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The effect of lithium-intercalation on the mechanical properties of carbon fibres.

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Abstract

Carbon fibres (CFs) can be used as lightweight structural electrodes since they have high specific tensile stiffness and ultimate tensile strength (UTS), and high lithium (Li)-intercalation capability. This paper investigates the relationship between the amount of intercalated Li and the changes induced in the tensile stiffness and UTS of polyacrylonitrilebased CF tows. After a few electrochemical cycles the stiffness was not degraded and independent of the measured capacity. A drop in the UTS of lithiated CFs was only partly recovered during delithiation and clearly larger at the highest measured capacities, but remained less than 40% at full charge. The reversibility of this drop with the C-rate and measured capacity supports that the fibres are not damaged, that some Li is irreversibly trapped in the delithiated CFs and that reversible strains develop in the fibre. However, the drop in the strength does not vary linearly with the measured capacity and the drop in the ultimate tensile strain remains lower than the CF longitudinal expansion at full charge. These results suggest that the loss of strength might relate to the degree of lithiation of defectives areas which govern the tensile failure mode of the CFs.

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1. Introduction

Lightweight designs are essential in system performance. They can allow lower energy consumption and higher energy storage capabilities which are facing ever growing needs. Many systems like hybrid vehicles and mobile phones include two kinds of subsystems with high mass contribution and completely separate functions: rechargeable batteries and mechanical structures. Thus, the storage of electric energy directly in the structure of the system e.g., in the casing of a laptop would allow significant mass reductions. A novel solution is to develop a lightweight material, called structural battery, with the energy storage capacity of lithium (Li)-ion batteries and the mechanical performance of carbon fibre (CF) composites. Rechargeable Li-ion batteries have high operating voltage, high specific energy and very slow self-discharge [1]. They often use porous composites based on carbon materials as negative electrode and the CF, which is a high-performing lightweight structural reinforcement for composite materials, is a potential candidate material. CFs have a micro structure with carbon content higher than 90% [2] which enables reversible Li-intercalation reactions. Therefore, the concept of structural Li-ion batteries is based on the use of the CFs as structural electrodes.

The electrochemical performance of the CF is complex and depends on the structure, the texture and the heteroatom content of the material [3–6]. The electrochemical energy storage capacity of CFs, that is the amount of Li reversibly incorporated during lithiation, has been studied previously [7–9] on a wide range of CF grades. Intermediate modulus polyacrylonitrile (PAN)-based CFs (which combine high performance in terms of specific tensile stiffness and strength) appeared to be the most favourable for use as structural electrode. The turbostratic microstructure of these fibres has actually been suggested to be more favourable for Li-ion intercalation than ordered crystalline structures found in highly graphitized carbon fibres [10]. At a macroscopic scale, the diffusion of Li into a CF tow was found to be rate limiting, and the measured electrochemical capacity progressively decreases at higher cycling rates for which the CFs are less and less lithiated. This could be due to the diffusion of Li into a tightly packed CF bundle since the diffusion coefficient of Li in a CF filament is high [11]. The

electrochemical capacity was, however, not affected by external tensile loads applied to the CF tow [12].

The mechanical performance of a CF tow during electrochemical cycling was studied in previous research. Partly reversible transversal and longitudinal expansion were measured as function of the amount of intercalated Li and increased progressively with the measured specific capacity up to about 10% and 1%, respectively, when the CF tows were fully lithiated (first-cycle irreversible expansions were measured) [13,14]. In addition, the changes in the tensile properties during electrochemical cycling at a fixed rate and capacity were measured as function of the cycle count (up to 1000 electrochemical cycles at 1C-rate) [15]. The stiffness remained unchanged over time whereas a partly reversible drop about 20% of the ultimate tensile strength (UTS) was measured (irreversible drops were measured at the first cycle).

However, further understanding of the property changes in CFs induced by inserted Li is needed for the modelling of the CF structural electrode and the integration in more complex composite structures. In particular, it remains unclear whether the changes in the UTS of the CF depend, like the expansion, on the amount of intercalated Li. This knowledge could tell if the longitudinal expansion due to Li-ion intercalation corresponds to a tensile strain in the CF which is prestressed in tension after lithiation. Therefore, the aim of the present paper is to investigate the changes in the tensile stiffness and UTS as function of the specific capacity of CF tows at different C-rates.

