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Impact of lithium-ion intercalation on the tensile properties of carbon fibers for use in energy storage composite material

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Abstract

Carbon fibres are particularly well suited for use in a multifunctional lightweight design of a structural composite material able to store energy as a lithium-ion battery. The fibres will in this case act as both a high performance structural reinforcement and one of the battery electrodes. However, the electrochemical cycling consists of insertions and extractions of lithium ions in the microstructure of carbon fibres and its impact on the mechanical performance is unknown. This study investigates the changes in the tensile properties of carbon fibres after they have been subjected to a number of electrochemical cycles. Consistent carbon fibre specimens were manufactured with polyacrylonitrile-based carbon fibres. Sized T800H and desized IMS65 were selected for their mechanical properties and electrochemical capacities. At the first lithiation the ultimate tensile strength of the fibres was reduced of about 20% but after the first delithiation some strength was recovered. The losses and recoveries of strength remained unchanged with the number of cycles as long as the cell capacity remained reversible. Losses in the cell capacity after 1000 cycles were measured together with smaller losses in the tensile strength of the lithiated fibres. These results show that electrochemical cycling does not degrade the tensile properties which seem to depend on the amount of lithium ions inserted and extracted. Both fibre grades exhibited the

same trends of results. The tensile stiffness was not affected by the cycling. Field emission scanning electron microscope images taken after electrochemical cycling did not show any obvious damage of the outer surface of the fibres.

Keywords: A. Carbon fibers, A. Hybrid composites, B. Strength, B. Mechanical properties, Electrochemical cycling.

1. Introduction

Reducing system mass has become a priority for a wide range of future applications. Many of them include load-bearing components in a system which requires electrical energy such as electric vehicles and laptops. Structure and energy storage are usually the subsystems with the highest mass contributions but energy storage devices have no structural function. A novel solution is a multifunctional lightweight design of a carbon fibre composite material able to simultaneously bear mechanical loads and store electrochemical energy as a rechargeable lithium-ion battery.

The advantages of secondary lithium-ion batteries are their high operating voltage, high specific energy, very slow self-discharge and no memory effect [1]. A lithium-ion battery consists of two electrodes between which a porous insulating separator prevents short-circuiting and an electrolyte conducts lithium ions from the negative electrode to the positive electrode during discharge and with a reversed flow during charge.

Electrons are transported via the current collectors to an outer circuit. Carbon fibres can be used as electrode because their structure is made of graphitic sheets and disordered carbon which enable lithium-ion intercalation [2]. The term lithiation is used for insertion of lithium ions and delithiation is used for extraction of the same.

Concepts of hybrid composite laminates have previously been studied [3,4], e.g. using a carbon fibre-fabric electrode to reinforce a solid polymer electrolyte (SPE). Pitch-based carbon fibres are commonly preferred for battery applications due to their higher degree of graphitization which give them a higher electrical conductivity [5]. Yet, previous research work has shown that polyacrylonitrile (PAN)-based fibres exhibit the best overall electrochemical capacities what suggests that their disordered carbon structure is more favourable for lithium-ion intercalation [2,6,7]. The mechanical properties of intermediate modulus PAN-based fibres also give them the widest range of applicability for structural batteries where both stiffness and strength are required.

However, possible changes in the structural performance of carbon fibres during cycling are still unknown. The graphitic microstructure is responsible for the mechanical properties of carbon fibres while it enables lithium-ion storage. Lithiations and delithiations are therefore expected to disrupt the morphology and the mechanical behaviour of the fibres. This study focuses on the impact of lithium-ion intercalation and extraction on the tensile properties of carbon fibres. Two grades of PAN-based fibres that exhibit good electrochemical capacities are selected, one sized unmodified and one desized (fibre sizing removed by solvent extraction). Tensile specimens made of dry fibre strands are used as carbon electrode and cycled in laboratory cells. Preliminary tensile tests are carried out on specimens which have never been cycled to check the consistency of stiffness and strength, the effects of desizing the fibres and of liquid electrolyte impregnation. Further tensile tests are performed on specimens after a number of cycles to measure the changes in the tensile properties. Field emission scanning electron microscope (FE-SEM) images of fibres after cycling are used to look at the changes of the fibre diameter and the possible damage of the fibre surface.

