1 Introduction

Reducing system mass for improvements in system performance has become a priority for future applications such as mobile phones or electric vehicles which require load bearing components and electrical energy storage devices. Structure and energy storage are usually subsystems with the highest mass contributions but energy storage components are structurally parasitic. A novel solution is a multifunctional lightweight design combining these two functions in a single material entity able to simultaneously bear mechanical loads as a carbon fiber composite component and store electrochemical energy as a lithium-ion battery.

Lithium-ion batteries consist of two electrodes in which lithium ions move from the negative electrode to the positive electrode during discharge and with a reversed flow during charge. An electrolyte conducts the ions and a porous insulating separator prevents short-circuiting of the electrodes. Carbon fibers have a conductive structure of graphite sheets which enables lithium-ion intercalation. The term lithiation is used for insertion of lithium ions and delithiation is used for extraction of the same. Previous studies evaluated the electrochemical capacities of carbon-fiber electrodes derived from a wide variety of grades [1]. High and intermediate modulus (IM) polyacrylonitrile (PAN)-based fibers appeared to be the best compromise for their best overall specific capacity and tensile strength and their wide range of applicability in structural batteries. Other research has shown that the copolymerization of two monomers with different properties can form a multifunctional solid polymer electrolyte (SPE) with good ionic conductivity and high mechanical stiffness [2]. The concept of structural batteries using a SPE as matrix material and carbon fibers as structural electrode has previously been studied [3]. The SPE turned out to be the weakest part with respect to both load transfer and ionic conductivity.

This work continues the investigation on the performance of carbon fibers as structural electrodes. The graphitic structure of carbon fibers deforms when an external load is applied. This paper focuses on the impact of mechanical loading on the electrochemical capacity of carbon fibers. One grade of PAN-based carbon fibers that exhibits a good capacity was selected. Tensile test specimens made of dry fiber bundles are loaded and cycled in pouch-type cells. The capacity of the fibers is measured for increasing and decreasing levels of strain for several electrochemical cycles. Any change in the capacity is correlated with the fiber deformation.

2 Experimental

2.1 Carbon fiber selected

IM PAN-based carbon fiber Toray T800HB 6K 40B P1 BB was used. The tow contains 6000 straight filaments with epoxy based sizing. This fiber was chosen for its good specific capacity in comparison wide a range of PAN-based fibers tested prior to this work by the authors. The fiber displayed a capacity of 135.0mAh/g with a good retention after 10 cycles.

2.2 Glovebox environment

Lithium is quickly oxidized in contact with air and water. Lithium ion-cells were manufactured inside a glovebox with inert argon atmosphere with less than 1 ppm [O₂] and [H₂O] at 27°C.
2.3 Tensile test rig and tensile specimens tabbing

The carbon fiber tensile specimens used as electrodes were manufactured with limited dimensions for acceptable consumption of cell materials. The tests were carried out using a 300N tensile stage from Deben UK. The fiber tow being made of straight and sized fibers it was possible to divide it properly into a lighter one with a consistent ultimate load measurable by the load cell. A consistent tabbing that fits in the jaws of the tester was developed for 46mm long dry carbon fiber bundles. End tabs 12 mm long × 10 mm wide × 0.7 mm thick were cut into insulating glass fiber composite plates made of cured Gurit SA80 prepreg. At the ends of each specimen two tabs were bonded to pre-stretched fibers using Gurit SE 84LV epoxy prepreg. The epoxy film was cured in a vacuum bag with a breather fabric at 120°C for 1h to allow good impregnation of the fibers in a stiff and insulating tabbing. Figure 1 shows a finished carbon fiber tensile specimen. The specimens completed were dried at 50°C under reduced pressure for 24h and placed inside the glovebox.

2.4 Lithium-ion pouch cell

Specimens were used as electrode in a layered electrochemical pouch cell design. The first layer is the working electrode made of a fiber specimen. 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 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 a lithium metal foil counter electrode. 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 placed in a polyethylene terephthalate (PET)/aluminum (Al)/polyethylene (PE) laminate from Skultuna Flexible 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 edges of the bag to prevent the liquid electrolyte from evaporating. Vacuum is drawn from the bag while it is sealed to ensure good contact between all layers.

2.5 Loading the carbon fiber electrode

The Microtest software from Deben UK was used for acquisition of load and extension and time data during tensile tests. A sample time of 100ms and a motorspeed of 0.1mm/min were used providing a strain rate of 1.5×10$^{-4}$ s$^{-1}$. Each pouch cell contained a fiber specimen. Fibers were loaded by clamping the vacuum bag containing the whole cell in the jaws of the tester on the specimen tabbing as illustrated figure 2. Flat jaws were used to avoid puncturing the bag. The specimen and the vacuum bag were both pulled. Once the target load and extension were reached, the motor was stopped. Load relaxation in the bag was recorded for 2h until the load was stabilized so that the cycling could be started.