CF tows are first lithiated separately at different C-rates and the changes in the stiffness and UTS are related to the measured capacities. Then, the reversibility of the tensile property changes with the measured capacities is investigated using sequences of high and low C-rates. Lastly, the drop in the ultimate tensile strain (UTStrain) at the different measured capacities is compared with the CF longitudinal expansion measured in [14] for a better understanding of the property changes induced by the inserted Li.

2. Materials and methods

2.1 CF tensile specimens used as electrode

Two grades of intermediate modulus PAN-based CFs, Toho Tenax IMS65 24 K 830tex unsized and sized Torayca T800HB 6 K 40B P1 BB 223tex were chosen for their

promising electrochemical capacities measured in [9], i.e., 177 and 136 mAh/g at a 1C-rate, respectively, with excellent capacity retention after 10 cycles. As describe in [15], CF specimens were manufactured from dry CF tows. The high number of filaments per cross section was considered to provide good mean results which are also representative of the scatter of the filament properties. 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 oxygen and water at ambient temperature. The tensile tests were carried out in the glovebox using a 300 N load-cell microtester from Deben UK. The number of filaments per specimen had to be typically lower than 4000 so that the ultimate tensile load can be measured by the load cell. CF tows with such a low number of filaments are not commercially available for the grades selected. However, it was possible to divide a bigger tow of straight fibres into lighter ones to manufacture consistent CF specimens with 22mm gauge length. The specimens were weighed to estimate the mass of CF electrode per specimen. The weight of the IMS65 and the T800H specimens were about 2.0 ± 0.1 mg, that is 2630 ± 130 filaments, and about 2.4 ± 0.1 mg, 2935 ± 120 filaments, respectively.

Fig. 1 – CF tensile specimen with dimensions.

Fig. 1 shows CF specimen with end tabs (12mm long $\times$ 10mm wide $\times$ 1mm thick) manufactured according to a bonding technique which allows good impregnation of the fibres in a stiff consistent and insulating tabbing fixture [14,15]. The end tabs consisted of a glass fibre composite laminate (Gurit SA80) bonded to the fibres using an epoxy film (Gurit SE 84LV) cured under vacuum at 120 °C for 1 h. Each specimen was taped on a support paper, which was cut away before a tensile test, to avoid damage of the fibres during handling. The specimens were dried at 50 °C under reduced pressure for 24 h and placed inside the glovebox prior to cell assembly. The consistency of the

specimens produced with this method was evaluated in previous work [15] and the coefficient of variation of the tensile stiffness and the UTS of specimens manufactured from the same tow was about 5%.

2.2 Electrochemical cells and galvanostatic cycling

Fig. 2 is a schematic of a test cell. Each cell consisted of about four consistent CF specimens used as the working electrode, a glass microfibre separator (Whatman GF/A, 260 μm thick) impregnated with 150 μL of 1.0 M LiPF_6 in EC:DEC (1:1 w/w, LP40 Merck) electrolyte and Li metal (120 μm thick) used as counter electrode. Copper and nickel foils were used as current collector tabs for the carbon and Li electrodes, respectively. The whole layup is placed inside a vacuum heat sealed laminate bag (Skultuna Flexible, PET/Al/PE, 12 μm /9 μm /75 μm thick), which is a barrier against air and water, and ensure good contact between all layers.

Fig. 2 – Schematic of a test cell with four CF specimens used as electrode.

A Solartron 1286 Electrochemical Interface potentiostat controlled with the CorrWare software was used for the electrochemical measurements. Each electrochemical cycle consisted of four consecutive steps: a galvanostatic lithiation, an open-circuit potential (OCP) allowing the cells to relax for 15 min, and a galvanostatic delithiation ending with another 15 min OCP. For the galvanostatic steps, the constant current applied to the cell was chosen according to the mass estimate of CF electrode and the desired C-rate. The term xC-rate is for x times the 1C-rate in mA/g. The fibres were considered lithiated at 0.002 V vs. Li/Li^+ and delithiated at 1.5 V vs. Li/Li^+ . The measured specific capacity is defined as the amount of electric charges received and delivered by the cell for lithiation and delithiation, respectively. It reflects the amount of Li intercalated in

the CFs and is calculated from the current applied times the charging time divided by the mass of CF electrode.

