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Expansion of carbon fibres induced by lithium intercalation for structural electrode applications

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Abstract

Carbon fibres (CFs) can work as lightweight structural electrodes in CF-reinforced composites able to store energy as lithium (Li)-ion batteries. The CF has high stiffness and strength-to-weight ratios and a carbonaceous microstructure which enables Li intercalation. An innovative in-situ technique for studying the longitudinal expansion of the CF and the relationship with the amount of intercalated Li is described in the present paper. The polyacrylonitrile-based CFs, T800H and unsized IMS65, were chosen for their electrochemical storage capacities. It was found that the CF expands during lithiation and contracts during delithiation. At the first electrochemical cycle, the expansion is partly irreversible which supports that the first-cycle capacity loss partly relates to Li trapped in the CF structure. For the following cycles, the capacity and the expansion are reversible. The expansion, which might relate to tensile stress, increases up to 1 % as the measured capacity approaches the theoretical limit of 372 mAh/g for Li storage in graphite. Minor additional expansions due to the uneven distribution of intercalated Li in the CF structure were measured before and after lithiations. Using scanning electron microscope images the transverse expansion of fully lithiated CFs was estimated to about 10 % of the cross-section area.

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1. Introduction

Rechargeable batteries are a leading solution for systems that require electrical energy storage, but many of these systems such as hybrid vehicles and laptops also include a mechanical structure. Energy storage devices and structural components have completely separate functions but they usually have the highest mass contributions. A novel solution to mass savings is to store electric energy directly in the structure of the system, e.g. in the roof of an electric car. This may be achieved with a structural battery: a lightweight material combining the mechanical performance of carbon fibre (CF)-reinforced polymers and the energy storage capacity of lithium (Li)-ion batteries.

Graphite-based materials are often used as negative and lithium metal oxides as positive electrodes in conventional rechargeable Li-ion batteries. The high operating voltage, high specific energy and very slow self-discharge [1] of Li-ion batteries put them in a favourable position for conversion into a structural battery. CFs are commonly used as structural reinforcement in composite materials because they have high tensile strength and stiffness-to-weight ratios. Thus, the concept of a structural Li-ion battery can be based on the use of CFs as structural electrodes since their carbonaceous microstructure [2] enables a reversible Li-intercalation reaction.

Previous work [3, 4, 5] has investigated the most favorable CF grades for use as structural electrodes. Intermediate modulus polyacrylonitrile (PAN)-based CFs fulfil both stiffness and strength requirements and exhibit the best overall electrochemical storage capacities at a 1C-rate (corresponds to a 1h charge time). The more disordered carbon structure has actually been suggested to be more favourable for Li-ion intercalation than the highly graphitized structures of pitch-based fibres [6]. As previously reported [7], the impact of electrochemical cycling over time (up to 1000 cycles at 1C-rate) on the tensile properties of CFs has been investigated. It was found that the tensile stiffness of the CF remains unchanged, but the ultimate tensile strength of CFs dropped about 20 % during lithiation and is only partly recovered after delithiation. Furthermore, when the fibres were subjected to a tensile load the capacity of the CF, at 1C-rate, remained unchanged and reversible, while a lengthwise expansion and contraction were observed during lithiation and delithiation, respectively [8, 9]. However, the impact of the amount of intercalated Li on the mechanical performance of

the CF is still unknown. Previous research [4] showed that the measured specific capacity of a CF tow depends on the electrochemical cycling rate (C-rate). The CF tow may be fully lithiated at very low rates but for higher rates the diffusion of Li in the fibre tow becomes rate limiting and the fibres are only partly lithiated. This paper focuses on the longitudinal expansion of the CF and the relationship with the measured capacity. The magnitude of the expansion of the CFs is of primary interest since it may cause internal stresses and deformation in a multifunctional electrode.

In this study, two grades of PAN-based CFs that exhibit good electrochemical and mechanical properties were selected, one sized and one unsized. The longitudinal expansion of the CFs was measured separately in situ at different C-rates for several lithiations and delithiations, and the results were correlated with the measured capacity. In further tests, the electrochemical cycling consisted of sequences of high and low rates to investigate the reversibility of the capacity and the longitudinal expansion measured. The longitudinal expansion of the CFs during cell relaxation was also investigated after delithiation and lithiation when the concentration gradient in the fibre of the initially unevenly distributed Li relaxes. In addition to the study of the longitudinal expansion, field emission scanning electron microscope (FE-SEM) cross-sectional images were used to statistically estimate the transverse expansion of fully lithiated CFs.