2. Experimental

2.1. Glove box environment

Lithium is quickly oxidized in contact with air and water. Manufacturing of cells and tensile tests of fibre specimens after cycling were therefore carried out inside a glove box with inert argon atmosphere at 25 °C and less than 1 ppm [O₂] and [H₂O].

2.2. Tensile test rig

Tensile tests were carried out inside the glove box using a micro tensile stage from Deben UK equipped with a 10 mm travel extensometer and a 300 N load cell. An air tight electrical junction was built to fit in the wall of the glove box and to connect the tester inside the box to its control unit standing outside.

2.3. Carbon fibers

The study focuses on continuous and straight intermediate modulus PAN-based carbon fibres tailored to suit applications where both stiffness and strength are of priority. The specific capacities of a wide range of sized and desized PAN-based fibres have been measured by the authors in [8] with the same cell configuration, electrolyte and test

parameters as in this study. Two types of fibre grades were selected for their good capacity in comparison with the theoretical saturated value of 372 mAh/g for pure graphite [1]. The first grade was Toho Tenax IMS65 E23 24 K desized by the authors. The specific capacity of desized IMS65 fibres was particularly good, 131 mAh/g at a moderate rate with excellent capacity retention after 10 cycles. The second grade was Torayca T800HB 6 K 40B P1 BB. The sized T800H fibre exhibited a specific capacity of 136 mAh/g with similar retention behaviour after 10 cycles as the desized IMS65 fibre.

2.4. Splitting yarns

Tensile specimens were manufactured from dry carbon fibres strands. A single filaments exhibits a scatter of about 5% on its diameter and may be more sensitive to micro defects and sizing distributions, but the high number of filaments in a strand may have a predominant ameliorative effect on the mean results. The number of filament 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 carbon fibres yarns containing such a low number of filaments for the two grades selected. However, since the filaments were straight and sized it was possible to divide each yarn properly into a lighter one with lower number of filaments over a sufficient length, typically of 8 m, to manufacture the required amount of consistent tensile specimens having a 22 mm gauge length. The consistency of the specimens was checked with a series of tensile tests. The cross-section area of the specimens could then be considered as constant but it was not determined because it is the relative changes of the tensile properties which are needed for modelling work. The relative changes in the fibre modulus and the strength were thus assumed to be the same as in the stiffness and the ultimate force of the specimens. They were directly measured between consistent specimens taken before and after cycling.

However, 22 mm long strands collected at the middle and the ends of the lighter yarns were weighed to predict the mass of carbon fibre electrode in each specimen and the scatter due to the splitting process. The strands of IMS65 specimens were of about 2.6 ± 0.1 mg that is 3417 ± 131 filaments considering the nominal linear density of the full 24,000 filaments yarn is 830 tex (1 tex = 1 g/1000 m). So the scatter was roughly of $\pm 3.8\%$. The strands of T800H specimens were of about 1.9 ± 0.1 mg that is 2324 ± 122

filaments and a scatter of roughly $\pm 5.2\%$ considering the nominal linear density of the full 6000 filaments yarn is 223 tex. These variations were measured along 8 m of yarn, but the specimens of a cell were collected over the same 30 cm of yarn which might reduce the scatter.

2.5. Fibers desizing

Sized T800H and desized IMS65 were selected for this study. The sizing was removed from IMS65 carbon fibres using solvent extraction. Fibres were put in a vessel of acetone placed on a shaking table for 4 days. After the extraction, the fibres were dried at 50 °C under reduced pressure for 24 h to drive off excess solvent and water. FE-SEM imaging and tensile tests were carried out on fibres before and after treatment to check the extent of sizing removal and the impact on the tensile properties.