2.3 Changes in the tensile properties after electrochemical cycling

For each test cell, the CF specimens were subjected to tensile tests inside the glovebox after finishing the electrochemical cycling. Tensile tests were also carried out on virgin specimens for reference. During the test, the load, extension and time data were sampled. A constant displacement rate of 0.1 mm/min was used to keep a slow strain rate. For each CF specimen, the ultimate tensile load, the tensile stiffness and the UTStrain were extracted from the force–displacement relation. A tensile-property change for a sample of CF specimens cycled in a cell was estimated with the normalized property according to Eq. (1):

$$P_n = P_{\text{cycling}} / P_{\text{virgin}} \pm \mu / P_{\text{virgin}} \quad (1)$$

where P_n is the normalized property, P_{cycling} and μ are the property mean value and standard deviation for the specimens after electrochemical cycling, respectively. P_{virgin} is the property mean value for the consistent virgin specimens used as reference.

2.4. Experimental procedures

Two experiment procedures were carried out for each CF grade. In a first procedure (procedure 1), the tensile-property changes were measured as function of the specific capacity after electrochemical cycling at constant C-rate. This was repeated with different cells for different C-rates and measured capacities. For each C-rate, two cells with three to four CF specimens each were run until the last-cycle delithiation was completed, and one of the two cells was run for an additional lithiation. Thus, the changes in the tensile stiffness and UTS induced by Li intercalation were measured on the lithiated and delithiated samples separately at each C-rate. The tensile tests were carried out more than 24 h after the last cycle to relax any post-cycling Li diffusion that may occur.

In a second experiment procedure (procedure 2), some CF specimens were subjected to electrochemical cycling during which the C-rate was varied according to a C-rate sequence A, and other CF specimens were subjected to electrochemical cycling during

which the C-rate was varied according to a C-rate sequence B. All specimens were subjected to tensile tests in the glovebox after the whole sequence of electrochemical cycling was completed, some in the lithiated state and some in the delithiated state. Electrochemical cycling at the C-rate sequence A consisted of five high-rate cycles (at 3.14C for IMS65 and 3.37C for T800H) followed by one low-rate cycle (at 0.10C for IMS65 and 0.09C for T800H). Electrochemical cycling at the C-rate sequence B consisted of three low-rate cycles (at 0.07C for IMS65 and 0.12C for T800H) followed by one high-rate cycle (at 2.11C for IMS65 and 3.93C for T800H).

3. Results and discussion

3.1 Cell capacity measurements during electrochemical cycling

Table 1 presents the cell capacities measured during electrochemical cycling for the different rates applied. For cycling of the cells, similar C-rates as in [14] were intentionally used to allow comparisons between the changes in the tensile properties and the fibre expansion. For the first cycle some Li is irreversibly used to form the solid-electrolyte interphase (SEI) at the surface of the CFs [16] and some Li is irreversibly trapped [14] resulting in a first-cycle capacity loss. For the next cycles the cell capacities can be considered as reversible between charge and discharge with good retention. The results at the last cycle (third cycle at 0.1C and fifth cycle for the other C-rates), show as in [9,14] that at higher current rates the diffusion of Li into the CF tows is rate limiting and the measured capacities are progressively lower. At lower rates, the measured capacities increase and approach the saturated value of lithium storage in pure graphite (372 mAh/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 specific capacity [mAh/g]	
	C-rate	Current rate [mA/g]			Lithiation	Delithiation
IMS65	5.93C	1050	0.05	55	53	53
	2.31C	409	0.28	102	113	112
	1.03C	182	0.93	144	169	167

	0.37C	66	4.02	118	265	263
	0.13C	22	13.88	110	309	304
	6.99C	951	0.05	51	48	48
	3.20C	435	0.23	99	101	97
T800H	0.87C	118	1.47	138	174	173
	0.38C	52	5.01	157	262	259
	0.13C	17	20.77	153	353	345

3.2. Procedure 1: changes in the tensile properties as function of the measured capacity during electrochemical cycling at constant C-rate

The changes in the tensile stiffness and UTS induced by Li intercalation were measured on lithiated and delithiated samples separately at each C-rate presented in Table 1 and for both CF grades according to the procedure 1 described in Section 2.4.