2. Materials and methods

2.1 CF specimens

Two types of intermediate modulus PAN-based CFs, that demonstrated the best capacities measured previously [4], were selected for this study: Toho Tenax IMS65 24K 830tex unsized (fibers which have never been sized) and Torayca T800HB 6K 40B P1 BB 223tex with sizing. The IMS65 and T800H CFs exhibited a specific capacity of 177 mAh/g and 136 mAh/g, respectively, at a 1C-rate with excellent capacity retention after 10 cycles.

Tensile specimens were manufactured from dry CF tows. A single filament may be more sensitive to micro-defects whereas the high number of filaments in the tows used in this study may have a predominantly ameliorative effect on the mean results. The CF specimens were loaded using a microtester, a 300 N tensile stage from Deben UK. The

number of filaments per specimen had to be typically lower than 4000 so that the ultimate tensile load was below the 300 N of the load cell. Manufacturers do not produce tows containing such a low number of filaments for the CF grades selected. However, it was possible to divide the tows properly into lighter ones over a sufficient length, typically 60cm, to manufacture the required amount of CF specimens with 22 mm gauge length. Strands of 22mm were collected along the lighter tows and weighed to estimate the mass of CF electrode in each specimen. For consistency, almost all the specimens used were from the same tow, and therefore the error in the mass remained within the range of accuracy of the balance, $\pm 0.1\text{mg}$. The weights of the IMS65 and the T800H specimens were about $2.0 \pm 0.1\text{mg}$, that is 2630 ± 130 filaments, and about $2.5 \pm 0.1\text{mg}$, 3360 ± 120 filaments, respectively.

Figure 1 shows an image of a prepared CF specimen with its end tabs (made to fit in the microtester) as presented in [7, 8]. The end tabs (12 mm long $\times$ 10 mm wide $\times$ 1 mm thick) were cut from insulating glass fibre composite plates made from cured Gurit SA80 prepreg. The lighter CF tows were slightly pre-stretched with tape during the bonding procedure of the end tabs. Gurit SE 84LV epoxy films were used for impregnation of the fibres between end tabs followed by curing in a vacuum bag at 120 °C for 1h. A breather fabric was used to absorb the excess resin which could otherwise flow along the fibres during cure. This bonding technique allowed good impregnation of the fibres in a stiff, consistent and insulating tabbing fixture. To avoid damage and keep the fibres straight during handling the end tabs were taped on a support paper, which was cut away before the mechanical test. The specimens were dried at 60 °C under reduced pressure for 24 h and placed inside the glovebox prior to cell assembly.

Fig. 1. CF tensile specimen with its dimensions.

2.2 Cell assembly and electrochemical cycling

The CF specimens were used as electrodes in laboratory Li-ion cells which were manufactured in a glovebox under inert argon atmosphere with less than 1 ppm [O₂] and [H₂O] at ambient temperature as presented in [8]. Each cell consisted of a CF specimen electrode, a glass microfibre separator 260µm thick (Whatman GF/A) impregnated with 150 µL 1.0 M LiPF₆ in EC:DEC (1:1 w/w, LP40 Merck) electrolyte, and 120µm thick Li metal foil counter electrode. The electrodes are connected to the outer circuit via current collector tabs consisting of copper foil and nickel foil for the carbon and the Li electrodes, respectively. The assembly was heat sealed inside a laminate bag (polyethylene terephthalate/aluminium/polyethylene, 12 µm / 9 µm / 75 µm thick from Skultuna Flexible), functioning as a barrier against air and water, and vacuum was drawn inside the bag to ensure good contact between all layers.

All electrochemical measurements were performed using a Solartron 1286 Electrochemical Interface controlled with the CorrWare software. The cycling of the cells was performed at a constant current, chosen according to the mass estimate of the CF electrode and the desired C-rate. Each cycle contained four consecutive steps: a galvanostatic lithiation, an open-circuit potential (OCP) allowing the cells to relax for 15 minutes, a galvanostatic delithiation, ending with another 15 minute OCP. The fibres were considered lithiated at 0.002 V vs. Li/Li⁺ and delithiated at 1.5 V vs. Li/ Li⁺. The cells were cycled for three to ten cycles with the currents corresponding to about 6C, 3C, 1C, 0.4C, 0.1C rates. The term x C-rate is for x times the 1C-rate in mA/g. The measured specific capacity C_s^{measured} , which is defined as the amount of electric charges received and delivered by the cell for lithiation and delithiation, respectively, is calculated from the constant current applied times the charging time divided by the mass of the CF electrode; it reflects the amount of Li intercalated in the CFs.

