PAN-BASED CARBON FIBERS FOR STRUCTURAL LITHIUM-ION BATTERIES

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Abstract
Structural batteries have the potential to become an integrated part of the device, functioning as both a structural element and as energy storage by combining electrochemical properties and mechanical properties in the same material. In addition, an increase of power and energy density on a system level could be achieved. The electrochemical properties of seven different commercially available PAN-based carbon fibers have been investigated as negative electrodes for structural lithium-ion batteries. All of the tested fibers showed some ability to intercalate lithium ions. The performance varied significantly between the different grades of fiber. Fibers with intermediate modulus showed the most promising results.

1 Introduction
Multifunctional materials have in recent years attracted more and more attention due the possibility to combine several properties into one single entity. Portable electronics and hybrid electrical vehicles are some areas that would greatly benefit by the use of multifunctional materials in the form of structural batteries. Conventional batteries are considered to be purely structurally parasitic since they only add to the weight of the device and not to the structural integrity. Structural batteries have the potential to become an integrated part of the device, functioning as both a structural element and as energy storage by combining electrochemical properties and mechanical properties in the same material. In addition, an increase of power and energy density on a system level could be achieved.

Conventional lithium-ion batteries consist of three major components: a positive electrode (usually based on metal oxides like $LiCoO_2$, $LiFePO_4$), a negative electrode (carbon-based materials) and an electrolyte (a lithium-ion conducting medium in liquid or solid form). Both electrodes are so-called lithium-ion intercalating materials i.e. they can store lithium-ions in their crystal lattice. The working principle is based on the transport of lithium ions from one of the electrodes through the electrolyte to the other electrode and depending on the direction the cell is either charged (positive to negative) or discharged (negative to positive). A more detailed description on the principles of lithium-ion batteries can be found elsewhere [1].

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 (crystallinity), but research has shown that the disordered structure of PAN-based fibers is more favorable for lithium-ion intercalation [2,3]. The mechanical properties of the PAN-based fibers also make them more suitable for structural composite batteries since both strength and stiffness are of great importance.

A first step in introducing mechanical properties into a lithium-ion battery would be to replace the ordinary carbon-based negative electrode by continuous carbon fiber tows, generating a negative electrode with the desired multifunctional properties. Carbon-fiber based electrodes can be designed so that no current collectors or conductive additives will be needed since carbon fibers themselves have reasonably good electrical conductivity. In figure 1 a SEM image of a conventional negative electrode consisting of graphite powder and a polymeric binder can be seen together with an image of PAN-based carbon fibers. By comparing these two images it is clear that the latter will present the electrode with the required mechanical properties needed in a structural battery.

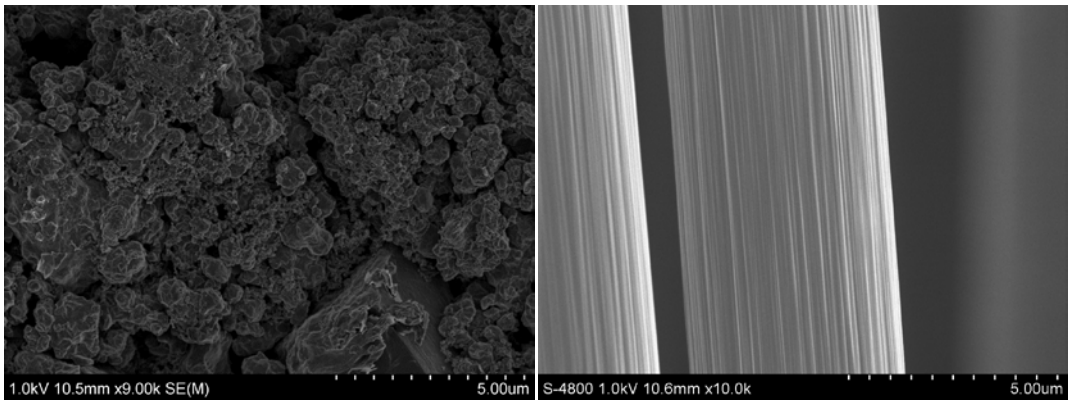

Figure 1. Left: SEM picture of a conventional negative electrode used in lithium-ion batteries. Right: SEM picture of a PAN-based carbon fiber negative electrode for structural lithium-ion batteries.

The study presented here is mainly focused on evaluating the electrochemical properties and performance of PAN-based carbon fibers for future use in structural lithium-ion batteries. The impact of lithium-ion insertion (lithiation) and extraction (delithiation) on the tensile properties of the fibers have also been investigated.

2 Experimental

2.1 Electrochemical testing

The electrochemical performance was tested for seven different grades of commercially available PAN-based fibers. The tested carbon fibers are listed in table 1. The carbon fibers were used either as received or with the sizing removed prior to sample preparation to evaluate the impact of sizing on capacity. “Desized” refers to a fiber where the sizing has been removed by washing in acetone and “unsized” refers to a fiber which has been taken out of production by the manufacturer prior to the sizing step, and these distinctions will be used henceforth.

