EFFECT OF LITHIUM-ION INTERCALATION ON THE TENSILE PROPERTIES OF CARBON FIBRES FOR ENERGY STORAGE COMPOSITES

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Abstract
Carbon fibres can be used as structural electrodes because they have a high tensile properties-to-weight ratio and a graphitic structure which enables lithium-ion intercalation. Carbon fibre specimens were used as electrodes in laboratory cells. It was found that the fibre undergoes an ultimate tensile strength drop and an axial expansion which depend on the measured capacity. The results suggest that a tensile strain develops in the carbon fibre which is pre-stressed in tension and that this pre-stress correlates with the amount of lithium-ions intercalated.

1 Introduction
1.1 Scope
Mass savings is a key issue in the development of many systems that require electrical energy and a structure able to bear mechanical loads such as hybrid vehicles or laptops. Structure and energy storage devices are generally the heaviest components but their functions are entirely separate. Mass reduction is therefore possible by combining these two functions in a multifunctional lightweight material able to simultaneously bear mechanical loads as carbon fiber composites and store electrochemical energy as rechargeable lithium-ion batteries.

1.2 Background
Carbon fibers can be used as electrode in lithium-ion batteries because they have a conductive graphitic structure which enables lithium-ion insertion and extraction during lithiation (charge) and delithiation (discharged) respectively. Previous work [1, 2] has shown that intermediate modulus (IM) Polyacrylonitrile (PAN)-based carbon fibres are particularly suited for structural batteries applications where both stiffness and strength are required. They exhibit the best overall electrochemical capacities which suggests that their disordered carbon structure is more favorable for lithium-ion intercalation than the highly graphitized structures of Pitch-based fibres. However, the capacity of PAN-based fibres depends on the charge rate [3]. The term 1C-charge rate is used when the charge time is one hour and the term xC-charge rate is for x times the 1C-charge rate in mA/g. It was shown in [4] that the tensile stiffness of the carbon fibre is unchanged during electrochemical cycling. The tensile strength drops during lithiation and is partly recovered after delithiation but does not degrade with the cycle

count. The fibre also swells and shrinks in the length direction during lithiation and delithiation, respectively [5].

1.3 Aims
This paper continues the investigation on the mechanical performance of carbon fiber structural electrodes. The work focuses on the change in the fibre ultimate tensile strength and the fibre axial expansion during lithium-ion intercalation. Both are expected to depend on the measured capacity, i.e. the amount of lithium ions intercalated. One grade of PAN-based carbon fibers that exhibits a good capacity was selected. Tensile specimens made of dry carbon fiber strands are used as electrode in laboratory lithium-ion cells and cycled at 6C, 3C, 1C and about 0.40C-charge rates. Some specimens are subjected to tensile tests after cycling to measure the tensile stiffness and ultimate strength in lithiated and delithiated states. Other specimens are subjected to a tensile load during cycling for measurement of the axial expansion. The results are presented as function of the capacity measured during cycling.

2 Theoretical
2.1 Cell potential and redox reaction
Lithium metal has the lowest standard electrode potential and is therefore the negative electrode with the fiber as the positive electrode. The cell potential is the difference between the potentials of the positive and the negative electrode. Lithium metal is considered as an infinite source of lithium ions which has a constant potential. The concentration of lithium in the electrolyte is also constant. Thus, any change in the cell potential is attributed to the potential of the carbon fiber electrode which depends on the concentration of lithium ions in the fibers during cycling. Reaction (1) is the total redox reaction in the cell:

$$\text{Li}_{x(s)} + \text{C}_{6(s)} \xrightleftharpoons[\text{delithiation}]{\text{lithiation}} \text{C}_6\text{Li}_{x(s)} \tag{1}$$

where *x* is an unknown parameter which depends on the chemical composition of the fiber.

2.2 Specific electrochemical capacity
The specific capacity measured $C_s^{measured}$ is defined as the amount of electric charges received and delivered by the cell for lihtiation and delithiation, respectively. It reflects the amount of lithium ions which are intercalated in the carbon fibers and is calculated with equation (2):

$$C_s^{measured} = I * t / m \tag{2}$$

where *I* is the constant current, *t* is the charge time and *m* is the mass of the fiber electrode. A passivation layer about 10nm thick, the solid-electrolyte interphase (SEI), caused by a decomposition of the electrolyte is formed during the first cycle at the surfaces of the carbon fibre electrode [6]. Some lithium ions are used for the first lithiation to form the SEI layer and some other are irreversibly trapped in the carbon fibre microstructure. This process causes an irreversible first-cycle capacity loss which depends on the electrolyte formulation and on the specific surface area of the carbon electrode. For the next cycles the cells exhibit a capacity that can be considered as reversible between charge and discharge and with good retention.