2.3 Measuring the CF longitudinal expansion induced by Li intercalation

As describe elsewhere [8], the longitudinal expansion of CFs may be measured in situ, using CF specimens as structural electrode in the Li-ion cells. The tensile load carried by a CF specimen varies during lithiation and delithiation while subjected to a constant tensile strain. The force variations are attributed to a longitudinal expansion of the CFs since the tensile stiffness of the specimen remains unchanged [7]. The expansion [%] is

calculated as the variation of the tensile load divided by the tensile stiffness of the CF specimen, measured in a tensile test. The tensile stiffness of a CF specimen is defined herein as the slope of the tensile curve (force [N]) vs. (percent elongation [%]) where the deformation is linearly elastic and was calculated with the method of linear least squares to fit data points, between load limits of about 400 mN/tex and 800 mN/tex, as suggested for a single filament [10].

Figure 2 is a schematic of a sectional view of the experimental setup. All measurements were made separately for the different C-rates, using a new cell with a single CF specimen electrode. The laminate bag of the cell was clamped onto the tabs of the specimen inside the jaws of the microtester. Flat clamps were used to avoid puncturing the bag. A constant tensile extension was applied in parallel to the CF specimen and the bag. A slow motorspeed of 0.1mm/min was used to keep a slow strain rate because of the small gauge length of the specimen. The Deben UK Microtest software was used for acquisition of load, extension and time data. The load relaxation in the bag was recorded for 3h to let it stabilize before starting the electrochemical cycling of the cell. The CF specimens were subjected to a tensile test to evaluate the tensile stiffness after finishing the electrochemical cycling. The load carried by the bag alone at the applied constant extension was measured in a separate load relaxation test.

Fig. 2. Section schematic of a laboratory cell in the clamps of the microtester.

2.4 FE-SEM imaging of the CF transverse expansion

FE-SEM (Hitachi S-4800) was used to make cross-sectional images of the two CF grades in an attempt to estimate the transverse expansion induced by Li-ion

intercalation. The conductive CF samples were not coated prior to examination. The mean cross-section areas of virgin and fully lithiated (at a 0.1C-lithiation rate) CFs were compared statistically to evaluate the relative change from a number of images. The lithiated CFs were cleaned with dimethyl carbonate (DMC) solvent to remove any electrolyte residues deposited on the outer surface of the fibre. The fibres were mounted on a SEM stub and the cross sections were cut with a scalpel. All samples were prepared in the glovebox and place in a sealed bag to minimize the contact with air during transfer into the FE-SEM.

3. Results and discussion

3.1 Electrochemical cycling at different rates

Table 1 presents the capacities measured during electrochemical cycling for the different rates applied. The results for the last cycles show larger capacity at lower rates, as in [4] and at the lowest rates the measured capacities are close to the saturated value of lithium storage in pure graphite (372mAh/g).

Table 1. Cell capacity measurements for the different cycling rates.

Grade	Cycling rate		Charging time [h]	1 st -cycle capacity loss [mAh/g]	Last cycle capacity ^a [mAh/g]	
	C-rate	[mA/g]			Lithiation	Delithiation
IMS65	5.94C	1052	0.05	46	56	55
	2.97C	526	0.19	80	98	98
	1.08C	192	0.88	135	168	166
	0.31C	54	5.35	128	289	283
	0.08C	14	22.70	118	360	345
T800H	6.91C	940	0.06	56	56	56
	3.09C	420	0.26	150	110	110
	0.94C	128	1.27	174	163	160
	0.39C	53	5.10	162	269	271
	0.11C	15	24.43	154	354	369

^a For each CF grade, the reversible capacity is measured at the 3rd cycle for the 0.1C-rate and at the 5th cycle for all the other C-rates.