Manufacturer	Grade	Diameter (μm)	Strength (MPa)	Modulus (GPa)	Sizing	Electrical Resistivity (Ωcm $\times 10^3$)
Toray	**T300**B 1K 50B	7	3530	230	Epoxy	1.5
Toray	**T800**HB 6K 40B P1 BB	5	5490	294	Epoxy	1.4
Toray	**M40**JB 6K 50B P1 BB	5	4410	377	Epoxy	0.8
Toray	**M46**JB 6K 50B P1 BB	5	4210	436	Epoxy	0.9
Toho Tenax	**UTS50** F13 12K 800tex	7	4800	240	PU	1.6
Toho Tenax	**IMS65** E23 24K 830tex	5	6000	290	Epoxy	1.45
Toho Tenax	**UMS45** F22 12K 385tex	4.7	4500	430	PU	0.97

Table 1. Carbon fiber properties as specified by the manufacturers.

All fiber grades were cycled with a constant current normalized by the mass of fiber in each sample between 0.002-1.5V. Lithium foil was used as the counter electrode, a glass-microfiber filter (Whatman) as separator and 1.0 M $LiPF_6$ in EC:DEC (1:1 w/w, LP40 Merck) was used as electrolyte. Cell assembly was performed in a glove box with an inert argon atmosphere (<1 ppm H_2O) at ambient temperature. The electrochemical testing of the fibers was performed in vacuum sealed pouch cells using tabbed specimens (figure 2). The sample preparation, desizing procedure and electrochemical testing has been described in detail elsewhere [4].

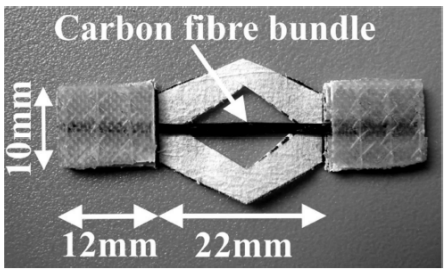

Figure 2. Tabbed carbon fiber specimen used for electrochemical testing.

The performance of the fibers will be presented in terms of specific capacity. The specific electrochemical capacity (mAh g^{-1}) is a commonly used figure of merit for battery materials and corresponds to the amount of lithium ions that can be intercalated (inserted) in a carbon fiber, normalized by the mass of fiber. The terms lithiation and delithiation will be used for fibers being charged and discharged with lithium ions, respectively.

2.2 Tensile test

The 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. Load, extension and time data during tensile tests until failure of the specimen were sampled every 100 ms with the Microtest software (Deben UK). Tensile tests were carried out after 1, 10, 100 and 1000 electrochemical cycles on lithiated and delithiated specimens of desized IMS65 and T800. Benchmarking of uncycled fibers was performed prior to the cycling and tensile testing. Further details on this study can be found elsewhere [5].

3 Results

3.1 Capacity evaluation

All of the tested fibers showed some ability to intercalate lithium ions. However, the reversible capacity varied significantly between the different 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. The capacity retention over ten cycles for a selection of fibers can be seen in figure 3. In figure 4 the cycle behavior of unsized IMS65 (blue curve) can be seen together with a conventional graphite electrode (red curve). The carbon fiber displays a similar behavior as the graphite electrode but has a more sloping appearance. Of all the tested fibers IMS65 and T800 were the most promising ones. Unsized IMS65 displayed the highest capacity but 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. The results also indicate that fibers with intermediate modulus (T800 and IMS65) have better electrochemical properties than those with a high modulus (UMS45). 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 [6], properties that will have a distinct affect on the ability to intercalate lithium ions.

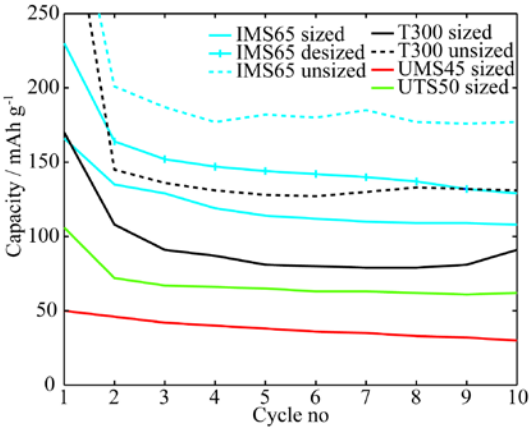

Figure 3. Capacity retention over ten cycles for a selection of the tested fibers.

3.2 Impact of sizing on capacity

Comparing the obtained results for the sized, desized and the unsized samples of the IMS65 fiber, it is evident that the sizing has a large influence on the reversible capacity for this specific fiber. Similar results were observed for sized and unsized T300, where the latter had a capacity of 130 mAh g^{-1} compared to less than 100 mAh g^{-1} for the former. For some of the other fibers (T800 and UMS45) the impact of sizing was less pronounced than for IMS65 and T300, indicating that sizing has a varying impact on the capacity. Hence, removing the sizing will not always result in an increased capacity and depends on the type of fiber and sizing.

