated with a view to potential applications in secondary batteries [21,22,44–46], but these systems were inferior to LIBs, in particular with regard to energy density [47]. However, recent work has demonstrated remarkable cycling stabilities of dual-ion cells with acceptor-type GICs [14,15,22]. In 2015, Lin et al. showed that secondary batteries based on anion intercalation can also show extraordinary high charging rates [19]. They developed an aluminum-ion battery which can be fully charged in less than one minute using intercalation of AlCl₄⁻ into graphite [19]. In combination with the low cost of the electrode materials and the avoidance of heavy metals, batteries based on anion intercalation are promising candidates for stationary energy storage applications.

In this paper, we focus on a cell that was introduced by Placke et al. in 2012 [14,15]. This cell consists of a lithium metal anode and
a graphite cathode combined with a solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in the room temperature ionic liquid (RTIL) 1-butyl-1-methylpyrrolidinium TFSI (Pyr$_1$,4TFSI) as electrolyte. During charging, lithium is plated on the metallic lithium electrode, while TFSI$^-$ anions are intercalated into graphite. This implies that the lithium salt LiTFSI is extracted from the electrolyte during charging and released back into the electrolyte during discharging. This leads to strong concentration changes and local concentration gradients during cycling [48]. During the first cycles, this system shows a significant irreversible capacity [14–16,49]. Placke et al. showed that these irreversible processes are not related to the formation of a solid electrolyte interphase (SEI) [16], which is commonly formed on graphite anodes in LiBs. In a recent paper, we demonstrated that the irreversible processes take place mainly at the graphite electrode [48]. However, further studies are needed to understand the exact origin of the irreversible processes.

In 2014, Placke et al. studied charging behavior during the electrochemical intercalation of TFSI$^-$ and other anions in dual-ion cells by means of in-situ powder x-ray diffraction (XRD) [23]. Staging of GICs is a well-known phenomenon first described by Rüdorff and Hofmann in 1938 [43]. The stage number indicates how many graphene layers are in between two intercalant layers (see Fig. 1). The XRD technique provides information about the staging mechanism and the amount of expansion of the graphite structure due to higher interlayer distances. Placke et al. investigated only a single charging/discharge cycle and did not analyze irreversible processes during this cycle. Huesker et al. investigated the same system by means of dilatometry [50]. They found that the expansion of the graphite matrix during charging is not completely reversible, but they did not give an explanation for this phenomenon.

Here we report on an in-situ Raman investigation of the intercalation of TFSI$^-$ into graphite. First studies on this field were carried out by Hardwick et al. [51]. However, they only investigated the first charging/discharging cycle with a focus on the unintentional intercalation of anions into conductive carbon inside high-voltage cathodes for lithium-ion batteries. Instead we focus on the intentional intercalation of TFSI$^-$ into graphite in dual-ion cells. We show that in the first charging/discharge cycle, the intercalation of TFSI$^-$ is not completely reversible, implying that a certain amount of TFSI$^-$ anions remain trapped in the graphite matrix during discharging. This is in contrast to Li$^+$ intercalation/deintercalation in graphite. We also find clear evidence for mechanical strain and changes in the electronic charge density induced by the anion intercalation. Finally, we show that during charging, lattice defects are formed, which do not disappear after discharging, but which can be healed by long rest times of the cell. There seems to be an anti-correlation between the number of these defects and the kinetic barrier height for anion intercalation.