2.6. Specimen tabbing

The purpose of the tabbing was to properly transfer the load from the jaws of the tester to the fibres and to minimize the risk of stray fibres causing short-circuits once the specimens were put into an electrochemical cell. [Fig. 1](#) presents an image of a finished tensile specimen with its end tabs and dimensions. A consistent tabbing that fits in the jaws of the tester was developed for 46 mm long fibre specimens. End tabs 12 mm long $\times$ 10 mm wide $\times$ 0.7 mm thick were cut from insulating glass fibre composite plates made of cured Gurit SA80 prepreg. The fibre yarns were slightly pre-stretched with tape. Two end tabs were bonded to the fibres at the ends of each specimen. An adhesive film of Gurit SE 84LV epoxy was used for impregnation of the fibres between the end tabs. The epoxy was cured in a vacuum bag at 120 °C for 1 h. A release film and a breather fabric were used to absorb the extra amount of resin which could flow from the end tabs along the fibre strand during cure. Each specimen was taped on paper to keep the fibres straight and avoid damage during handling. The support paper was cut away before each tensile test. This bonding technique allowed good impregnation of the fibres in a stiff and insulating tabbing fixture. The specimens were dried at 50 °C under reduced pressure for 24 h and placed inside the glove box prior to cell assembly.

Fig. 1. Finished tensile specimen with its end tabs and dimensions.

2.7. Pouch cells

Specimens were used as electrode in a layered electrochemical pouch cell design shown in a sectional view in Fig. 2. The first layer is the combined reference and counter electrode made of a 120 μm thick lithium metal foil. The second layer is the separator which is a 260 μm thick glass micro fibre filter with porosity of 90% from Whatman impregnated with 150 μL of liquid electrolyte made of ethylene carbonate and diethyl carbonate 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 (1 M). The third layer is the working electrode made of carbon fibre specimens also impregnated with electrolyte. The electrodes are connected to the outer circuit with current collector tabs consisting of a copper foil for the carbon electrode and a nickel foil for the lithium electrode. The whole assembly is in a PET/Al/PE laminated bag from Skultuna Flexible which is 12 μm /9 μm /75 μm thick, respectively. Aluminum is a barrier against water and oxygen whereas the thermoplastic layers allow heat sealing of the bag. Vacuum is drawn from the bag while it is sealed to ensure good contact between all layers and to prevent evaporation of the electrolyte.

Fig. 2. Schematic of the layered structure of a cell sealed under vacuum with a carbon fibre tensile specimen used as electrode.

2.8. Electrochemical cycling

Tensile tests were carried out after 1, 10, 100 and 1000 electrochemical cycles on lithiated and delithiated specimens. For each of these cycle counts, two pouch cells containing three to four specimens each were assembled in two separate vacuum sealed bags. They were connected in parallel with their current collectors and cycled simultaneously. The same experiments were performed for each fibre grade. The current collectors of the cells were connected to a Solartron 1286 Electrochemical Interface potentiostat controlled with the CorrWare software that runs the cycling and records the cells potential over time. Each cycle contained four consecutive steps. The first step is a galvanostatic lithiation. The current used for cycling depended on the mass estimate of the fibre electrode in the cell. It was chosen to have a charge rate of 136 mA/g for T800H-electrodes and 131 mA/g for desized IMS65-electrodes so that the charge time was of about 1 h. 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. During lithiations the fibres are considered completely charged at 0.002 V vs Li/Li⁺. During delithiations the fibres are completely discharged when the cell potential reaches 1.5 V vs Li/ Li⁺. When a cycle count was completed one cell was removed with delithiated specimens and the other one was run for an additional 1 h lithiation.

2.9. Tensile tests

The Microtest software from Deben UK was used for acquisition of load, extension and time data during tensile tests until failure of the specimen. The sample time was of 100 ms. A low displacement rate of 0.1 mm/min was used because of the small gauge length of the specimens so that the strain rate remained very low, of about $7.6 \times 10^{-5} \text{ s}^{-1}$. Before cycling a pouch cell, tensile tests were carried out on specimens never cycled and manufactured from the same yarn as the ones used as electrode in the cell. The purpose was to check the consistency of the specimens in the cell and to get reference values to normalize the tensile properties after cycling. When the cycling of a cell was completed, tensile tests were carried out inside the glovebox on the fibre specimens used as electrode immediately after the cell was opened.