During the first lithiation a passivation layer, the solid-electrolyte interphase (SEI), induced by a decomposition of the electrolyte is formed at the surfaces of the CF electrode [11], which causes an irreversible first-cycle capacity loss. The irreversible capacity is smaller for the highest rates (6C and 3C) and tends to stabilize for the lowest rates (1C, 0.4C and 0.1C). For the following cycles, the cells exhibit a capacity that may be considered reversible between charge and discharge with good retention. The charge efficiencies are slightly above 100% at low rates for the last tabulated cycles of T800H. However, at the previous cycles the battery efficiencies were below 100%, so that for the whole sequence of cycles more Li was inserted than extracted as expected. Efficiencies slightly higher than 100% are not commonly seen in these tests, but may occasionally happen and are attributed to flat electrode potential curves at low C-rates affecting the termination of the charging cycle.

3.2 Longitudinal expansion measurement

The longitudinal expansion of the CF was measured for both CF grades at about 6C, 3C, 1C, 0.4C and 0.1C-rates separately for several electrochemical cycles. For each C-rate, a new CF specimen and a new cell were used. Figure 3 shows the variations of the tensile load carried by the IMS65 CF specimens subjected to a constant extension during electrochemical cycling at the different rates. Similar results were found for T800H CFs. The green curve (with square markers) denotes the bag relaxation only (no fibres loaded), and is used as a reference to distinguish the variations of the load carried by the CF specimen and the residual load relaxation in the bag. For each C-rate, the relaxation of the load carried by the bag is obvious during the first 3h after which the electrochemical cycling is started. The force drops during lithiations, remains unchanged during potential relaxations and increases during delithiations. Since the CF stiffness may be considered as unchanged, these curves indicate a longitudinal expansion of the CFs during Li insertion which is partially recovered by a longitudinal contraction after extraction of the same.

Fig. 3. Tensile load carried by IMS65 CF specimens subjected to a constant extension during electrochemical cycling at different rates.

For each rate the drop in load during the first lithiation is not fully recovered by the load increase during the first delithiation. There is a first-cycle irreversible expansion which remains in the CFs. For the next cycles, the expansion is reversible as well as the measured capacity. The curves in figure 3 clearly show that the amplitude of the irreversible and reversible expansions increases with lower C-rates. However, the absolute value of the slope for lithiation and delithiation is not constant, a feature which is more noticeable at lower C-rates. The curves are less steep at about half the charge time during lithiations and at the end of delithiations.

3.3 CF longitudinal expansion and the relationship with the measured capacity at different C-rates

Figure 4a and 4b present the longitudinal expansion of IMS65 and T800H CFs with the specific capacities measured during the last lithiation at the different C-rates. The figures show the continuous expansion during the last lithiation at the different C-rates, which are indicated with different markers in the end of the lithiations. A dash-dot line connects these markers to show the total expansion of the lithiated CFs. The same markers are used for the different C-rates on a dashed line to present the irreversible expansion, remaining in the CFs after the last delithiation. Thus, the difference between the dash-dot line and the dashed line shows the last cycle-reversible expansion at the different C-rates. The tendencies of the measurements are similar for the two CF grades.

The total expansion of the lithiated CFs, which is the sum of the irreversible expansion of delithiated fibres and the reversible expansion during lithiation, increases with lower C-rates. At the highest C-rate, the measured capacity is about 56 mAh/g and the total expansion of the lithiated fibres is the smallest measured, about 0.15 % for both CF grades. At the lowest rate, the capacities are close to 372 mAh/g and the expansion is the highest, about 1.03 % for IMS65 fibres and 1.05 % for T800H fibres.

Fig. 4. Longitudinal expansion of IMS65 (a) and T800H (b) CFs with the capacity measured for the last lithiation at the different C-rates. The difference between the total expansion of the lithiated CFs (dotted line) and the irreversible expansion of the CFs after the last delithiation (dashed line) shows the last cycle-reversible expansion at the different C-rates.

The main point that emerges from these results is that the expansion increases with the amount of intercalated Li during lithiation. Another point is that the C-rate has an impact on the expansion because the slopes and the y-intercepts of the curves are not all the same. Indeed, the y-intercept, which is the irreversible expansion in the delithiated CFs before the last lithiation, increases with lower C-rates, suggesting that more Li is trapped in the delithiated CFs. This tendency is also clearly seen on the irreversible expansion after the last delithiation (dashed line). The expansion rate given by the slope is higher when the intercalation rate is slow enough (0.1C) to have a negligible effect on the total capacity [4]. At higher rates (0.3C and above) the curves are almost parallel and have slightly smaller slopes than at 0.1C-rate. The reason might be that at the rates higher than 0.3C the diffusion of Li in the CF tow becomes rate limiting. However, more research needs to be done on the diffusion of Li in the electrolyte within CF tows and in filaments for a better understanding of the effects of the C-rate.