2. Experimental

2.1 Synthesis

Graphitic foam was synthesized similar to the route described by Chen et al. [52]. Nickel foam (Ni-4753, Recemat BV) acted as a template for chemical vapor deposition (CVD) of carbon. Rectangular blanks of 40 mm × 20 mm and 1.6 mm thickness were laser-cut from a nickel foam sheet and placed in a horizontal quartz tube furnace of 35 mm inner diameter and 500 mm length. The templates were heated to 1000 °C at a rate of 30 °C min$^{-1}$ under forming gas (5% H$_2$/95% N$_2$) at a flow rate of 200 s.c.c.m. Carbon deposition on nickel was induced by adding 10 s.c.c.m CH$_4$ to the forming gas flow for a period of 7 minutes. Subsequently, the samples were cooled to room temperature at a rate of about 100 °C min$^{-1}$. As-prepared samples were drop-coated with a solution of 4 wt% poly(methyl methacrylate) (PMMA) in CHCl$_3$ and dried for 30 min at 180 °C in ambient air. PMMA-coated samples were immersed in HCl (3 mol/L) at 85 °C for 3 h in order to dissolve the nickel templates. Finally, the protective PMMA-coatings were removed by immersing the samples in acetone at 55 °C for 10 min.

2.2. Scanning Electron Microscopy

The nickel foam used as template for the graphitic foam and the graphitic foam itself were characterized by means of a JEOL-7500 F (JEFOL) scanning electron microscope (SEM). The SEM was operated at an accelerating voltage of 10.0 keV and at a working distance of 8.0 mm.

2.3. Electrochemical Measurements

For the electrochemical measurements, the synthesized graphitic foam was used as active cathode material. It was cut into 10 mm disks, dried at 80 °C for 24 h under a diffusion-pump vacuum. To contact the active material as working electrode, it was pressed onto an aluminum grid (EL-CELL GmbH). As an electrolyte, a solution of LiTFSI (Sigma-Aldrich, purity: 99.95%) in Pyr$_1$,4TFSI with a molar ratio LiTFSI:Pyr$_1$,4TFSI of 1:3.34 (1 mol/L) was used. The RTIL was synthesized and purified by Passerini et al. by means of a method described in [53,54] and was dried at a pressure of 10$^{-6}$ mbar at 80 °C. The water content of the RTIL was less than 15 ppm as measured by Karl-Fischer titration (Mettler-Toledo, C20 Coulometric Karl-Fischer-Titrator). As anode and as reference electrode, high-purity lithium foil (Chemetall) was used. The electrodes were separated by a glass fiber separator (EL-CELL GmbH).

All electrochemical measurements were performed in a three-electrode setup within an ECC-Opto-Std Cell (EL-CELL GmbH) by means of an IriumStat Electrochemical Interface (Irium Technologies). This cell allows for optical observation of the backside of the working electrode through an optical glass window of 0.3 mm thickness. The cells were assembled in a argon-filled glove box (UniLab, MBraun) and equilibrated for 24 h prior to further use. The cells had an open circuit potential (OCP) of approximately 3.0 V vs. Li$^+$/Li. Galvanostatic cycling was performed at room temperature (RT) with charging and discharging currents of 12.5 mA/g in a potential range from 3.4 V to 5.0 V vs. Li$^+$/Li.

2.4. In Situ Raman Measurements

The electrochemical cell used for the in-situ Raman measurements was assembled as described above. Raman spectra were recorded at OCP prior to cycling and at specific potentials during galvanostatic cycling with charging and discharging currents of
12.5 mA/g. After reaching a predefined potential, this potential was stabilized in a potentiostatic mode for 1.5 h before recording a Raman spectrum. After recording of the spectrum, the galvanostatic cycling was continued. Synchronization of the electrochemical measurement and the Raman measurements was achieved by means of self-written software.

Raman spectra were measured in backscattering geometry by means of a Raman microscope inVia (Renishaw), using a frequency-doubled Nd:YAG laser (532 nm wavelength) focused on the backside of the working electrode through a 20× objective (Leica). The spectra were recorded in confocal mode in a wave number range between 1230 cm⁻¹ and 2780 cm⁻¹. The laser power was reduced to 0.1 mW to prevent both heating of the sample area and degradation of electrolyte, which would produce fluorescence.

3. Results and Discussion

3.1. Characterization of Graphitic Foam

Fig. 2a and b show SEM images of the nickel foam used as template and of the synthesized graphitic foam, respectively. The overall morphology of the foams is virtually identical. As seen from Fig. 2b, some of the bars of the graphitic foam are cracked allowing the electrolyte to not only wet the outer surfaces of the bars, but also the inner surfaces.