3.3 Rate dependence

Figure 4 shows the results from the analysis of unsized IMS65 with different lithiation rates. A two-fold increase in capacity occurs when the current is reduced by a tenth (blue and black curves in figure 4); this trend was also observed for sized T800 and sized IMS65. The large variation in capacity shows that the design of a structural battery using PAN-fibers as negative electrode will need to be specifically designed to achieve optimal energy storage and structural performance.

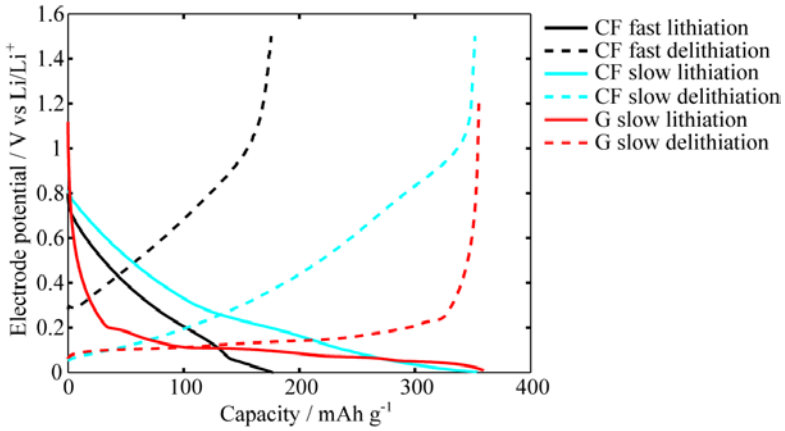

Figure 4. Cycle behavior of unsized IMS65 for two different lithiation rates (fast and slow) compared to the behavior of a conventional graphite electrode. CF: carbon fiber G: graphite

In addition to the results presented here, an ongoing study is focusing on determining the kinetics and transport properties of lithium ions in unsized IMS65 with electrochemical impedance spectroscopy (EIS). EIS results will be evaluated and quantified by a physically based electrochemical model.

3.4 Tensile tests after electrochemical cycling

In figure 5 some of the results from the tensile tests can be seen. Since the slope of the curves are unchanged it is clear that the tensile stiffness of the fibers are unaffected by lithium-ion intercalation/deintercalation.

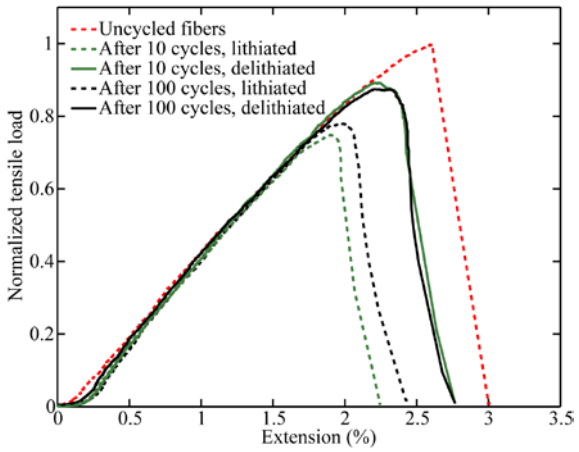

Figure 5. Tensile test of desized IMS65 for uncycled fibers and after 10 and 100 cycles at both lithiated (full of lithium ions) and delithiated (all lithium ions have been extracted) state.

However, the ultimate tensile strength is affected by cycling and also by the state of the fiber at the time of the test. A lithiated fiber exhibits a loss in the ultimate tensile strength which is partly recovered when the fiber is delithiated again. In addition to the losses in ultimate tensile strength between completely charged (lithiated) and discharged (delithiated) fibers, an initial irreversible loss occurs when the fibers are first lithiated. The number of cycles does not seem to have an impact on the tensile properties of the fibers. Similar results were obtained for T800.

Conclusions

To evaluate the possibility of using carbon fibers as electrodes in structural lithium-ion batteries a series of different grades of commercial available PAN-based carbon fibers have been studied. From the measurements performed it is evident that PAN-based carbon fibers can be used as the active negative material in a structural battery. Intermediate modulus fibers showed the highest reversible capacity. For some fibers the sizing can have an effect on the capacity. However, for other fibers the sizing has almost no impact at all on the capacity. The capacity is also found to be very rate dependent and a slow lithiation rate can increase the reversible capacity enormously. The tensile stiffness of the fibers is unaffected by cycling but the ultimate tensile strength displays an initial irreversible loss when the fiber is first lithiated. The ultimate tensile strength exhibits a loss when the fiber is in its lithiated state but can be partly recovered if the fiber is delithiated again.

Acknowledgements

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