In addition, the relationship between the reversible expansion of the CFs and the reversible measured capacity is not quite linear during lithiation, especially for the C-rates lower than 1C. Figure 5 presents the variation of the potential and the load carried by an IMS65 CF during the fifth cycle at 0.3C rate. The slope of both the force and the potential flattens for while at about half the charging time during lithiation then becoming steeper again. Thus, a force and a voltage plateau are observable for capacities between about 120 mAh/g and 180 mAh/g. These boundaries appear to remain the same for all C-rates because the plateau shape is obvious or partly seen at the rates lower than 1C and no longer visible at the rates higher than 3C. Such plateau shapes might reflect a phase transition of Li staging in the carbonaceous microstructure or some changes in the structure surrounding intercalated Li. Similar plateaus are visible between 70 mAh/g and 10 mAh/g during delithiation, but are only observable at rates lower than 1C. Thus, the potential and force curves exhibit a hysteresis which is attributed to irreversible energy losses during electrochemical cycling. Using all measurements at all C-rates for the two CF grades, an average linear least square approximation of the reversible expansion $\epsilon_{\text{reversible}}$ (in %) as function of the reversible measured capacity $C_{\text{reversible}}$ (in mAh/g) can be suggested for use in a modelling work:

$$\epsilon_{\text{reversible}} = 0.630 \times C_{\text{reversible}} / 372 \quad (1)$$

This model remains quite rough, especially at rates lower than 0.3C and could be improved considering the effects of the C-rate.

Fig. 5. Variation of the electrode potential of an IMS65 CF specimen and the force it carries during the fifth lithiation and delithiation at 0.3C-rate.

3.4 Irreversible longitudinal expansion and the relationship with the irreversible capacity loss measured during the first electrochemical cycle at different C-rates

Irreversibly intercalated Li has already been reported in low-temperature carbons [12] such as PAN-based CFs, and was attributed to the reaction of Li with active sites in the bulk of the carbon electrode, e.g. hydroxylic groups or carbon radicals. In the present study, the irreversible longitudinal expansion of the delithiated fibres after the first cycle supports that the first-cycle capacity loss is not only related to the formation of SEI, but also to Li actually irreversibly trapped in the CF structure. The total first-cycle irreversible capacity loss is measured, but the part of irreversible capacity dedicated to the SEI layer formation is unknown. As a consequence the other part of irreversible capacity, $C_{\text{trapped Li, cycle(1)}}$, which is dedicated to insert the Li trapped in the CF after the first delithiation cannot be directly calculated from the first cycle.

However, at the last lithiation, the SEI is already formed and the capacity is almost completely used for Li insertion. Thus, assuming a linear relationship between the capacity dedicated to intercalate Li and the expansion induced, $C_{\text{trapped Li, cycle(1)}}$ can be calculated from

$$C_{\text{trapped Li, cycle(1)}} / C_{\text{reversible, LastCycle}} = \epsilon_{\text{delithiated, cycle(1)}} / \epsilon_{\text{reversible, LastCycle}} \quad (2)$$

where $C_{\text{reversible, LastCycle}}$ is the reversible capacity at the last lithiation, $\epsilon_{\text{delithiated, cycle(1)}}$ is the irreversible expansion after the first delithiation, and $\epsilon_{\text{reversible, LastCycle}}$ is the reversible longitudinal expansion during the last lithiation. The ratio $\epsilon_{\text{delithiated, cycle(1)}} / \epsilon_{\text{reversible, LastCycle}}$ is measured for each C-rate and $C_{\text{reversible, LastCycle}}$ is also measured.