Fig. 3a and b present the normalized stiffness and UTS for the specific capacities measured at the different C-rates presented in Table 1. The symmetric error bars are twice the normalized standard deviation. The tensile stiffness of a CF specimen was defined herein as the slope of the force [N] vs. tensile strain-relation where the deformation is linear elastic and was calculated with the method of linear least squares to fit data points between load limits of about 400 and 800 mN/tex as suggested for single filament [17]. As in [15], the tensile stiffness does not degrade with Li intercalation whatever the measured capacity. The shifts of stiffness data points (for lithiated and delithiated fibres, and for different capacities) are in the range of 5–10% and are attributed to a small loss of consistency related to the compliance of the loading and gripping systems, especially since no external extensometer was used and the specimen gauge length was short. The UTS drops when Li is inserted in the CFs (lithiation), and increases when Li is extracted (delithiation). An irreversible drop in the strength is measured on the delithiated fibres. For IMS65, the drop in the strength of delithiated and lithiated CFs is larger for increasing measured capacities, and the maximum is about 17% and 35%, respectively, at 309 mAh/g (0.13C-rate). For T800H the drop in the UTS has a maximum of 9% and 22% at 174 mAh/g (0.87C-rate) for delithiated and lithiated CFs, respectively, and remains the same at higher capacities.

Fig. 3 – Normalized tensile stiffness (K) and UTS of (a) IMS65 and (b) T800H specimens as function of the specific capacity at the last electrochemical cycle.

Fig. 4a and b show representative normalized tensile curves of specimens before and after electrochemical cycling. No obvious changes can be seen on the tensile stiffness (represented by the initial slope of the curves) and the UTS clearly drops when the fibres are lithiated. In particular, it is clear on these curves that the failure at the ultimate tensile force looks sharp for the virgin specimens, whereas it occurs more continuously for the lithiated specimen. Similar effect was seen on virgin specimen left in liquid electrolyte suggesting that the viscosity of the electrolyte may affect the friction between fibres and make failure occur more gradually [15]. However, no obvious force drops indicating premature failure of a significant numbers of filaments can be seen before the ultimate force is reached.

Fig. 4 – Normalized tensile curves of (a) IMS65 and (b) T800H specimens lithiated at different C-rates.

In order to further investigate possible uneven loading of the filaments in the tows, Fig. 5a and b show the normalized tensile stiffness of the samples lithiated at the different C-rates as function of the normalized applied tensile strain. For each point the stiffness was calculated with the method of linear least squares to fit data points between ± 0.15 normalized strain. For IMS65, the normalized stiffness tends to be stable at a level slightly higher than unity and decreases continuously at normalized strain higher than 0.5 as failure approaches. For T800H the normalized stiffness is stable at a level slightly lower than unity and drops continuously at normalized strain higher than 0.6 as failure approaches. Despite some effects of the system compliance already mentioned, these plots do not show any significant changes or trends in the tensile stiffness which would indicate uneven mechanical loading of the filaments of the tows.

The drop in the UTS changes with the measured capacity, but not linearly, and may also depend on the C-rate. Some filaments might be less lithiated, have smaller longitudinal expansion [13], be loaded and fail earlier than those which are more lithiated, limiting the ultimate tensile force of the CF tow. However, the filaments are electrically connected and a concentration gradient of unevenly distributed Li between the filaments of the tow would relax within 24 h and before the mechanical testing.

Fig. 5 – Normalized tensile stiffness of (a) IMS65 and (b) T800H specimens as function of the normalized strain for the samples lithiated at the different C-rates.

3.3. Procedure 2: tensile property changes during electrochemical cycling at a varying C-rate

To investigate possible irreversible damaging of the CFs (such as cracks due to intercalated Li), the reversibility of the changes in the tensile properties with the measured capacity was investigated after electrochemical cycling at a varying C-rate according to the experiment procedure 2 described in Section 2.4. The measured capacities of the CF specimens are already characterised as function of the C-rate in Table 1.