2.6 Electrochemical cycling of a cell

The current collectors of the cell were connected to a Solartron 1286 Electrochemical Interface potentiostat controlled with the CorrWare software that runs the cycling of the cell and records the cell potential over time. Each cycle contained four steps. The first one is a galvanostatic lithiation using a constant current chosen to make it last about one hour according to the mass of carbon fiber electrode, which was measured with a high accuracy scale. The second one is an open-circuit potential (OCP) that allows the cell to relax for 15 min. The third one is a one hour galvanostatic delithiation ending with another 15 min OCP.

2.7 Measurement

Benchmark tests were performed prior to any cycling on fiber specimens alone, on specimens inside a vacuum bag and on the vacuum bag alone. Stiffness and strength were measured as well as the load relaxation of the bag at the extensions studied and the consistency of the results. Three load cases were studied using three cells, one for each case, to estimate the impact of a strain in the fiber on its specific capacity. A first cell was cycled before and after loading the fibers. Two further cells were cycled before, while and after two levels of strain respectively were applied to the fibers and released.

3 Theoretical

3.1 Redox reactions

Lithium metal has the lowest standard electrode potential in comparison to the carbon fiber and is...
therefore the negative electrode with the fibers as the positive electrode. For a lithiation, reaction (1) and (2) give the reduction and oxidation reactions at the positive and negative electrodes respectively. Reaction (3) is the total redox reaction in the cell:

\[ C_6(s) + x\text{Li}^+(aq) + xe^- \rightarrow C_6\text{Li}_x(s) \]  

(1)

\[ \text{Li}_x(s) \rightarrow x\text{Li}^+(aq) + xe^- \]  

(2)

\[ \text{Li}_x(s) + C_6(s) \rightarrow C_6\text{Li}_x(s) \]  

(3)

where \( x \) is an unknown parameter which depends on the chemical composition of the carbon fibers. For a delithiation the opposite reactions occur.

3.2 Cell potential

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 and will therefore display a constant potential so that any changes in the cell potential can be attributed to the carbon fiber electrode. The change in the potential during lithiation and delithiation depends on the concentration of lithium ions in the fibers. For lithiation the fibers are considered to be completely charged at 0.002V vs. Li/Li\(^+\) and for delithiation the fibers are discharged when the cell potential reaches 1.5V vs. Li/Li\(^+\).

3.3 Specific electrochemical capacity

The specific electrochemical capacity measured for a lithiation \( C_{x_{\text{measured}}} \) is defined as the amount of electric charges that is received by the cell for the duration \( t \) of the experiment normalized by the mass \( m \) of the carbon fiber electrode. The capacity characterizes the amount of lithium ions that can be intercalated in the carbon fibers and is calculated with equation (4):

\[ C_{x_{\text{measured}}} = \frac{I \cdot t}{m} \]  

(4)

where \( I \) is the constant current used for cycling the cell. The capacity for a delithiation refers to the amount of electric charges delivered by the cell.

3.4 Capacity retention

Lithium is thermodynamically unstable when used with both liquid and polymer electrolyte. A passivation layer about 10nm thick, the solid-electrolyte interphase (SEI), caused by a decomposition of the electrolyte is formed for the first cycle of a cell at the surfaces of the carbon electrode that allows it to work in its stability range [4]. Some lithium ions are incorporated into the SEI. This process causes an irreversible loss of capacity which depends on the electrolyte formulation and on the specific surface area of the carbon electrode. For the following cycles the cells exhibit a capacity that can be considered as reversible.

3.5 Strain applied to the fibers

The strain applied to the fibers was defined as their extension divided by their initial length of 22mm. It was calculated using the specimen stiffness and the load carried by the fibers when pulled with the bag. The stiffness of a fiber specimen was defined as the slope of its tensile curve (force) vs. (strain) where the deformation is linear elastic and was calculated with the least square method using data points between load limits of 400mN/tex and 800mN/tex. The load carried by the fibers when pulled together with the vacuum bag was estimated by testing the vacuum bag separately to deduct its contribution at different levels of extension.

4 Results and discussion

Each measured property \( x_i \) is presented in the text, figures and tables according to equation (5):

\[ x_i = \frac{X_i \pm c_v \%}{n} \]  

(5)

where the sample mean \( X \) is denoted with the sample number of tests \( n \) in subscript lowercase and the sample coefficient of variation (CV) \( c_v \) in % is calculated from the sample standard deviation.

4.1 Benchmark tests on bags and fiber specimens

4.1.1 Specimens manufactured and never cycled

A first curve in figure 3 characterizes a manufactured specimen that has never been cycled. It demonstrates an ultimate extension of 0.42mm corresponding to an ultimate strain of 1.9%. Tensile tests were performed on a sample of these specimens. The sample stiffness measured in N was 9660±3.02% and the sample ultimate tensile load in N was 180±2.35%. The CV were good enough to consider the specimens manufactured consistent.