The results are presented on figure 6 which shows the capacity of the first delithiation for each C-rate, the first-cycle total irreversible capacity loss, and the irreversible capacity corresponding to the trapped Li. The first-cycle capacity loss is smaller for the high rates (6C, 3C) and increases but stabilizes at a saturated value for the rates lower than 1C. However, more and more Li is irreversibly intercalated in the CF structure when the C-rate is lower, down to 0.1C. The difference between the irreversible capacity and the trapped Li is attributed to the SEI layer formation, which is higher for intermediate rates (around 1C) but smaller at the high (3C to 6C) and the low (0.3C to 0.1C) rates. This suggests that for the highest and the lowest rates the capacity loss is more dedicated to Li trapped in the structure and less to the SEI layer formation. The reason might be that the SEI layer is hastily formed at high rates and consumes only little capacity, as suggested elsewhere [13]. On the contrary, at low rates the SEI layer may be formed more efficiently, that is minimizing the capacity loss.

Fig. 6. Irreversible capacity loss, Li trapped in the CF and capacity for the delithiation at the first cycle for different C-rates.

Using all measurements at all C-rates for the two CF grades, an average linear least square approximation of the irreversible expansion $\epsilon_{\text{delithiated}}$ (in %) in the delithiated CFs as function of the maximum reversible capacity (in mAh/g) measured for the last lithiation, $C_{\text{reversible, Max}}$ (in mAh/g), can also be suggested:

$$\epsilon_{\text{delithiated}} = 0.303 \times C_{\text{reversible, Max}} / 372 \quad (3)$$

The total expansion in the lithiated CFs, $\epsilon_{\text{lithiated}}$ (in %) during the last lithiation can be calculated from equation (1) and (3) as:

$$\epsilon_{\text{lithiated}} = \epsilon_{\text{delithiated}} + \epsilon_{\text{reversible}} \quad (4)$$

Combining equations (1) and (3) after the last lithiation gives $\epsilon_{\text{delithiated, LastCycle}} / \epsilon_{\text{reversible, LastCycle}} = 0.481$. Assuming $\epsilon_{\text{delithiated, LastCycle}} = \epsilon_{\text{delithiated, cycle(1)}}$ (no irreversible expansion adding after the first cycle), equation (2) gives

$$C_{\text{trapped Li, cycle(1)}} = 0.481 \times C_{\text{reversible, LastCycle}} \quad (5)$$

The coefficient 0.481 is only a rough approximation at all C-rates which could be used in a modelling work of structural electrodes.

3.5 Impact of a varying charge rate on the CF longitudinal expansion

For each CF grade, further measurements of the longitudinal expansion were made with varying high and low rates during electrochemical cycling. Table 2 presents the expansion measured in the CFs at each step of the electrochemical cycling. One cell was subjected to sequence A (fast cycling followed by slow cycling) and another cell was subjected to sequence B (slow cycling followed by fast cycling). For IMS65 CFs the high and low rates were 3.05C and 0.29C, respectively. For T800H CFs the low rate was 0.31C, and the high rate was 2.50C in sequence A and 3.25C in sequence B. Figure 7 shows the curves of the load carried by CF specimens subjected to a constant extension for the two sequences A and B. The results are similar for both CF grades.

Table 2. CF longitudinal expansion for electrochemical cycling with varying rates.

Electrochemical cycling		Longitudinal expansion measured [%]			
		IMS65 fibres		T800H fibres	
		Delithiated	Lithiated	Delithiated	Lithiated
Sequence A	5 fast cycles	0.09	0.32	0.18	0.47
	+ 2 slow cycles	0.12	0.67	0.25	0.83
	+ 3 fast cycles	0.16	0.38	0.28	0.60
	+ 2 slow cycles	0.15	0.69	0.27	0.84
Sequence B	4 slow cycles	0.21	0.80	0.26	0.84
	+ 4 fast cycles	0.25	0.47	0.29	0.63
	+ 2 slow cycles	0.23	0.81	0.28	0.86
	+ 3 fast cycles	0.26	0.49	0.31	0.68

The main result is that the first rate of the sequence governs the value of both the irreversible capacity loss and the irreversible expansion which are mainly determined by the first electrochemical cycle (Table 2). When the first rate of the sequence is the higher (sequence A), the irreversible expansion is smaller.

Another effect is a minor increase in the irreversible expansion of the delithiated fibres visible the first time the rate is changed from high to low in sequence A. The reason might be that cycling at low rate allows intercalation of more Li which diffuses deeper into the fibres, increasing the amount of irreversibly intercalated Li after delithiation.

