PAN-Based Carbon Fiber Negative Electrodes for Structural Lithium-Ion Batteries

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Several grades of commercially-available polyacrylonitrile (PAN)-based carbon fibers have been studied for structural lithium-ion batteries to understand how the sizing, different lithiation rates and number of fibers per tow affect the available reversible capacity, when used as both current collector and electrode, for use in structural batteries. The study shows that at moderate lithiation rates, 100 mA g⁻¹, most of the carbon fibers display a reversible capacity close to or above 100 mAh g⁻¹ after ten full cycles. For most of the fibers, removing the sizing increased the capacity to some extent. However, the main factor affecting the measured capacity was the lithiation rate. Decreasing the current by a tenth yielded an increase of capacity of around 100% for all the tested grades. From the measurements performed in this study it is evident that carbon fibers can be used as the active negative material and current collector in structural batteries.

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For nearly two decades, different types of graphitized carbons have been used as the negative electrode in secondary lithium-ion batteries for modern-day energy storage. The advantage of using carbon is due to the ability to intercalate lithium ions at a very low electrode potential, close to that of the metallic lithium electrode (~3.045 V vs. standard hydrogen electrodes). Extensive research has focused on improving the lifetime, capacity and safety, and to decrease the cost of carbon materials.

In addition to finding new carbon materials with superior electrochemical properties, another approach would be to find battery materials with multifunctional properties. By letting the battery become an integrated load-carrying part of a device, forming a structural battery, an increase in both the power and energy density at a system level could be achieved. The concept of structural batteries has previously been studied with various approaches and results. Replacing the ordinary electrochemically active materials with materials that can form a structural battery will result in a product that cannot be expected to perform as well as a state-of-the-art battery cell, because of the trade-off between the electrochemical and mechanical performance.

A battery with good mechanical properties can be achieved by continuous carbon fiber tows acting as the negative electrode and giving the desired multifunctional properties. An electrode like this could be designed so that no current collectors or conductive additives will be needed since carbon fibers themselves have reasonably good electrical conductivity. The two most commonly used precursors for continuous carbon fibers are pitch and polyacrylonitrile (PAN). Pitch-based fibers have traditionally been favored by the battery community due to a higher degree of graphitization, but research have shown that the disordered structure of PAN-based fibers are more favorable for lithium-ion intercalation. The mechanical properties of the PAN-based fibers also make them more suitable for structural composite batteries where both strength and stiffness are of great importance.

Previous studies have shown that PAN-based carbon fibers can be used as active material in conventional lithium-ion batteries. Most of these studies have often centered on increasing the capacity of the carbon fibers with different approaches like acid and heat treatments or electrolyte composition. However, no studies have been made to evaluate the capacity when the carbon fiber is used as both current collector and electrode; a feature necessary for the structural battery proposed.

This paper presents a study where the electrochemical properties of several different grades of commercially available PAN-based fibers, used as both current collector and electrode, have been investigated. A cell design was developed to mimic the usage of carbon fibers in a structural battery. The cell design would also have to function as an in-situ test cell for future investigation of mechanical properties during cycling. The impact of sizing versus removal of sizing, different lithiation rates, and number of fibers per tow were analyzed to determine their effect on capacity. This study is a pre-study for further work on carbon fibers as negative electrodes for structural batteries. Further work on the more promising carbon fibers in this study will include investigations of the impact of lithium-ion intercalation on the tensile properties of carbon fibers.

Experimental

The PAN-based fibers used in this study were supplied by two different manufacturers, Toray Tenax Europe and Soficar (a subsidiary of the Toray group). The selection process was based on the mechanical properties of the carbon fibers so that a range of modulus and strength was covered. Table 1 lists the carbon fibers tested in this study. PAN-based carbon fibers are usually equipped with a coating, also known as sizing, consisting of either epoxy or polyurethane (PU) resin to ease the handling and enhance the bonding between the fiber and the surrounding matrix in composite manufacturing. When discussing the sizing on carbon fibers the term desized refers to a fiber where the sizing has been removed by washing in acetone and the term unsized refers to a fiber which has been taken out of production by the manufacturer prior to the sizing step.

The carbon fibers were used either as received or with the polymeric sizing removed prior to sample preparation. Removal of the sizing was done by solvent extraction using a vessel with acetone placed on a shaking table for four days. To eliminate excess solvent, the fibers were dried under reduced pressure for 24 hours at 50°C after the extraction was completed.