The magnification of the optical microscope (see Fig. 2c) allows for focusing on the surface of a single bar. This is important for achieving a good signal to noise ratio in the Raman measurements. During the in-situ Raman measurements, the laser was focused onto the black marked spot. The Raman spectrum of the pristine graphitic foam is shown in Fig. 3. The main peaks observed are the G band at 1582 cm⁻¹ and the 2D band. The latter band can be fitted by two peaks at 2682 cm⁻¹ and 2722 cm⁻¹. Such a Raman spectrum is typical for graphitic carbon [55–58]. The G band corresponds to the first-order E₂g optical mode and is associated with a relative motion of sp² carbon atoms. The 2D peak is the overtone of the so-called D peak that is located at ca. 1350 cm⁻¹ [57]. Even though the D band is related to defects in graphite, the 2D band is observed in defect-free graphite as well [58]. Here, the absence of the D band is a clear indication of highly ordered defect-free graphite. The origin of the small peak at 2449 cm⁻¹ is not known and will not be further discussed in this paper.

Here, it is worth mentioning that all bands of graphite are due to resonant Raman scattering, leading to very high intensities. Raman bands of the electrolytes, which are expected in the considered spectral range are caused by non-resonant scattering. Since these bands exhibit a much lower intensity, they cannot be observed under the experimental conditions in this study.

3.2. Galvanostatic Cycling

In order to obtain information about the potentials, at which intercalation and deintercalation of TFSI⁻ in graphite takes place, a dual-ion cell was cycled for two complete charging/discharging cycles using a current of 12.5 mA/g. Fig. 4 shows the differential capacity curves of both cycles. During the first charging, intercalation of TFSI⁻ starts at approximately 4.41 V vs. Li⁺/Li, followed by a sharp peak at ca. 4.44 V. At higher potentials between 4.5 V and 4.7 V, the peak shows a weak shoulder, while between 4.7 V and the cutoff potential of 5.0 V, the differential capacity is almost constant. During discharging, a total of five peaks is detected: (i) a weak peak at 4.67 V; (ii) a sharp peak at 4.50 V; (iii) another sharp peak at 4.47 V; (iv) a broad peak at 4.34 V; (v) a weak and broad peak at 4.07 V. In the literature [15], the occurrence of the different peaks is assigned to the existence of different stages of the GIC. This will be discussed in more detail in section 3.3.1.

The differential capacity curve of the second cycle is quite similar to that of the first cycle, except for one important difference. Intercalation of TFSI⁻ starts at lower potentials (ca.
4.36 V) than in the first cycle, resulting in a broad peak at 4.44 V. This effect was explained by Placke et al. [15] in terms of a kinetic hindrance of TFSI\textsuperscript{−} intercalation during the first cycle. According to this explanation, the kinetic barrier is caused by an opening process of partially closed interlayer gaps during the first charging cycle. This kinetic hindrance is then absent during the second and subsequent cycles [15].

3.3. In-situ Raman Measurements

Fig. 5 shows an overview of selected Raman spectra recorded during the first (Fig. 5a) and the second cycle (Fig. 5b). The most important changes of the spectra during cycling will be discussed in the following subsections and compared to phenomena observed during the intercalation of Li\textsuperscript{+} into graphite.

3.3.1. Staging Behavior and Charge Density of Layers from G Band

The most prominent change in Raman spectra during charging of the dual-ion cell is the splitting of the so-called G peak, accompanied by a blue shift of both resulting peaks (see Fig. 5). Splitting of the G peak is a well-known phenomenon observed for GICs and is related to the formation of staged compounds with stage numbers larger than 3. The origin of the splitting can be described by means of the nearest layer model [59]. The peak at lower wave numbers results from a vibrational mode of the inner graphene layers (E\textsubscript{2g}(i)) adjacent to other graphene layers, while the peak at higher wave numbers is due to a vibrational mode of the boundary graphene layers (E\textsubscript{2g}(b)) adjacent to intercalant layers. GICs with a stage of 2 or 1 exhibit only boundary layers and therefore do not show two E\textsubscript{2g} modes.