2.10. FE-SEM imaging of the surface of the fibres

The possible changes in the surface of the fibres due to cycling were studied with IMS65 fibres which have circular cross-sections. FE-SEM Hitachi S-4800 was used to observe surfaces and cross-sections before and after cycling. Lithiated fibres were mounted on stubs with holders inside the glovebox and placed in sealed bags to minimize the time of contact with open air during the transfer into the FE-SEM.

3. Theoretical

3.1. Redox reactions

Lithium metal has a lower standard electrode potential than the carbon fibre and is therefore the negative electrode with the fibres as the positive electrode. During a lithiation, reactions (1) and (2) give the reduction and oxidation reactions that occur at the positive and negative electrodes respectively. Reaction (3) is the total cell reaction:

where x is an unknown parameter which depends on the chemical composition of the carbon fibres. During a delithiation the reversed reactions occur in the cell.

3.2. Cell potential

The cell potential is the difference between the potentials of the positive electrode and the negative electrode. Lithium metal can be considered as an infinite source of lithium ions which exhibits a constant potential. Any changes in the cell potential can be attributed to the carbon fibre electrode as the concentration of lithium in the electrolyte is constant. The change in the potential during lithiation and delithiation depends on the concentration of lithium ions inserted in the fibres.

3.3. Specific electrochemical capacity

The specific electrochemical capacity measured for a lithiation C_s^{measured} is defined as the amount of electric charges received by the cell for the duration t of the lithiation normalized by the mass m of the carbon fibre electrode. The capacity reflects the amount of lithium ions inserted in the fibres and is calculated with equation:

$$C_s^{\text{measured}} = I \times t / m \quad (4)$$

where I is the constant current used to cycle the cell. The specific capacity measured for a delithiation refers to the amount of electric charges delivered by the cell.

3.4. Capacity retention

A thin passivation layer about 10 nm thick, the solid-electrolyte interphase (SEI), caused by a decomposition of the electrolyte is formed during the first cycle of a cell at the surfaces of the carbon electrode which can thus work in its stability range [9]. Some lithium ions are incorporated into the SEI. This process causes an irreversible loss of capacity which depends primarily on the electrolyte formulation and on the specific surface area of the carbon electrode. Over the first tens of cycles the capacity exhibited less than 5% of variation between charge and discharge and between consecutive cycles. The capacity could therefore be considered as reversible with good retention.

3.5. Ultimate tensile load and tensile stiffness

The ultimate tensile load was defined as the maximum tensile load that the specimen can withstand before failure. The tensile stiffness of a specimen was defined as the slope of the tensile curve (force (N)) vs. (extension (%)) where the deformation is linearly elastic. The extension is the relative displacement between the jaws of the tester in percentage of the original gauge length. It is affected in absolute by the compliance of the tester and the tabbing fixture but these appeared to be consistent for all tests. The

stiffness was calculated with the least square method between load limits of 400 mN/tex and 800 mN/tex as it is suggested for a single filament in [10].

4. Results

4.1. Consistency of specimens never cycled

Table 1 reports sample means for the ultimate tensile load and the tensile stiffness of virgin specimens that were never cycled. These values were used to normalize the results obtained for samples tested after electrochemical cycling. The same yarn and reference sample of virgin specimens could be used for all IMS65 samples that have been cycled. For T800H fibres separated yarns and reference samples of virgin specimens were used, on the one hand for the samples tested after 1, 10 and 1000 cycles and on the other hand for the samples tested after 100 cycles. Tensile tests showed that the tabbing fixture did not slip in the clamps and failure occurred properly in the middle of the specimens. The consistency of the stiffness measurement made it unnecessary to use an external extensometer. The number of virgin specimens tested and the samples coefficients of variation indicated that the specimens were consistent enough to distinguish any significant impact of the cycling on the tensile properties.

Table 1. Tensile properties of samples never cycled.

Benchmark virgin sample	Measured tensile property ^a	
	K ^b (N)	F _{max} (N)
Desized sample used to normalize results of all IMS65 samples	10 430 ₉ ± 4.50%	230.3 ₉ ± 0.83%
Sized T800H, used for samples after 1, 10 and 1000 cycles	9 880 ₅ ± 4.26%	181.45 ₅ ± 1.41%
Sized T800H, used for samples after 100 cycles	13 610 ₃ ± 5.35%	256.57 ₃ ± 1.37%

^a Each measurement is sample mean denoted with number of specimens in subscript lowercase and with sample coefficient of variation in %.