Table 2 presents the normalized UTS and stiffness measured for each fibre grade after electrochemical cycling at the different C-rate sequences. The results are similar for both CF grades. The stiffness remains unaffected by Li-intercalation whatever the C-rate sequence. The drop in UTS appears to depend mainly on the last measured capacity of the sequence and is therefore larger in lithiated fibres after sequence A than after sequence B (37% against 20%, respectively, for lithiated IMS65 CFs for instance). In delithiated fibres, the drop in strength is also higher after sequence A (up to 15% for IMS65 fibres) than after sequence B and exhibits reversibility with the measured capacity and C-rate.

Table 2 – Normalized tensile properties after electrochemical cycling with varying C-rate.

	IMS65 fibres		T800H fibres	
	Lithiated	Delithiated	Lithiated	Delithiated
<u>Sequence A:</u>				
K	0.99 ± 0.06	1.01 ± 0.07	1.08 ± 0.05	1.08 ± 0.01
UTS	0.63 ± 0.01	0.85 ± 0.03	0.81 ± 0.02	0.92 ± 0.01
<u>Sequence B:</u>				
K	1.01 ± 0.07	1.03 ± 0.05	1.03 ± 0.05	1.10 ± 0.09
UTS	0.80 ± 0.01	0.91 ± 0.02	0.91 ± 0.03	0.98 ± 0.02

^a K is for the normalized tensile stiffness and UTS is for the normalized tensile strength.

From these results, the intercalated Li does not seem to create irreversible damages such as new cracks in the fibre, as already suggested after 1000 electrochemical cycles in [15]. If irreversible damages were created, the drop in the UTS of delithiated CFs after sequence B would be as low as after sequence A, i.e., governed by the lowest C-rate, but it is not. Thus, in sequence B some Li trapped in delithiated fibres during low-rate cycles is extracted again during high-rate cycles. These results suggest that intercalated Li simply induces free elastic (reversible) strains in the microstructure of CFs which consequently are pre-stressed in tension and exhibit lower strength in tensile tests. Therefore, some strength is recovered during delithiation as Li is extracted, and the remaining strength loss after delithiation is attributed (as also shown in [14]) to some residual Li trapped in the delithiated fibres pre-stressed in tension (and not irreversibly damaged by the formation of new cracks in the microstructure).

3.4 Comparison between the drop in the UTS and the CF expansion

The drop in strength might relate to a free elastic strain induced by the intercalated Li in the microstructure of the CF filaments which would therefore be pre-stressed after lithiation and exhibit lower UTS and UTStrain in tensile test. The longitudinal expansion of the CFs measured in [14] has also been suggested to be a measurement of the tensile pre-strain which grows progressively in the structure of CFs during Li-intercalation. In this case, the expansion strain in a lithiated specimen should compare with the drop of UTStrain in tensile tests, $\Delta\epsilon_u$, which was calculated from the elastic

stiffness of the specimen (as for calculation of the expansion in [14]) according to Eq. (2) as suggested in [18]:

$$\Delta\epsilon_u = \Delta F_{\max} / K \quad (2)$$

where $\Delta F_{\max}$ is the difference between the ultimate tensile force (N) of the virgin sample and the one of the specimen and K (Nm/m) is the specimen stiffness.

Fig. 6a and b compares the drop in the UTStrain measured in the tensile tests with the CF longitudinal expansion [14] for the lithiated IMS65 and T800H samples, respectively, as function of the measured capacities during electrochemical cycling. For each point representing the drop in the UTStrain, the symmetric error bars are twice the sample standard deviation long and centred on the sample mean. The overall trends and orders of magnitude of the plots are comparable. Both the longitudinal expansion and the UTStrain drop tend to increase with the measured capacity and the overall results seem to confirm that both the longitudinal expansion and the UTStrain drop relate to a tensile strain growth in the CF filaments.

Fig. 6 – Comparison between the measured drop in the UTStrain ($\Delta\epsilon_u$) and the longitudinal expansion (exp.) measured in [14]. The results are given for lithiated (li.) and delithiated (deli.) (a) IMS65 and (b) T800H specimens as function of the measured specific capacity after about 5 electrochemical cycles.