2.3 Tensile stiffness of the carbon fiber specimens
The tensile stiffness of a carbon fiber specimen was defined herein as the slope of the tensile curve (force [N]) vs. (percent elongation [%]) where the deformation is linear elastic. It was

calculated with the method of linear least squares to fit data points between load limits of 400mN/tex and 800mN/tex as suggested for single filament in [7].

2.4 Axial expansion of the carbon fiber caused by lithium-ion intercalation
The carbon fibre swells and shrinks in the length direction because of lithium-ion intercalation but the tensile stiffness remains unchanged as mentioned in 1.2. One way to measure this axial expansion is to charge and discharge carbon fibres while they are subjected to a constant tensile strain. The tensile load carried by the fibres is measured during lithiation and delithiation. It varies because of the fibre axial expansion which is calculated as the variation of the tensile load divided by the tensile stiffness of the specimen.

3 Experimental
*3.1 Glovebox and tensile test rig*
Lithium is oxidized in contact with air and water. Lithium ion-cells were manufactured inside a glovebox that is in inert argon atmosphere with less than1 ppm $[O_2]$ and $[H_2O]$ at ambient temperature. Tensile tests on lithiated and delithiated carbon fibres were also carried out inside the glovebox using a microtester which is a 300N tensile stage from Deben UK.

3.2 Carbon fibre electrode material
IM PAN-based carbon fiber Toho Tenax IMS65 24K 830tex unsized, that is a yarn containing 24000 filaments (24K) which have never been sized, was chosen for its good specific capacity in comparison with other fibres tested prior to this work by the authors [3]. The fiber exhibited a capacity of 177mAh/g with a good retention after 10 cycles at 1C-charge rate.

3.3 Carbon fibre tensile specimens
Tensile specimens were manufactured from a dry carbon fibre strand. The number of filament per specimen had to be typically lower than 4000 so that the ultimate tensile load was below the 300N of the load cell. Manufacturers do not produce a yarn containing such a low number of filaments for the carbon fibre grade selected. However, it was possible to divide the 24K yarn properly into a lighter one over a length sufficient to manufacture the required amount of consistent tensile specimens with 22mm gauge length. The consistency of the specimens was checked with a series of tensile tests. Strands were collected at the middle and the ends of the lighter yarn and weighed to predict the mass of carbon fibre electrode in each specimen and the scatter due to the splitting process. It was of 2.0±0.1mg per specimen that is 2687±134 filaments. Figure 1 shows an image of a specimen with end tabs which fit in the microtester.
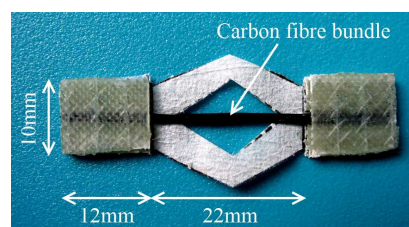
Figure 1. IMS65 carbon fibre tensile specimens with the end tabs and dimensions.

12mm long×10mm wide×0.7mm thick end tabs were cut from insulating glass fibre composite plates made by curing Gurit SA80 prepreg. The light carbon fibre yarn was slightly pre-stretched with tape while end tabs were bonded to the fibres along the yarn. Gurit SE 84LV epoxy prepreg was used for impregnation of the fibres between end tabs. The epoxy films were cured in a vacuum bag at 120°C for 1h. A breather fabric was used to absorb the resin which could flow along the fibres during cure. Each specimen had its end tabs taped on

paper to keep the fibres straight and avoid damage during handling. The support paper was cut away before tensile test. This bonding technique allowed good impregnation of the fibres in a stiff consistent and insulating tabbing fixture. The specimens were dried at 50°C under reduced pressure for 24h and placed inside the glovebox prior to cell assembly.

3.4 Lithium-ion pouch cell

The carbon fibre specimens were used as electrode in laboratory lithium-ion cells made of four layers. A first layer is the working electrode, i.e. the carbon fibre specimens. A second layer is the separator which is a 260 µm thick glass microfibers filter with porosity of 90% from Whatman impregnated with 150 µL of liquid electrolyte. The electrolyte is made of ethylene carbonate (EC) and diethyl carbonate (DEC) in 1 to 1 relation by weight (1:1 wt. %) with a concentration of lithium hexafluorophosphate $LiPF_6$ in the solvents that is 1 mol/dm^3 (1M). A third layer is the counter electrode which is a lithium metal foil. The electrodes are connected to the outer circuit via current collector tabs consisting of a copper foil and a nickel foil for the carbon and the lithium electrode, respectively. The assembly is placed inside a laminate bag from Skultuna Flexible made of polyethylene terephthalate (PET)/aluminum (Al)/polyethylene (PE) which is 12µm/9µm/75µm thick, respectively. The aluminum foil is a barrier against water and oxygen while the thermoplastic layers allow heat sealing of the bag to prevent the electrolyte from evaporating. Vacuum is drawn from the bag while it is sealed to ensure good contact between all layers.