^b “K” indicates stiffness and “F_{max}” is for ultimate load.

4.2. Tensile tests of sized specimens and of specimens left in electrolyte

Table 2 presents the normalized properties of virgin IMS65 specimens. One sample was made of sized fibres and another one was made of desized fibres left in a bath of electrolyte for 48 h. The results show that the samples stiffness is not affected by the desizing process or by the electrolyte. Sized fibre specimens exhibited slightly higher failure loads than those that had been desized. The ultimate load was even higher for desized specimens left in the electrolyte for 48 h. One explanation for this result could be that the viscosity of the liquid electrolyte may affect the friction between fibres making the failure occur more gradually. From these results it was deduced that the desizing process and the electrolyte did not damage the fibres.

Table 2. Impact of desizing process and of electrolyte impregnation on virgin samples.

Sample feature	Measured tensile property ^a	
	k	f _{max}
Sized IMS65	1.01 ₄ ± 4.69%	1.10 ₄ ± 1.52%
Desized IMS65 left in liquid electrolyte	1.02 ₃ ± 1.86%	1.15 ₃ ± 2.99%

^a Each measurement is sample mean normalized by benchmark virgin sample mean, with number of specimens in subscript lowercase and coefficient of variation in %.

^b a “k” is for normalized stiffness and “f_{max}” is for normalized ultimate load.

4.3. Electrochemical cycling

Fig. 3 illustrates the changes in the cell capacity measured during lithiations and delithiations after a number of electrochemical cycles for IMS65 and T800H positive electrodes. These capacities may differ slightly from the expected ones because they depend on the charge rates used as shown in [8] and thus on the accuracy of the estimated masses of carbon fibre electrodes cycled. The capacity at the second lithiation was only about half that of the first lithiation because some more lithium ions are used for the first lithiation to form the SEI layer and some other are irreversibly trapped in the carbon fibre microstructure. These ions cannot be extracted and are responsible for an irreversible loss in the cell capacity. For the next hundred cycles the cells exhibited

good capacity retention. The same trends of results were found for both grades of fibres. However obvious losses in the capacity of the cells occurred continuously from about 200 cycles to 1000 cycles. Fewer and fewer lithium ions were inserted in the fibres apparently because of the wear of the electrolyte and the lithium metal electrode.

Fig. 3. Cell capacity measured during lithiations and delithiations of desized IMS65 and T800H after 1, 2, 10, 100, 500 and 1000 electrochemical cycles.

4.4. Tensile tests of specimens after electrochemical cycling

Fig. 4a and b present normalized tensile test curves of IMS65 and T800H specimens respectively that are representative of the tensile stiffness of the specimens, reflected by the slopes where the deformation is linearly elastic, remains unchanged with the number of cycles. There are losses of 9% measured in the stiffness of T800H specimens but only after 1000 cycles. These losses are not measured for IMS65 specimens and are therefore not systematic. They might be due to unexpected wear of the screws of the tester clamps, or they could reflect a small impact of a long term-cycling suggesting for example an irreversible disruption in the orientation of graphene layers or in the cross-section area of fibres. The impact of cycling is seen in the changes of the ultimate tensile load which drops for lithiations and is partly recovered for delithiations.

Fig. 4. Representative tensile curves of virgin (dashed line), delithiated (solid line) and lithiated (dotted line) specimens made of IMS65 (a) and T800H (b) for a number of cycles.

Table 3 reports the normalized stiffness and ultimate load of both T800H and IMS65 samples after cycling. The trends of the changes in the tensile properties were similar for both fibre grades which suggests that these trends are not influenced by the filament sizing. After the first lithiation the specimens demonstrated a loss in their ultimate tensile load of about 20% which was only partly recovered after the first delithiation. Carbon fibres lose strength during the first lithiation when lithium ions are inserted and regain only a part of this strength during the first delithiation namely when lithium ions are extracted again from the inner structure.