However, at the highest measured capacities the drop in the UTStrain is significantly lower than the longitudinal expansion. The drop in the UTStrain increases until

measured capacities of about 270 and 180 mAh/g for IMS65 and T800H, respectively. For higher capacities (cycling at about 0.3C and 0.1C-rates), the longitudinal expansion keeps on increasing to about 1% whereas the UTStrain drop stabilizes around 0.5–0.7%, so that some of the intercalated Li expands the fibre without further affecting the UTS. When measuring $\Delta\epsilon_c$ directly from tensile curves the overall trends and values are similar and lead to the same conclusions.

In order to further interpret the differences between the expansion and the drop in the UTStrain, it is possible to look at the total strain in the CFs at failure. The total strain at tensile failure in the virgin fibres is only the applied mechanical strain (failure strain measured in tensile test). However, the total strain at tensile failure in the fibres after electrochemical cycling should be the sum of the applied mechanical strain (failure strain measured in tensile test) and the lithium-intercalation expansion strain (measured in [14]). Fig. 7a and b plot the total strain at tensile failure in the specimens after electrochemical cycling normalized by the total strain at failure in the virgin specimens (assuming measurement at the same capacities). We can see that in the fibres after electrochemical cycling the expansion strain does not simply superimpose over the mechanical strain, otherwise the sum of these two strains would be equal to the failure strain of the virgin fibres and the values plotted would be equal to 1. After lithiation, the values are lower than 1 at low capacities (less than 150–200 mAh/g) for which failure is happening at lower total strain than in the virgin fibres. As a consequence, lithiation may be causing early failure via an additional mechanism which adds to simple expansion strain. At higher capacities, the values plotted are higher than 1 which indicates that failure of lithiated fibres occurs at higher total strain than failure of virgin fibres. This indicates that the fibres further expand without or faster than strength degradation, which may indicate an apparent toughening.

3.5. Discussion of the possible mechanisms governing the strength and the total strain at failure in lithiated CFs

In order to discuss these results as a whole, it may be useful to first look at the microstructure–tensile property relationships in virgin carbon fibres, i.e., the micro-mechanisms of strength and strain. PAN-based CFs can be seen as having a microcomposite structure, made of turbostratic folded and interlinked carbon layers forming fibrils of graphitic crystallites almost aligned with the fibre axis and immersed

in a micromatrix of quasi-amorphous carbon [19]. Useful lamellar models based on the microtexture of the CFs explaining the experimental data and tensile properties can be found [20,21]. The CFs modulus is mainly determined by the crystallites size and their degree of orientation with respect to the fibre axis. The tensile strength of the fibre depends on the amount of flaws. It also increases with the density of so-called “defective areas”, i.e., lateral bonds (such as tetrahedral bonds) between adjacent layers which provide lateral cohesion, enhance sensitivity (impede transversal microcracks propagation) and permit a larger elongation before catastrophic fracture. Lateral bonds in the CF microstructure have high chances to arise during heat treatment in a turbostratic and compact texture with high number of folds per crystallites. For high tensile strength fibres which have small crystallite size, the strength was found to increase with a relative visual criterion called “compactness index” defined on transverse cross-sections. No compactness indexes are available for comparison between IMS65 and T800H, but this description suggests that the drop in the UTS of Li-intercalated CFs might also relate to the transversal expansion of the CF which corresponds to a drop of compactness. Measurement of transverse expansion on fully lithiated fibres in [14] exhibit high coefficient of variation and no data is available at different capacities. This transverse expansion might for example, as already reported for graphite electrodes [22,23], drive carbon layers locally closer to delamination at small capacities. This would cause premature failure in tensile test, with lithiated fibres breaking at lower strength and lower total strain than virgin fibres as shown in Figs. 3 and 7, respectively. In the same time, increasing Li-concentration in graphite intercalation compounds was reported to significantly strengthen the interlayer bonding but slightly soften the intralayer bonding [24]. This improvement in the filament lateral cohesion at high capacities could explain a limited drop of strength and the higher total strain at failure than in virgin fibres shown in Fig. 7. No evidence is available for this discussion, but a possible relationship between the transverse expansion and the strength and strain to failure of a lithiated fibre should be considered in future research.