At last, every time the rate changes from low to high (in both sequences A and sequence B) there is a small but observable increase of about 0.04% (shown with arrows in Figure 7) in the expansion of the delithiated fibres which occurs during the first cycle of the fast cycling. During this fast cycle, the capacity measured during lithiation is a bit higher than expected at such a high rate. The reason might be that for the previous slow cycles the Li trapped in the delithiated fibres is distributed deeper in the CF structure freeing up space for more Li to be inserted during the fast lithiation. During the fast delithiation which follows a small capacity loss occurs. Only a part of the inserted Li, which should be the closest to the surface, has time to be extracted again. The capacity remains unchanged for the following fast cycles as expected at such a high rate.

However, this small capacity loss and the increase in the expansion of the delithiated fibres are almost reversible when the rate changes to low again. A slight contraction of about 0.01% is measured in the delithiated fibres. Some of the Li which was trapped in the CFs after the fast delithiations seems to have time to be extracted again during the following slow delithiation.

Fig. 7. Tensile load carried by CF specimens subjected to a constant extension during the cycling-rate sequence A (IMS65) and B (T800H).

Finally, it was found that any change in the expansion of the CFs correlates with a similar change in the capacity. The measured capacity and the expansion of the CFs may be considered as reversible with C-rate. However, a varying rate might affect the distribution and the amount of Li trapped in the delithiated fibres, causing only minor and reversible effects on the capacity loss and the expansion of the delithiated fibres.

3.6 Longitudinal expansion of the CFs during OCP

In other measurements, a few electrochemical cycles were run at about 1C-rate with about 6h OCP after each lithiation and delithiation in order to measure the longitudinal expansion of the CF caused by the relaxation of the Li concentration gradients in the fibre during potential relaxation. The 1C-rate is a good compromise between charging time and specific capacity for exhibiting the effects of the Li diffusion. Figure 8 shows the curve of the tensile load carried by an IMS65 CF specimen subjected to constant extension during an electrochemical cycle with subsequent OCP. The cycle starts with lithiation during which the load drops significantly as the fibres expand in the longitudinal direction. After the lithiation, the load goes up slightly during OCP,

reflecting a longitudinal contraction of about 0.03% of the CFs as the intercalated Li diffuses. When the delithiation starts, the load increases significantly as the fibres contract during extraction of the Li. After the delithiation, there is a slight decrease of load reflecting a longitudinal expansion of about 0.03% during the diffusion of the Li still remaining in the CFs. The same tendencies were seen for T800H fibres.

Fig. 8. Tensile load carried by an IMS65 CF specimen subjected to a constant extension during electrochemical cycling at a 1C-rate with about 6h OCP.

During cycling at higher rates, Li concentration gradients will form in the CF electrode. Li will diffuse in the CF during OCP relaxation steps until the concentration becomes uniform. This diffusion is exhibited as a small contraction or expansion of the CF after lithiation or delithiation, respectively. Plausible explanations may lie in the description of the microstructure of PAN-based fibres given in previous studies [14, 15, 16]. The graphitic layer planes may be essentially parallel to the surface in the shell region and increasingly folded closer to the centre of the core region where the diffusion of Li might be slower. The shell region is just a minor part of the CF cross-sectional area, but the modulus might be higher close to the shell where the layer planes are more parallel and aligned with the fibre longitudinal axis [15, 17]. After lithiation, the shell region might be more lithiated and over-expanded, which causes the fibre to contract when Li diffuses towards the core. On the contrary, after delithiation the concentration of Li might be higher in the core and the CF might expand slightly due to the diffusion of Li towards the shell of the fibre.

3.7 Transverse expansion measurements with FE-SEM images

Figure 9a and 9b show cross-sectional images of virgin and fully lithiated IMS65 CFs, respectively. The mean cross-section areas of virgin, fully lithiated and delithiated CFs at 0.1C-rate were estimated after 3 electrochemical cycles with FE-SEM images. For each image the clear and usable cross-sections were reproduced by layer on a binary image with the software Paint.NET. About 70 and 25 cross-section areas at $\times 2,000$ and $\times 6,000$ magnifications (Magn.), respectively, were processed with Matlab. Table 3 presents the mean cross-sections areas $\bar{A}_{\text{virgin}}$, $\bar{A}_{\text{li.}}$, $\bar{A}_{\text{deli.}}$ and their coefficient of variation (CV) measured on the virgin, lithiated and delithiated fibres, respectively.