3.5 Electrochemical cycling

The current collectors of the cells were connected to a Solartron 1286 Electrochemical Interface potentiostat controlled with the CorrWare software that cycles the cells and records the potential over time. Each cycle contained four consecutive steps. The first step is a galvanostatic lithiation. The current used for cycling was chosen according to the mass estimate of fibre electrode in the cell and the desired the charge rate in mA/g. The second step is an open-circuit potential (OCP) that allows the cells to relax for 15 min. The third step is a galvanostatic delithiation ending with another 15 min OCP. The fibres are considered completely charged at 0.002V vs. Li/Li$^+$ during lithiations and completely discharged at 1.5V vs. Li/ Li$^+$ during delithiations. When a cycle count was completed one cell was removed with delithiated specimens and the other one was run for an additional one hour lithiation.

3.6 Measuring carbon fibre tensile properties after cycling

Only the relative changes of the tensile properties are sought for herein. The specimens being consistent, their cross-section area could be considered as constant so that the relative changes in the fibre modulus and ultimate strength were the same as in the specimens' stiffness and ultimate load. They were directly measured between consistent specimens taken before and after cycling. Tensile tests were carried out on specimens in lithiated and delithiated states after electrochemical cycling at 6C, 3C, 1C and about 0.40C-charge rates. For each of these states a cell containing four specimens was assembled in a vacuum sealed bag and run for 5 cycles. The Microtest software from Deben UK was used for acquisition of load and extension and time data during tensile tests. A motorspeed of 0.1mm/min was used so that the strain rate remained very low because of the small gauge length of the specimens.

3.7 Measuring the carbon fibre axial expansion during electrochemical cycling

The axial expansion of the carbon fibre caused by lithium-ion intercalation was measured with a carbon fibre specimen subjected to a constant tensile extension during electrochemical cycling as explained in 2.4. For each charge rate, the measurement was made with a pouch cell containing a single carbon fibre specimen electrode. The vacuum bag containing the cell

components was clamped on the specimen tabbing inside the jaws of the microtester as illustrated in Figure 2. Flat clamps were used to avoid puncturing the bag.
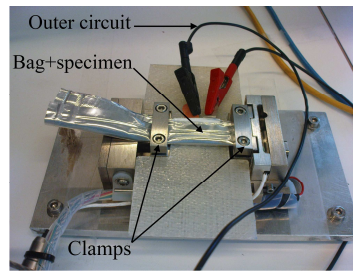
Figure 2. Cell with a specimen clamped in the microtester during electrochemical cycling.

A constant tensile extension was applied to the fibre specimen and the bag which were pulled in parallel. The load relaxation in the bag was recorded for 3h until it stabilized and the electrochemical cycling of the cell was started. Obvious variations of the tensile load were measured during lithium-ion intercalation and attributed to the axial expansion of the fibres.

4 Results

4.1 Charge rate and capacity measured during cycling

Table 1 reports first-cycle capacity loss and the capacity measured during lithiations after 5 cycles for the different charge rates used. For axial expansion measurement, a lower charge rate of 0.30C was used instead of 0.40C.

Charge rate		Measured charge time [h]	First-cycle capacity loss [mAh/g]	Measured capacity [mAh/g]	
C-rate	[mA/g]			5th delithiation	6th lithiation
5.93C	1050	0.054	55	52	44
2.82C	500	0.25	103	106	100
1.06C	188	0.98	152	175	169
0.40C	70	3.90	148	259	264
0.30C	60	5.6	146	295	285

Table 1. Cell capacity measurement at different charge rates.

The results show as in [3] that the lower the charge rate, the higher the charge time and capacity, i.e. the amount of lithium ions intercalated. For example at 0.40C-charge rate the capacity is more than twice the one at 2.82C-charge rate. It is also seen that the first-cycle capacity loss is higher for lower charge rates which correlates with the fact that more lithium ions are transferred during charge and discharge. From the second cycle the capacity was almost consistent with the cycle count and reversible between lithiations and delithiations.