To facilitate handling and to minimize the risk of stray fibers causing short circuits, laminate tabs were attached to both ends of the sample, 22 mm apart (Figure 1). Tabbing the carbon fibers like this is a method commonly used for tensile testing of fiber-composites specimens (ISO_10618:2004(E) and ISO_11566:1996(E)). The tabs consisted of two glass fiber laminates (Gurit SE 84 LV glass fibers prepreg) and a foil of Gurit SA80 epoxy. Curing of the epoxy resin was performed in a vacuum bag at 120°C for one hour to achieve...
The measurements show that the electrochemical capacity varies considerably between grades of fibers when cycled at 100 mA per gram of fiber, ranging from 177 mAh g$^{-1}$ for unsized IMS65 to only 24 mAh g$^{-1}$ for desized UTS50 after 10 cycles. Results for all the fibers can be seen in Table II. Furthermore, by using tabbed samples the reproducibility between cells containing the same kind of fibers were excellent, with less than 1 mAh g$^{-1}$ difference in capacity between cells. Therefore, the results reported for single cells and not as an average of several cells. Only the results for the 1st and 10th cycle are shown since all fibers showed a stable reversible capacity, disregarding the first lithiation.

Figure 2 shows representative SEM images of sized, desized and unsized carbon fibers. A comparison between the pictures show that the dark agglomerated sizing on the sized fibers have been removed making the desized fibers look more like the unsized. Since no visible difference could be detected between the desized and the unsized fibers it is deemed that the desizing process did not change the fibers. The desizing was also noticeable when handling the fibers since desized fibers became more unruly and loose due to the lack of sizing.

Table I displays some of the properties of the carbon fibers as specified by the manufacturers. The reported values for the electrical resistivity are sufficiently low to function adequately as current collectors and any differences in electrochemical properties between the grades could then be attributed to electrochemical properties the fibers. As opposed to the results obtained for IMS65, removing the sizing on UTS50 seems to degrade the fiber in some way, resulting in a decreased reversible capacity. This decrease might be related to the type of sizing used for this specific fiber, which consists of PU, and may therefore possibly need a different approach to be removed, compared to an epoxy-based sizing.

Figure 3 shows the lithiation and delithiation curves for the 1st and the 10th cycle for T800 and UMS45. The measured capacity is even higher for the unsized fibers than for the desized fiber. The observed difference in capacity between the unsized and desized samples may originate in sizing residues not seen with the SEM or surface transformation during the sizing process, which would interfere with the intercalation process for the desized fiber. For T800 and UMS45 the impact of sizing was less pronounced than for IMS65, M40, M46 and T300. Lithiation and delithiation curves for the 1st and the 10th cycle for T800 can be seen in Figure 4. These results are in agreement with those seen in a previous study\textsuperscript{17} i.e. that the sizing has very little impact on the capacity, but is clearly not a general rule for all fiber grades since about half the tested grades in this study showed an increase in capacity when the sizing was removed.

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**Table I. Carbon fiber properties as specified by the manufacturers.**

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Grade</th>
<th>Diameter (μm)</th>
<th>Strength (MPa)</th>
<th>Modulus (GPa)</th>
<th>Sizing</th>
<th>Electrical Resistivity (Ωcm × 10$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toray</td>
<td>T300B 1K 50B</td>
<td>7</td>
<td>3530</td>
<td>230</td>
<td>epoxy</td>
<td>1.5</td>
</tr>
<tr>
<td>Toray</td>
<td>T800HB 6K 40B P1</td>
<td>5</td>
<td>5490</td>
<td>294</td>
<td>epoxy</td>
<td>1.4</td>
</tr>
<tr>
<td>Toray</td>
<td>M40JB 6K 50B P1</td>
<td>5</td>
<td>4410</td>
<td>377</td>
<td>epoxy</td>
<td>0.8</td>
</tr>
<tr>
<td>Toray</td>
<td>M46JB 6K 50B P1</td>
<td>5</td>
<td>4210</td>
<td>436</td>
<td>epoxy</td>
<td>0.9</td>
</tr>
<tr>
<td>Toho Tenax</td>
<td>UTS50 F13 12K 800tex</td>
<td>7</td>
<td>4800</td>
<td>240</td>
<td>PU</td>
<td>1.6</td>
</tr>
<tr>
<td>Toho Tenax</td>
<td>IMS65 E23 24K 830tex</td>
<td>5</td>
<td>6000</td>
<td>290</td>
<td>epoxy</td>
<td>1.45</td>
</tr>
<tr>
<td>Toho Tenax</td>
<td>UMS45 F22 12K 385tex</td>
<td>4.7</td>
<td>4500</td>
<td>430</td>
<td>PU</td>
<td>0.97</td>
</tr>
</tbody>
</table>

**Results and Discussion**

The measurements show that the electrochemical capacity varies considerably between grades of fibers when cycled at 100 mA per gram of fiber, ranging from 177 mAh g$^{-1}$ for unsized IMS65 to only 24 mAh g$^{-1}$ for desized UTS50 after 10 cycles. Results for all the fibers can be seen in Table II. Furthermore, by using tabbed samples the reproducibility between cells containing the same kind of fibers were excellent, with less than 1 mAh g$^{-1}$ difference in capacity between cells. Therefore, the results reported for single cells and not as an average of several cells. Only the results for the 1st and 10th cycle are shown since all fibers showed a stable reversible capacity, disregarding the first lithiation.