In the first cycle, splitting of the G peak starts at 4.40 V, at which the steep incline of the differential capacity is observed (see Fig. 4). At higher potentials (starting at 4.70 V), the E\textsubscript{2g}(i) mode nearly vanishes and only manifests as a shoulder of the E\textsubscript{2g}(b) mode, making it difficult to fit this peak in a reliable fashion.

Before the G peak splits up into two peaks, its wave number remains constant at 1584 cm\textsuperscript{−1} (see Fig. 6). This is a significant difference to the electrochemical intercalation of Li\textsuperscript{+}, which manifests as a gradual blue shift of the G peak, before it splits up due to the formation of a dilute stage 1 GIC [40,41]. During TFSI\textsuperscript{−} intercalation, no dilute stage 1 compound is formed, but compounds with stage numbers n > 3 are instantaneously formed. As soon as the G peak splits up during the first charging cycle, there is a sudden blue shift followed by a more gradual increase of the wave number with increasing potential, up to a value of 1592 cm\textsuperscript{−1}. The peak at higher wave numbers appears at 1607 cm\textsuperscript{−1} and blue shifts almost linearly with potential up to a value of 1623 cm\textsuperscript{−1}. During the first discharging cycle, the E\textsubscript{2g}(b) mode shows a gradual red shift between 5 V and 4.3 V. At 4.3 V and 4.2 V, there are sudden red shifts of the boundary-layer mode (to 1609 cm\textsuperscript{−1}) and of the inner-layer mode (to 1587 cm\textsuperscript{−1}), respectively. These sudden changes seem to be related to the broad deintercalation peak visible in the differential capacity curve (see Fig. 4). Remarkably, there is no big difference between the spectra recorded at 4.6 V and at 4.4 V (see Fig. 5), even though the differential capacity curve exhibits two sharp peaks in this potential range. At lower potentials, the position of the E\textsubscript{2g}(i)
mode remains fairly constant at 1586 cm\(^{-1}\), while the position of the E\(_{2g}\) mode further red shifts to 1606 cm\(^{-1}\).

The blue shift of the peaks during intercalation can be explained by an increasingly positive electronic charge density of the graphene layers [57,60]. It is most likely caused by a breakdown of the adiabatic Born-Oppenheimer approximation due to strong electron-phonon coupling [61]. The positive charge is located almost entirely at the boundary graphene layers, while the inner layers remain nearly unchanged [62]. This also explains the more pronounced shift of the E\(_{2g}\) mode (nearly 20 cm\(^{-1}\)) compared to the E\(_{2g}\) mode (less than 10 cm\(^{-1}\)).

At the end of the first discharging process, the Raman spectrum (see Fig. 5a) still exhibits two E\(_{2g}\) modes that strongly overlap. This gives strong indication that the deintercalation of TFSI\(^{-}\) anions is not complete, implying that residual TFSI\(^{-}\) anions remain in the graphite matrix. This is also in accordance with the position of the E\(_{2g}\) mode at the end of the discharging process, which is still slightly higher than the position of the G peak before cycling.

The trends observed during the second cycle are similar, except for a small difference (see Fig. 6) which manifest mainly during discharging, even though the differential discharge capacity curves of the first and the second cycle (see Fig. 4) are virtually identical. During the second discharging cycle, the red shift of the E\(_{2g}\) modes (especially of the E\(_{2g}\) mode) are somewhat more gradual below 4.3 V. Even the significant differences between the first and the second charging cycle regarding the kinetic hindrance effect does only manifest in a slightly more gradual blue shift of the E\(_{2g}\) mode.