4.2 Tensile properties

Figure 3 illustrates the normalized stiffness and ultimate load for lithiated and delithiated samples after cycling at the different charge rates. Each measurement corresponds to the sample mean of four tensile specimens after cycling normalized by the sample mean of the reference virgin specimens. The vertical bar is the sample coefficient of variation.
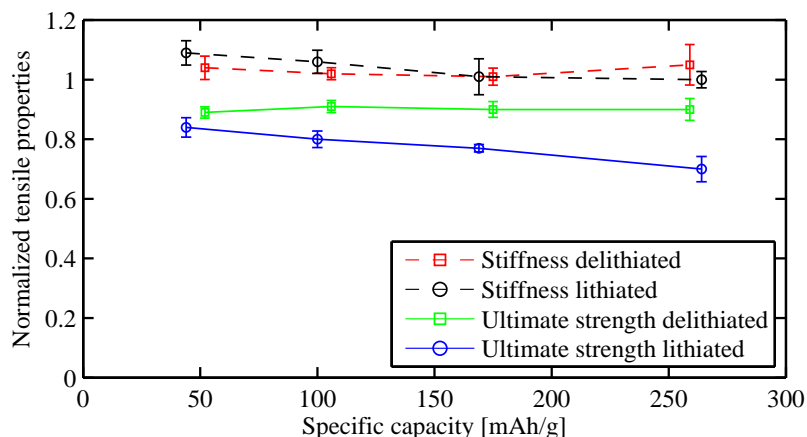
Figure 3. Normalized tensile properties of IMS65 carbon fibre for different measured capacities.

The tensile stiffness of charged and discharged specimens can be considered as unaffected whatever the charged rate. However, the ultimate tensile strength drops during lithiations when lithium ions are inserted and is only partly recovered during delithiations when lithium ions are extracted again from the structure of the carbon fibre. As for the electrochemical capacity, an irreversible loss of strength occurs by the first cycles. In the delithiated state the ultimate strength of the fibres drops about 10% and appears to be quite consistent with the capacity measured. The main impact of the capacity can be seen in the lithiated state. When the fibres are charged the ultimate strength drops only 16% for a capacity of 44mAh/g and about 30% for a capacity of 264mAh/g for example. Thus, the higher the capacity measured the higher the loss measured in the ultimate tensile strength.
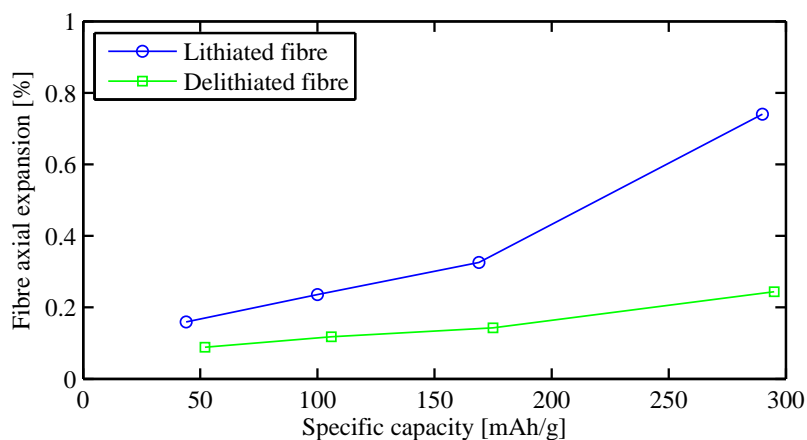
4.3 Axial expansion
Figure 4 shows the variation of the force carried by fibre specimens subjected to a constant extension during cycling at different charge rate. The force relaxation in the bag is obvious for the first 3h. The blue curve is for the bag relaxation only (when no fibres are loaded). It is used as reference to distinguish the variations of actual force carried by the fibre specimen. For each charge rate the force drops during lithiations when the fibres swell, is unchanged during potential relaxations and increases during delithiations when the fibres shrink.
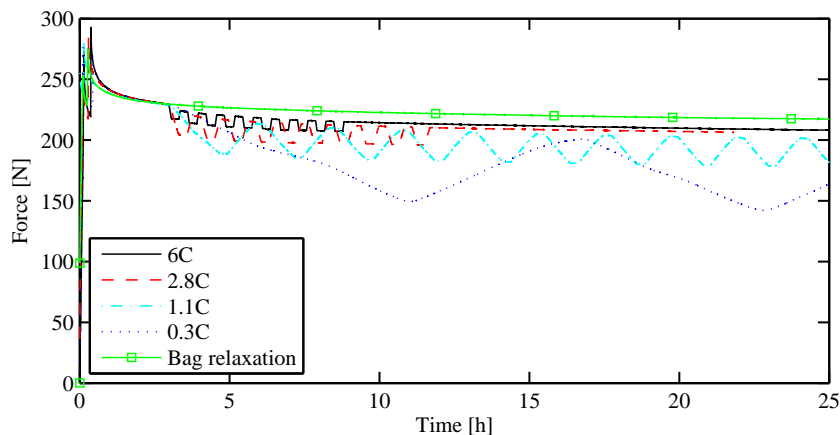
Figure 4. Tensile load carried by carbon fibre specimens under constant extension for electrochemical cycling.