Measurements at 10 and 100 cycles show that additional cycles up to 100 do not add any losses. They have a reversible effect on the ultimate strength which goes up and down during delithiations and lithiations respectively between unchanged values of the lithiated and the delithiated states. This illustrates the significance of the first cycle which is primarily responsible for an irreversible loss in the ultimate tensile strength. However, after 1000 cycles the lithiated fibres exhibit a reduced loss. Their ultimate tensile strength is still lower but much closer to the one of delithiated fibres which did not obviously change since the first cycle has occurred. It turns out that the increasing number of electrochemical cycles does not degrade the tensile properties of the carbon fibres.

Table 3. Tensile properties of samples after different numbers of cycles.

Measured properties of samples after cycling					
Number of cycles ^a		IMS65		T800	
		k	f _{max}	k	f _{max}
1	L	1.04 ₃ ± 2.34%	0.82 ₃ ± 1.34%	1.04 ₄ ± 2.91%	0.77 ₄ ± 3.99%
	D	0.99 ₃ ± 4.90%	0.90 ₃ ± 3.45%	1.03 ₄ ± 4.50%	0.92 ₄ ± 2.82%
10	L	1.01 ₃ ± 3.53%	0.74 ₃ ± 1.76%	1.01 ₃ ± 3.59%	0.81 ₃ ± 3.47%
	D	1.05 ₃ ± 1.98%	0.89 ₃ ± 1.81%	1.03 ₃ ± 5.89%	0.93 ₃ ± 2.31%
100	L	0.99 ₄ ± 4.95%	0.80 ₄ ± 2.04%	0.97 ₃ ± 4.52%	0.83 ₃ ± 2.70%
	D	1.01 ₃ ± 6.19%	0.91 ₃ ± 4.97%	0.99 ₃ ± 4.67%	0.93 ₃ ± 3.35%
1000	L	1.00 ₃ ± 5.77%	0.92 ₃ ± 0.44%	0.92 ₄ ± 9.07%	0.89 ₄ ± 2.22%
	D	0.99 ₃ ± 2.46%	0.95 ₃ ± 1.57%	0.91 ₄ ± 6.87%	0.94 ₃ ± 2.85%
Average over all cycles	L	1.01 ± 1.90%	0.82 ± 9.12%	0.98 ± 5.27%	0.82 ± 6.06%
	D	1.01 ± 2.80%	0.91 ± 2.88%	0.99 ± 5.71%	0.93 ± 0.88%

^a Each measurement is sample mean normalized by benchmark virgin sample mean, with number of specimens in subscript lowercase and coefficient of variation in %.

^b ‘‘L’’ is for lithiated fibres and ‘‘D’’ is for delithiated fibres.

4.5. Appearance of fibres after cycling

Fig. 5a and b present SE-FEM images of desized IMS65 fibres respectively virgin and lithiated after 1000 cycles. The outer surface of the virgin fibre in Fig. 5a consists of a homogeneous and relatively smooth texture slightly crenulated. Cross-sectional images did not exhibit any obvious evidence of porosity or a skin-core structure in either of the fibres. In Fig. 5b a black deposits of material can be seen on the outer surface of the lithiated fibre that might be some electrolyte residues like LiPF₆ and ethylene carbonate. These residues could be cleaned quite well with dimethyl carbonate (DMC) solvent. Even though the surface texture looks slightly rougher than for virgin fibres, no obvious wear, damage or defects were seen after electrochemical cycling.

Fig. 5. FE-SEM images at 1 kV with $\times 10,000$ magnification. Desized IMS65 carbon fibre before cycling (a) and lithiated after 1000 cycles (b).

5. Discussion

5.1. Impact of lithium ion intercalation on tensile properties

The mechanisms of lithium-ion intercalation in the structure of carbon fibres are still not well understood. Charging specimens has no significant effect on their stiffness. This suggests that the atomic microstructure of fibres and the strength of its interatomic bonds are conserved. In particular the tensile modulus of a carbon fibre is mainly related to the degree of orientation of the graphitic layer planes [11]. It seems that neither lithium-ion intercalation nor the cycle count affect this feature.