The intensity ratio \(R\) of the E\(_{2g}\) mode and the E\(_{2g}\) mode gives detailed information about the staging of the GIC. \(R\) depends on the stage number \(n\) of the GIC in a linear fashion [63]:

\[
R = \frac{I_i}{I_b} = \frac{\sigma_i n - 2}{\sigma_b 2}
\]

\(I_i\) and \(I_b\) denote the intensities of the E\(_{2g}\)(i) mode and the E\(_{2g}\)(b) mode, respectively. The stage independent value \(\sigma_i/\sigma_b\) represents the ratio of the cross sections for Raman scattering of the inner and the boundary layers. Sole et al. claimed that this ratio is unity in case of lithium intercalation [40]. This is not strictly correct, since the ratio of scattering cross sections depends on the wavelength of the laser [62]. However, since Sole et al. obtained reasonable values for the stage numbers, their claim is plausible.

Fig. 7a shows the ratio of peak intensities of the E\(_{2g}\)(i) mode to the E\(_{2g}\)(b) mode plotted versus potential. On the right ordinate, the stage number is plotted under the assumption that the ratio \(\sigma_i/\sigma_b\) is unity. Under this assumption, the obtained stage numbers are in a plausible range between two and five. During the first charging cycle, the stage number drops rapidly to a virtually constant number slightly larger than two (at potentials above approximately 4.6 V). This value is in good agreement with the in-situ XRD study performed by Placke et al. [23] showing a stage 2 GIC for TFSI\(^{-}\) intercalation at a potential of 5.1 V. During the second charging cycle, the stage is fairly constant below 4.5 V and drops to similar values as in the first cycle at potentials above 4.5 V.

The two discharging cycles are rather similar and show a gradually increasing stage number with decreasing potential with an indicated plateau region starting at ca. 4.2 V with a stage number in the range of 3–4. This, in fact, takes place at potentials below the occurrence of the broad deintercalation peak in the

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**Fig. 6.** Wave number of the (a) E\(_{2g}\)(i) mode and the (b) E\(_{2g}\)(b) mode plotted versus potential.

**Fig. 7.** Plot of the intensity ratio of the E\(_{2g}\)(i) mode to the E\(_{2g}\)(b) mode versus (a) potential and (b) composition of the GIC(TFSI\(_{x}\)C\(_{24}\)). The composition is calculated under the assumption that the charge flow is exclusively caused by the intercalation and deintercalation of TFSI\(^{-}\). The stage number on the right y-axis was calculated under the assumption that the ratio of the Raman scatter cross sections of the inner layers to the boundary layers, \(\sigma_i/\sigma_b\) is unity.
differential capacity curve during discharging (see Fig. 4). It should again be mentioned that stage 2 compounds should not exhibit two E_{2g} modes. However, it is possible that domains of stage 2 and domains of stage 3 GICs coexist and are simultaneously probed by the laser.

The stage number in dependence of the composition of the GIC is shown in Fig. 7b. Remarkably, during discharging, low stage numbers seem to be stable over a broad composition range and then quickly rise in a composition range between x=0.4 and x=0.55.

3.3.2. Relative changes in conductivity from peak intensities

The change in absolute intensity of a set of peaks gives valuable information about changes in conductivity, since the optical skin depth δ correlates with the conductivity σ of a material as follows [64]:

\[ \delta = \sqrt{\frac{2}{\mu \omega}} \]

Here, μ and ω are the magnetic permeability and the angular frequency, respectively. According to Eq. (2), a reduction of the electronic conductivity will result in an increase of optical skin depth and consequently of the detected Raman intensity.

As soon as the intercalation of TFSI\(^-\) starts (at approximately 4.5 V in the first charging cycle), the sum of the intensities of the E_{2g} band increases gradually by a factor of up to 8 (see Fig. 8), suggesting a strong decrease of the electronic conductivity of the GIC with increasing amount of intercalated TFSI\(^-\). During deintercalation, the sum of intensities decreases again, indicating an increase of the electronic conductivity. This finding is remarkable, since donor-type GICs as well as acceptor-type GICs are commonly known to exhibit higher electronic conductivities than pure graphite [65–67]. Indeed, in-situ Raman measurements on Li\(^+\) intercalation/deintercalation in graphite showed that the peak intensities decrease during Li\(^+\) intercalation and increase during Li\(^+\) deintercalation [40]. At high amounts of intercalated Li\(^+\) ions, Raman peaks are not detectable anymore. The origin of the opposite trend observed here for TFSI\(^-\) intercalation/deintercalation is not clear at present. Therefore, further experimental and theoretical studies on the electronic charge density on graphite during anion intercalation are highly desirable.