The fibres swell in the axial direction during insertion of lithium-ion in their structure and shrink during extraction of the same. The axial expansion of the fibre was calculated dividing

the force variation by the tensile stiffness of the specimen which was measured in a tensile test after cycling. Figure 5 presents the results for the swelling and the shrinkage of the fibre due to lithium-ion intercalation after 5 cycles.

Figure 5. Axial expansion of IMS65 carbon fibre for different measured capacities.

The amplitude of the expansion depends on the capacity measured that is on the amount of lithium ions intercalated. There is an obvious first-cycle irreversible swelling measured in the delithiated state because the fibre swelling for the first lithiation is larger than the shrinkage for the first delithiation. For the next cycles the axial expansion is almost reversible.

5 Discussion

5.1 Predominant influence of the capacity

The results suggest that the capacity i.e. the amount of lithium ions intercalated in the fibre, has an impact on both the tensile strength and the axial expansion of the carbon fibre. During the first-cycle the irreversible loss of capacity results in an irreversible drop of the ultimate tensile strength and an irreversible axial swelling of the fibre. These variations depend on the charge rate and correlate in terms of percentage changes. For example when a higher first-cycle capacity loss is measured a larger amount of lithium ions may be irreversibly trapped in the fibres and a higher irreversible axial swelling is also measured. After the first cycle the capacity is almost reversible with good retention. The same behavior is illustrated by Figure 3 for the fibre axial expansion and was shown in [4] for the fibre tensile strength at 1C-charge rate. In addition, the amplitude of the axial expansion and the tensile strength loss vary almost linearly with the capacity measured. These tendencies support the idea that the amount of lithium ions intercalated has a predominant effect on the axial expansion and the ultimate tensile strength of the fibres. The diffusion of the ions in the fibre microstructure might have an impact that is minor because no obvious axial expansion was measured after charge during 15 min open cell potential relaxation.

5.2 Correlating the loss of ultimate strain with the fibre axial expansion

Figure 6 presents the losses measured in the fibre ultimate tensile strain after electrochemical cycling and the fibre axial expansion caused by lithium-ion intercalation. The plots correlate to some extent which suggests that the fibre axial expansion due to lithium-ion intercalation corresponds to an elastic tensile strain.
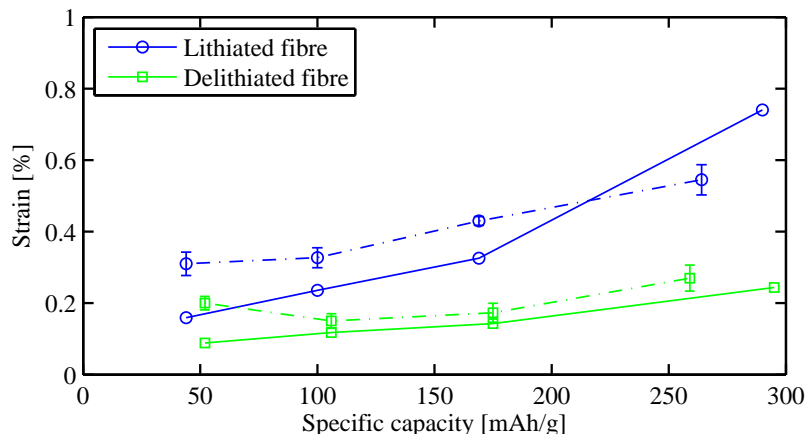
Figure 6. Losses in the carbon fibre ultimate tensile strain (dash-dot line) and fibre axial expansion (solid line) for different capacities.

The lithium ions inserted in the carbon fibre might create an elastic deformation and act as a tensile load. Thus, the fibres might be pre-stressed in tension after cycling and therefore exhibit a lower ultimate tensile strength in a tensile test.

6 Conclusion

Carbon fibre loses strength and swells in its length direction during lithiations whereas it recovers some strength and shrinks during delithiation. The amplitudes and variations of these losses and expansion depend directly and primarily on the capacity measured that is on the amount of lithium ions intercalated. These results suggest that the lithium ions inserted create tensile strain in the fibre which is therefore pre-stressed in tension.

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