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To further evaluate the changes in capacity at different lithiation rates T800 (sized) and IMS65 (sized and unsized) were chosen and tested with the current rate of 1 mV s$^{-1}$ for graphite. To further evaluate the changes in capacity at different lithiation rates T800 (sized) and IMS65 (desized) were also chosen and tested with the current that corresponds to 0.1 C, 0.2 C, 0.5 C and 1 C, based on the capacities obtained during the initial screening of the fibers. T800 (sized) and IMS65 (desized) were also chosen to evaluate how the number of fibers per tow would affect the capacity. Cyclic voltammetry (CV) was used to determine the impact of tow size and sizing on the fiber performance. Two different CV sweeps was carried out, the first between 2−3 V vs. Li/Li$^+$ at a sweep rate of 10 mV s$^{-1}$ to investigate the electrochemical surface area, which can be seen as the double-layer capacitance, and the second between 0-3 V vs. Li/Li$^+$ at a sweep rate of 1 mV s$^{-1}$ to investigate the effect of fiber grade and sizing on the kinetics of intercalation. All measurements were performed using a Solartron 1287 Electrochemical Interface controlled with the CorrWare software.

**Figure 1. Schematic of sample with (a) tab structure and (b) top view of real sample.**
Table II. Measured capacities for the 1st and the 10th cycle.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Capacity (mAh g(^{-1}))</th>
<th>Lithiation</th>
<th>1st cycle</th>
<th>10th cycle</th>
<th>Capacity (mAh g(^{-1}))</th>
<th>Delithiation</th>
<th>1st cycle</th>
<th>10th cycle</th>
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<tr>
<td>T300</td>
<td>170</td>
<td>91</td>
<td>79</td>
<td>87</td>
<td>350</td>
<td>130</td>
<td>150</td>
<td>130</td>
</tr>
<tr>
<td>T300 unsized</td>
<td>170</td>
<td>98</td>
<td>88</td>
<td>97</td>
<td>252</td>
<td>136</td>
<td>131</td>
<td>135</td>
</tr>
<tr>
<td>T800</td>
<td>194</td>
<td>112</td>
<td>128</td>
<td>110</td>
<td>194</td>
<td>112</td>
<td>128</td>
<td>110</td>
</tr>
<tr>
<td>T800 divided tow</td>
<td>46</td>
<td>36</td>
<td>37</td>
<td>36</td>
<td>46</td>
<td>36</td>
<td>37</td>
<td>36</td>
</tr>
<tr>
<td>M40</td>
<td>87</td>
<td>69</td>
<td>73</td>
<td>68</td>
<td>87</td>
<td>69</td>
<td>73</td>
<td>68</td>
</tr>
<tr>
<td>M40 desized</td>
<td>31</td>
<td>26</td>
<td>22</td>
<td>26</td>
<td>31</td>
<td>26</td>
<td>22</td>
<td>26</td>
</tr>
<tr>
<td>M46</td>
<td>87</td>
<td>72</td>
<td>77</td>
<td>72</td>
<td>87</td>
<td>72</td>
<td>77</td>
<td>72</td>
</tr>
<tr>
<td>UTS50</td>
<td>106</td>
<td>62</td>
<td>62</td>
<td>61</td>
<td>48</td>
<td>24</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>UTS50 desized</td>
<td>166</td>
<td>108</td>
<td>109</td>
<td>108</td>
<td>120</td>
<td>78</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td>IMS65</td>
<td>230</td>
<td>129</td>
<td>163</td>
<td>127</td>
<td>216</td>
<td>131</td>
<td>127</td>
<td>130</td>
</tr>
<tr>
<td>IMS65 desized divided tow</td>
<td>360</td>
<td>177</td>
<td>228</td>
<td>177</td>
<td>41</td>
<td>30</td>
<td>41</td>
<td>28</td>
</tr>
<tr>
<td>IMS65 desized</td>
<td>44</td>
<td>30</td>
<td>41</td>
<td>28</td>
<td>44</td>
<td>30</td>
<td>44</td>
<td>30</td>
</tr>
<tr>
<td>IMS65 desized divided tow</td>
<td>49</td>
<td>33</td>
<td>38</td>
<td>33</td>
<td>49</td>
<td>33</td>
<td>49</td>
<td>33</td>
</tr>
<tr>
<td>UMS45</td>
<td>106</td>
<td>62</td>
<td>62</td>
<td>61</td>
<td>48</td>
<td>24</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>UMS45 desized</td>
<td>166</td>
<td>108</td>
<td>109</td>
<td>108</td>
<td>120</td>
<td>78</td>
<td>78</td>
<td>78</td>
</tr>
</tbody>
</table>