4.1.2 Vacuum bag pulled separately

A second tensile curve in figure 3 represents the load carried by a sealed bag after vacuum has been drawn
for a static test. The fibers of a specimen inside were cut prior to the test so that only the bag was pulled.

4.1.3 Specimens pulled with the vacuum bag
A third curve is representative of a specimen pulled inside a vacuum sealed bag. An abrupt increase in the stiffness occurs at 0.35mm of extension as the loading of fibers adds to the loading of the bag. Eventually the ultimate tensile load which corresponds to the failure of the fibers increases of about 135N due to the bag contribution.

4.1.4 Load relaxation in the bag
Load relaxation tests showed that only the bag relaxes load, from 40N to 60N before stabilizing after about 2h depending on the strain rate, the load carried and the extension. Thus the load relaxed by the bag when pulled with a fiber specimen inside was measured for 2h after each loading and deducted from the bag contribution in the load path.

4.1.5 Strain applied to the fibers for each load case
Three cells were cycled and loaded according to three respective load cases. In the first load case, a load of 208N at 0.67mm extension was applied to the cell. At this extension the bag carries about 120N and it relaxed 48N. The load stabilized at 160N after 2h with 72N in the bag and 88N in the fibers. This load in the fibers corresponds to an extension of 0.22mm that is a strain of 1.0%. Similarly strains of 0.72% and 0.90% were applied to the fibers in the second and third load case respectively.

4.2 Electrochemical impact of fiber deformation
Table 1 summarizes the specific capacities of the fiber electrode measured for several cycles for the three load cases studied. For the first cycling without loading, all three carbon fiber electrodes exhibited a specific capacity of about 140mAh/g for 1h-lithiations and delithiations as expected. For the intermediate cycling with loading, the second and third load cases show that fiber electrodes fibers did not exhibit any noticeable change in their capacity as suggested by the low coefficients of variation measured. Also the capacity also did not change once the loading of the fibers was released what means that the amount of lithium ions intercalated in the carbon fiber graphitic structure is unaffected. However for all load cases, when the strain in the fiber was changed only a drop in the cell potential occurred for the next lithiation to be started. This drop always resolved at the end of this lithiation and did not affect the capacity. It was of about 7% in the second load case and of 11% and 10% in the first and third load cases where higher strain is applied to the fibers. This might be related to a change in the surface energy of the fiber due to the deformation of its microstructure. Figure 4 illustrates this drop for the third load case.

4.3 Swelling and shrinkage of the fiber length
Figure 5 presents the load in the cells vs. time. After the loading of the second cell at 170N and the bag relaxation for about 2h the load stabilized at about 155N. When the cycling starts at about 9000s, it is seen that the load carried decreases for the first lithiation, remains unaffected for the OCP and increases again for the first delithiation. These changes can only be attributed to the load carried by the fibers and they occur identically for the following cycles. These results show that the fiber length swells for a lithiation and shrinks for a delithiation, which is confirmed with the third cell.

The stiffness of the specimens used was measured in tensile tests after cycling to calculate the strain, in % of a specimen length, corresponding to the load drops and recoveries. Using a sample of several lithiations, the fiber swelling corresponds to strains of 0.33±2.59% and 0.33±1.02% for the second and third load case respectively. Calculations for a sample of delithiations show that the fiber shrinkage corresponds to a strain of -0.33±2.02% for the second case and -0.28±1.03% for the third one.

5 Conclusion
The strain applied to the fibers did not affect their specific capacity. Swelling of the fiber length of 0.33% for lithiations and shrinkage of about 0.30% for delithiations were measured. These results encourage the ongoing development of energy storage composite materials.

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Table 1. Measured specific electrochemical capacities (mAh/g) of the fiber electrode at different strains

<table>
<thead>
<tr>
<th>Load case</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>145.0±1.20%</td>
<td>144.3±1.32%</td>
<td>144.4±3.29%</td>
</tr>
<tr>
<td>D</td>
<td>139.7±0.90%</td>
<td>140.4±1.50%</td>
<td>136.3±2.50%</td>
</tr>
</tbody>
</table>

Intermediate cycling with loading

| Strain (%) | 1.0 | 0.72 | 0.90 |
| L          | No cycling | 141.9±1.00% | 141.8±1.94% |
| D          | No cycling | 139.3±0.8%  | 137.9±1.87% |

Last cycling after unloading

|          | 140.1±2.14% | 147.3±6.02% | 136.0±0.78% |
| L        | 138.7±1.90% | 144.9±6.20% | 134.3±0.87% |

a “L” indicates lithiation and “D” indicates delithiation.
b Three cells were used, one for each load case. Sample means are calculated for several cycles and denoted with number of cycles in subscript lowercase.
Fig.3. Benchmark tensile tests on a vacuum bag and a fiber specimen pulled separately and together.

Fig.4. Representative lithiation and delithiation curves of the carbon fiber electrode for load case 3, before, and during loading with small potential drop and after unloading.

Fig.5. Load relaxation in the bag and load variations due to fiber swelling and shrinkage for the cycling.

References