Fig. 9. Cross-sectional FE-SEM of IMS65 CFs virgin (a) and fully lithiated (b) at 1kV with $\times 2,000$ magnification.

Table 3. Cross-sectional expansions measured on CFs fully lithiated at 0.1C-rate.

Fibre grade	Magn.	Virgin fibres		Lithiated fibres		Delithiated fibres	
		$\bar{A}_{\text{virgin}}$ [μm^2]	$\text{CV}_{\text{virgin}}$ [%]	$\bar{A}_{\text{li.}} / \bar{A}_{\text{virgin}}$	$\text{CV}_{\text{li.}}$ [%]	$\bar{A}_{\text{deli.}} / \bar{A}_{\text{virgin}}$	$\text{CV}_{\text{deli.}}$ [%]
IMS65	$\times 2,000$	20.38	± 6.74	1.088	± 8.51	1.027	± 6.07
	$\times 6,000$	19.91	± 6.75	1.094	± 5.25	1.022	± 6.27
T800H	$\times 2,000$	20.60	± 4.10	1.112	± 5.9	1.033	± 4.94
	$\times 6,000$	19.90	± 3.74	1.126	± 3.9	1.031	± 6.81

The results reflect a transverse expansion between 8 % and 13 % of the cross-section area for lithiated CFs, but much lower, between 2 % and 4 %, for delithiated CFs which indicates that the measured expansion is induced by the intercalated Li. The quality

control of Toho Tenax as to density per running meter of IMS65 CFs leads to a CV on the cross-section area of about 9 % which is one reason for the deviations measured. Therefore, cross-sectional FE-SEM images of partially lithiated CFs should not be the optimal technique for measurement of the transverse expansion which is expected to decrease almost linearly with the amount of intercalated Li, just like for the longitudinal expansion.

3.8 Correlation with the expansion of the structure of intercalated graphite

Previous research [18, 19, 20] has shown that volume changes occur in the intercalated graphite compound LiC_6 . As Li is intercalated into graphite, the interlayer spacing increases by about 10%, with a simultaneous expansion of about 1% of the basal planes. In the microstructure of CFs, the graphitic layers tend to be oriented more parallel to the longitudinal axis of the fibre [14, 15, 16]. Therefore, the correlation between the longitudinal expansion of fully lithiated CFs and the expansion of the graphite network in LiC_6 which are both about 1 % is noteworthy. In addition, the transverse expansion observed on CFs saturated with Li is obviously higher, between 8% and 13% (Table 3), and in the same order of magnitude as the increase in the interlayer spacing of the Li-intercalated graphite compound. Some differences might be due to amorphous carbon or to the turbostratic structure of the fibre in which the graphitic layers are in complete rotational disorder inside each stack. Nevertheless, these results suggest that the expansion of the CF caused by Li-ion intercalation is governed by the expansion of the graphitic layer planes and the longitudinal expansion might correspond to an internal tensile stress in the CF. The idea is also supported by the recent findings [7] showing that the ultimate tensile strength of CFs drops during lithiation and recovers during delithiation, but further work is required to clarify the expansion-strength relationship.

4. Conclusion

The work presented in this paper has resulted in a greater understanding of the Li-insertion and diffusion processes in the CF on one hand, and of the impact on the morphology and mechanical performance on the other hand. The CFs were found to expand in the longitudinal direction during lithiation and to contract during delithiation. After the first cycle some longitudinal expansion was irreversible which supports that

the first-cycle capacity loss is not only related to the formation of SEI, but also to Li being actually trapped in the CF structure. The expansion increased almost linearly with the measured capacity during lithiation suggesting that the inserted Li creates a tensile stress in the CF. A transverse expansion of the CF cross-section area was also observed with FE-SEM images from fully lithiated fibres. Both the transverse and longitudinal expansions are similar to those occurring when LiC_6 is formed from graphite.

The longitudinal expansion of the CF was also affected by minor effects related to the distribution and the diffusion of intercalated Li in the CF structure. Varying the rates highlighted the influence of the depth of the Li initially trapped in the CF structure on the measured capacity and the expansion during lithiation. During potential relaxation after delithiation and lithiation when the concentration gradient in the CFs of the unevenly distributed Li decreases, minor longitudinal expansions and contractions were measured, respectively. These results open the way for further investigation of the structural-electrochemical property relationship in CF.

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