3.3.3. Strain and Electron Concentration from 2D Band

The intensity ratio of the dominant 2D band to the sum of the intensities of the E_{2g} bands decreases with potential by a factor of approximately three, see Fig. 9. Such an effect has also been observed upon p doping of bilayer graphene top gated by a polymer electrolyte [60], suggesting that the change in intensity ratio observed here results from the decreasing electron concentration during anion intercalation.

Upon p doping of bilayer graphene, the decreasing electron concentration leads in addition to a blue shift the 2D band [60]. However in the present study, we observe an abrupt red shift of the dominant 2D peak from ~2725 cm\(^{-1}\) to ~2700 cm\(^{-1}\), as soon as TFSI\(^-\) intercalation starts. Subsequently, the position of the dominant 2D peak remains fairly constant throughout both cycles. Of course, the abrupt red shift cannot be explained by a change of the electron concentration, but most likely it is related to a mechanical strain due to a deformation of the graphene layers during TFSI\(^-\) intercalation. It is well known that strain leads to a significant red shift of the 2D band [68,69]. This strain can be explained in the framework of the Daumas-Héroid model of intercalation into graphite [70]. According to this model, layers are not sequentially filled as proposed by the Rüdorff model [43]. Instead, ions intercalate between all graphene layers at the same time, deforming the layers around the intercalant (see Fig. 10). Staging then occurs by means of a lateral diffusion of the intercalant ions. This model also allows for an easy transition between stages by means of lateral diffusion (in contrast to diffusion along the c-axis in the Rüdorff model) and for coexistence of domains of different stages in a single crystallite.

The fairly constant position of the dominant 2D peak after the initial red shift could be due to the compensation of two effects: (i) Blue shift due to decreasing electron concentration, and (ii) red shift due to increasing strain.

![Fig. 8. Plot of the normalized sum of intensities of the E_{2g} bands in dependence of (a) the potential and (b) the composition.](image)

![Fig. 9. Ratio of the intensity of the dominant 2D band to the sum of intensities of the E_{2g} bands, plotted vs. potential.](image)
3.3.4. Disorder and Inter-defect Distance from D Band

The D band represents a vibrational mode that is forbidden in defect-free graphite. The mode is only then active, if defects exist, such as crystallite edges, point defects or stacking faults [71–73]. The absence of the D band in the pristine sample (see Fig. 3 and Fig. 5a at OCP) indicates that the graphite consists of large crystallites with very few defects.

During the first charging cycle, the D peak emerges at a potential of 4.9 V, and its relative intensity compared to the E2g modes increases with increasing TFSI− content, see Fig. 11. Obviously, defects are induced by the initial TFSI− intercalation. In the second cycle, the intensity ratio of the D peak to the E2g peaks decreases during TFSI− intercalation and increases during TFSI− deintercalation, indicating that the amount of defects is reduced during intercalation and enhanced during deintercalation. The nature of these defects will be discussed below.

Apart from its intensity, also the position of the D peak changes during charging/discharging. There is a blue shift of the D peak during TFSI− intercalation and a red shift during TFSI− deintercalation (reversible behavior), see Fig. 11b. Since this shift shows similar trends as the shift of the E2g modes, it results most likely from the varying electronic charge density of the graphene layers.

3.3.5. Raman Spectra after Long Rest Times of the Discharged Cell

After the second cycle was completed, the electrochemical cell was stored for two weeks at room temperature. After one and two weeks rest time, respectively, Raman spectra were collected, see Fig. 12. There are two significant changes over storage time. The most prominent change is the nearly complete disappearance of the D peak after storage. The ratio of the D peak intensity to the sum of the E2g peak intensities drops about one order of magnitude from ca. 0.28 to 0.029. This indicates that defects heal over time.