Fig. 7 – Sum of the tensile failure strain (ϵ_u) and the expansion strain (Exp.) measured in [14] normalized by the tensile failure strain of virgin specimens ($\epsilon_{u,\text{Vir}}$). The results are given for lithiated (li.) and delithiated (deli.) (a) IMS65 and (b) T800H specimens as function of the measured specific capacity after about 5 electrochemical cycles.

Another explanation of the results might also come from the tensile failure mode of CFs which is described by the Reynolds and Sharp mechanism [25–27]. When a tensile stress is applied to the fibre, the crystallites align until their movement is restricted by misoriented crystallites (carbon layers stacks linking crystallites parallel to the fibre axis) which will rupture prematurely and relieve shear stress. Catastrophic failure of the fibre occurs if the ruptured crystallite is (i) larger than the critical flaw size in the transverse directions or (ii) sufficiently continuous with the neighbouring crystallites for a crack to propagate. Misoriented crystallites were often found in the walls of the flaws which initiated failure [26], showing that structural organisation may be more important than flaw population. The strength of the CFs might be affected by the degree of lithiation of the misoriented crystallites which initiate failure, and the strength drop might depend on the occurrence and size of these. Lithiated CFs may fail at lower strength and lower total strain than virgin fibres at low capacities if the misoriented crystallites are preferentially lithiated by the beginning of a lithiation, i.e., at low capacities in Figs. 3 and 7. On the contrary, at higher capacities once these weak misoriented crystallites and their close surroundings are highly and uniformly lithiated,

further Li-intercalation in distant well-oriented crystallites or in the amorphous carbon matrix would still contribute to the global fibre longitudinal expansion but would not further affect the strength. Oriented crystallites, even fully lithiated, would not initiate failure and the lithiated fibres could then fail at higher total strain than the virgin fibres. This discussion is novel and no evidence is available, such as a mass fraction estimate of these misoriented crystallites. It may only be mentioned that lithiation mechanisms in graphite and disordered carbons were investigated in previous research [28–33]. Several authors report that the intercalation of Li in the ordered part of the carbon, i.e., between the layers of graphite crystallites, may occur more easily and prior to intercalation in the disordered areas (such as microvoids and amorphous carbon matrix where large amount of Li can also be accommodated and which could have a mass fraction in the order of 0.5 [19]). Therefore, the crystal structure which is driving failure might be likely to be saturated before the fibre is fully lithiated, but there is no clear evidence. Indeed, the strength of T800H and IMS65 CFs in Fig. 3 is only affected by Li-intercalation at measured specific capacities lower than about 150 and 275 mAh/g, respectively, which may also highlight some differences between the microstructure of IMS65 and T800H. The microstructural order of a CF increases significantly with the final temperature of heat treatment during manufacture. Therefore, it will be important in future research to compare the strength of lithiated CFs having different microstructures, i.e., different degrees of graphitization and crystallinity.

4. Conclusion

The use of CFs as structural electrodes is viable and the impact of Li intercalation on the tensile properties of the CF does not compromise the development of structural batteries. The tensile stiffness appears to remain unchanged with the measured specific capacity, contrary to the UTS which drops during lithiation but is partly recovered during delithiation. From a mechanical point of view, a drop in strength is in most cases much less severe than a loss of stiffness. The first-cycle capacity loss appears to be partly caused by Li irreversibly trapped in the delithiated CFs. The drop in the UTS (i) remained less than 40% when the CFs are lithiated to saturation at very low C-rate, (ii) was lower for smaller capacities measured at very high C-rates, and (iii) exhibited reversibility with the C-rate and the measured capacity. These results suggest that the

inserted Li creates elastic strains in the CF which is pre-stressed in tension rather than irreversible damage to the fibre.

However, the drop in the UTS did not vary linearly with the measured capacity and tend to stabilize at the highest measured capacities. When the CFs were fully lithiated (at the lowest C-rates) the drop in the UTStrain remained lower than the CF longitudinal expansion induced by the intercalated Li. This result suggests that the loss of strength might depend on the degree of lithiation of defective areas which govern the tensile failure mode of the CFs. Therefore, it remains of high interest to further understand the impact of intercalated Li on the CF microstructure in future research.

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