On the contrary after the first cycle, each lithiation causes a drop in the ultimate tensile load that is recovered for the delithiation that follows. One possible explanation could be that the lithium ions inserted between graphitic sheets might create stress concentrations near the agglomerates of lithium ions. Fibres would fail more quickly because of high local stress. However, the tensile strength of a carbon fibre depends mainly on the close packing and the stacking order of carbon layers within its cross-sections. In addition a large amount of distortions within a layer favour the strength by increasing lateral bonding between two adjacent sheets of layers [12]. This suggests another possible explanation which is that the lithium ions inserted between graphitic sheets may open up the layers and affect their lateral bonding. The swelling of the fibre in the length direction measured in [13] during lithium-ion intercalation could also reflect that a deformation of the fibre microstructure during a lithium ion intercalation is responsible for a loss in the strength. During a delithiation lithium ions are removed from the fibre which may release internal deformation and allow the recovery of

strength. However, the magnitude of the losses measured in the fibre strength remains low enough not to compromise the applicability of the carbon fibre as structural electrode.

5.2. Correlation between electrochemical capacity and tensile properties

At the first cycle, the lithium ions trapped in the fibre electrode are responsible for the irreversible loss in the cell capacity as they will not be extracted and inserted in the fibres again during the next cycles. A similar irreversible drop occurs in the fibre ultimate strength during the first cycle which appears to be responsible for a permanent loss of strength in delithiated fibres. For the next cycles until 100 the cell capacity is reversible and unchanged as well as the ultimate strength of fibres in the lithiated and delithiated states. After 1000 cycles lower losses were measured in the ultimate strength of lithiated fibres that matches with the decrease of the cell capacity illustrated by Fig.

3. The amount of lithium ion inserted during a lithiation was about half lower after 1000 cycles which could be the reason for the lower losses of strength measured in lithiated fibres. These comparisons suggest that the magnitude of the drops and recoveries in the fibre ultimate strength is influenced by the cell capacity during cycling and may therefore depend on the amount of lithium ions inserted in and extracted from the fibre. This possible explanation is investigated in a separate study. However T800H and desized IMS65 exhibited some of the best specific capacities measured within a large range of PAN-based fibres and could therefore be considered as representative for the biggest losses of strength that might be measured in the same cycling conditions.

5.3. Changes in the specific capacity and appearance of the fibres with cycling

No damage of the outer surface of fibres was clearly noticed after 1000 cycles and the increasing cycle count did not degrade the tensile properties either. The cell capacity reduction from 200 to 1000 cycles is attributed to the wear of the liquid electrolyte and the lithium metal electrode which looked clearly worn. The cycle life of lithium metal electrodes in liquid electrolyte is commonly known to be limited due to passivation, corrosion or dendrite growth as mentioned in [14]. Measurements on FE-SEM images confirmed that the diameter of IMS65 fibres is of about 5 μm after manufacturing. The quality control of Toho Tenax on the density with running meters of IMS65 fibres allowed the calculation of a manufacturing tolerance on the diameter of 4.50% i.e. 0.22

µm. This scatter is larger than any visible swelling of the fibre diameter that might be caused by the insertion of lithium ions.

Conclusion

This work highlights the usability and performance of carbon fibres in structural lithium-ion batteries. The tensile stiffness of carbon fibres does not appear to be affected either by lithium-ion intercalation or by electrochemical cycling. The ultimate tensile strength undergoes a total loss of about 20% during the lithiations which is partly recovered during delithiations. This drop is not accentuated by the cycling. Thus the increasing number of electrochemical cycles does not degrade the fibre tensile properties. The outer surface of the carbon fibre electrode itself did not either appear to be damaged by the cycling on FE-SEM images after 1000 cycles.

The magnitude of the losses in the strength of fibres seems to be related to the changes of the cell capacity and may depend on the amount of lithium ions inserted in and extracted from the microstructure of fibres. The trend of the results were the same for two grades of intermediate modulus PAN-based fibres, sized and desized with different cross-section geometries and provided by two different manufacturers. These findings are therefore useful and promising for the modelling and development of carbon fibres as structural electrode in multifunctional energy storage composites.

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