The second important observation is that the two E2g modes, which are present due to residual TFSI− anions in the graphite matrix, become sharper and better separated. This is most likely due to ordering of TFSI− anions by lateral diffusion resulting in a better defined stage structure.

The position of all observed peaks remains identical. Thus, neither the electron concentration nor the strain of the graphene layers seems to change significantly over time.

After two weeks of storage, two more charge/discharge cycles were performed with a charging current of 12.5 mA/g. Fig. 13 shows the differential capacity curves of these cycles 3 and 4. Remarkably, the kinetic hindrance of TFSI− intercalation observed for the pristine graphite shows up again after long-time storage of the discharged cell, even though residual TFSI− ions are in the graphite matrix. This seems to contradict the theory of Placke et al. [15] that the kinetic hindrance is due to an initial opening of the interlayer gaps. Placke et al. proposed that mechanical impact due to milling of commercial graphite particles leads to a partial closure of the interlayer gaps. An alternative explanation for the kinetic hindrance given in [15] is the insufficient wetting of the
electrode. However, both of these explanations do not account for the reappearance of the kinetic hindrance after long-time storage of the discharged cell. There rather seems to be a anti-correlation between the number of defects and the kinetic hindrance. The formation of defects induced by the intercalation and deintercalation of TFSI$^-$ anions seem to play an important role for the removal of the kinetic hindrance. Consequently, the healing of the defects during storage increases the kinetic barrier for the intercalation. These defects could be stacking faults [71,72] due to a lateral movement of graphene layers during intercalation. A healing of such stacking faults during long-time storage requires only lateral movement of graphene layers and appears to be a highly plausible explanation for the reappearance of the kinetic hindrance.

4. Conclusion

We have investigated changes in structure and physical properties of a graphite electrode during intercalation and deintercalation of TFSI$^-$ in the first two charging/discharging cycles of a dual-ion cell by means of in-situ Raman spectroscopy. As known from Li$^+$ intercalation, the formation of stages can be clearly observed by G band splitting during intercalation. However, in contrast to Li$^+$ intercalation, no dilute stage 1 compound [40] forms at the beginning of the intercalation process, but immediately distinct stages are formed. A remanent splitting of the G band at the end of the deintercalation process shows that the intercalation of TFSI$^-$ is not completely reversible, so that residual TFSI$^-$ remains within the graphite matrix.

On basis of total intensity of the observed peaks it is possible to gain information about conductivity changes. The increasing sum of intensities of the $E_{2g}$ bands suggests a decreasing electronic conductivity of the graphite electrode. This is a remarkable observation, since GICs usually exhibit a higher electronic conductivity than pristine graphite.

Peak shifts were used to investigate changes of the electronic charge of the graphite matrix. The blue shift of the $E_{2g}$ bands and the D band indicates a decreasing electron concentration within the graphite during intercalation. In contrast, the 2D band shows a sudden red shift as soon as intercalation takes place in the first cycle. This is a clear indication of strain induced by intercalation due to the formation of a Daumas-Hérold type GIC.

A D band is not observed in the Raman spectra of the pristine graphitic foam due to a very small number of defects. The first intercalation process gives rise to the D peak, revealing the formation of intercalation-induced defects. Subsequently, the number of defects increases during deintercalation and decreases during intercalation. During storage of the discharged cell at room temperature over two weeks, the D band disappears almost completely. Thus, despite residual anions remaining in the graphite matrix, there is defect healing during long-time storage of the cell. In addition, the stored cell shows a kinetic hindrance of TFSI$^-$ intercalation during a third charging cycle. These findings provide strong indication that there is a anti-correlation between the number of defects and the kinetic barrier for TFSI$^-$ intercalation and contradict the assumption that the kinetic hindrance is due to an initial opening of the interlayer gaps.

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Diffraction of In-Situ Itoh, N.

Dilatometry of In-Situ Itoh, N.

their performance of Nishina, T.

of graphite (1997) Hahn, B.


Dilatometric Itoh, N.