To investigate the impact of the amount of fiber filaments, cells with sized IMS65 from an undivided tow (24K = 24000 filaments) and with a divided tow (~3000 filaments) were assembled and cycled for ten full cycles. Mechanical tests on divided IMS65 and T800 displayed consistency in stiffness and strength showing that the tow could be divided properly without fiber damage. The results from the cells with different amount of IMS65 fiber filaments show no difference in capacity, as expected. However, similar cells made with sized T800 showed an increase in reversible capacity by almost 40%.

Figure 2. SEM images of sized, desized and unsized IMS65.

Figure 3. Lithiation/delithiation curves at 100 mA g\(^{-1}\) for the 1st and the 10th cycle for a) sized IMS65 and b) unsized IMS65.
Figure 4. Lithiation/delithiation curves at 100 mA g$^{-1}$ for the 1st and the 10th cycle for a) sized T800 and b) desized T800.

Figure 5. Capacity at different lithiation rates for T800, sized IMS65 and unsized IMS65 (the rates are based on the values in Table II). The current chosen for this study was deliberately set to 100 mA g$^{-1}$ since it is important to evaluate the capacity at realistic C-rates which would be required in an actual application instead of using very low rates to get high capacities.

The two grades of unsized fibers displayed a higher irreversible capacity loss between the first and the tenth lithiation than the sized and desized fibers. This phenomenon might be explained by results from previous studies, which concluded that a polymer coating...
can contribute to the formation of a more stable and flexible solid electrolyte interface (SEI) layer and therefore depress the irreversible capacity loss.22, 23

The results above show that even though the SEM images display a sizing-free fiber surface, which is supported by the fiber behavior after desizing, it is clear that the desizing process is not complete and that the desized fibers still have sizing residues. Due to the contradicting results for the desized fibers it is evident that the desizing process will require more work to ensure that a complete desizing is to be accomplished, regardless of sizing type.

Of all the tested fibers T800, unsized T300, desized IMS65 and unsized IMS65 were the most promising ones and will be further studied during the process of developing a functional structural battery. Unsized fibers are often hard to come by since it requires the manufacturers to stop the production and it will therefore be more practical and cost-effective to use sized fibers.

During this study it has become evident that fibers with intermediate modulus have better electrochemical properties than those with a high modulus. This can be seen if the results for IMS65 and T800 (intermediate modulus fibers) are compared to those for UMS45 and M46 (ultra high modulus fibers). However, the modulus is a property not only related to the microstructure and the degree of graphitization but also to the alignment of the graphite sheets in the fiber.24 Properties that will have a distinct affect on the ability to intercalate lithium ions. The results in Table II also show that regardless of manufacturer, fibers with similar tensile strength and modulus display similar electrochemical performance (IMS65 vs. T800; UMS45 vs. M46). A comparison of the cycling behavior seen in this paper to that reported in the literature shows that the fibers belong to the category of soft carbons.25

To further characterize the carbon fibers as a multifunctional electrode, an ongoing study is focusing on how the intercalation process affects the mechanical properties.

Conclusions

To evaluate the possibility of using carbon fibers as electrodes in structural lithium-ion batteries a series of different grades of commercial available carbon fibers have been studied. From the measurements performed in this study it is evident that carbon fibers can be used as the active negative material in further studies in the field of structural batteries. The following main conclusions can be drawn from this study:

- The cell design and using tabbed samples produced excellent reproducibility between cells containing the same kind of fibers.
- For some fibers the sizing will affect the capacity to a large extent. However, for other fibers the sizing has almost no impact at all on the capacity.
- Lithiation rate is extremely important. A slow lithiation rate will increase the reversible capacity enormously.
- Intermediate modulus fibers show better results than fibers with ultra high modulus.
- Fibers with similar tensile strength and modulus display similar electrochemical performance (IMS65 vs. T800; UMS45 vs. M46).
- Unsized fibers displayed a higher initial irreversible capacity loss compared to sized and desized fibers.

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References