Journal of The Electrochemical Society, **158** (12) A1455-A1460 (2011)
0013-4651/2011/158(12)/A1455/6/$28.00 © The Electrochemical Society

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

Maria H. Kjell,[a,*,z] Eric Jacques,[b] Dan Zenkert,[b] Mårten Behm,[a,] and Göran Lindbergh[a,**]**

[a]*School of Chemical Science and Engineering, Department of Chemical Engineering and Technology, Applied Electrochemistry and* [b]*School of Engineering Sciences, Department of Aeronautical and Vehicle Engineering, Lightweight Structures, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

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.
© 2011 The Electrochemical Society. [DOI: 10.1149/2.053112jes] All rights reserved.

Manuscript submitted May 25, 2011; revised manuscript received September 8, 2011. Published November 14, 2011. This was Paper 1239 presented at the Boston, Massachusetts, Meeting of the Society, October 9–14, 2011.

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.[1] 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).[2] Extensive research has focused on improving the lifetime, capacity and safety, and to decrease the cost of carbon materials.[3–7]

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.[8–12] 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.[13] The two most commonly used precursors for continuous carbon fibers are pitch and polyacrylonitrile (PAN).[14] Pitch-based fibers have traditionally been favored by the battery community due to a higher degree of graphitization,[15,16] but research have shown that the disordered structure of PAN-based fibers are more favorable for lithium-ion intercalation.[6,17] 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.[18–20] 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, Toho 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 I 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

* Electrochemical Society Student Member.
** Electrochemical Society Active Member.
z E-mail: mariakj@kth.se

Downloaded 23 Nov 2011 to 130.237.74.166. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

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

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

good impregnation of the fibers in the tabbing. In order to absorb all excess amounts of epoxy resin and to avoid resin from flowing along the fibers during cure, a breather fabric and a release film were used. To make sure that the fibers were kept straight and intact, the tabbing was attached onto a heat-resistant non-shrinking paper.

The carbon fiber samples were dried at 60°C in a vacuum oven overnight, prior to cell assembly to remove any water that would contaminate the electrolyte. A two-electrode pouch cell was chosen as the cell type for capacity testing, due to the sample design which requires a more versatile cell type. 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 dry argon atmosphere (<1 ppm H_2O) at ambient temperature.

Electrochemical capacity for the different carbon fibers was measured using galvanostatic cycling between 0.002–1.5 V vs. Li/Li^+ for ten full cycles with a current corresponding to 100 mA per gram of fiber. The current used corresponds to ∼0.25 C with respect to the theoretical capacity of 372 mAh g^{-1} for graphite. 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 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.

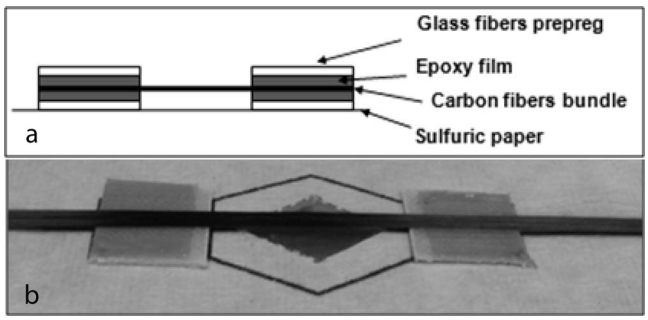

Figure 1. Schematic of sample with (a) tab structure and (b) top view of real sample.

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.

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 shown in previous work,[17] or any possible limitations due to electrolyte mass transport.

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. Figure 3 shows the lithiation and delithiation curves for the 1st and the 10th cycle for desized and unsized IMS65. 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[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.

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.

Downloaded 23 Nov 2011 to 130.237.74.166. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

Table II. Measured capacities for the 1st and the 10th cycle.

	Capacity (mAh g^{-1}) lithiation		Capacity (mAh g^{-1}) delithiation	
Grade	1st cycle	10th cycle	1st cycle	10th cycle
T300	170	91	79	87
T300 unsized	350	130	150	130
T800	170	98	88	97
T800 divided tow	252	136	131	135
T800 desized	194	112	128	110
M40	46	36	37	36
M40 desized	87	69	73	68
M46	31	26	22	26
M46 desized	87	72	77	72
UTS50	106	62	62	61
UTS50 desized	48	24	20	23
IMS65	166	108	109	108
IMS65 desized	230	129	163	127
IMS65 desized divided tow	216	131	127	130
IMS65 unsized	360	177	228	177
UMS45	44	30	41	28
UMS45 desized	49	33	38	33

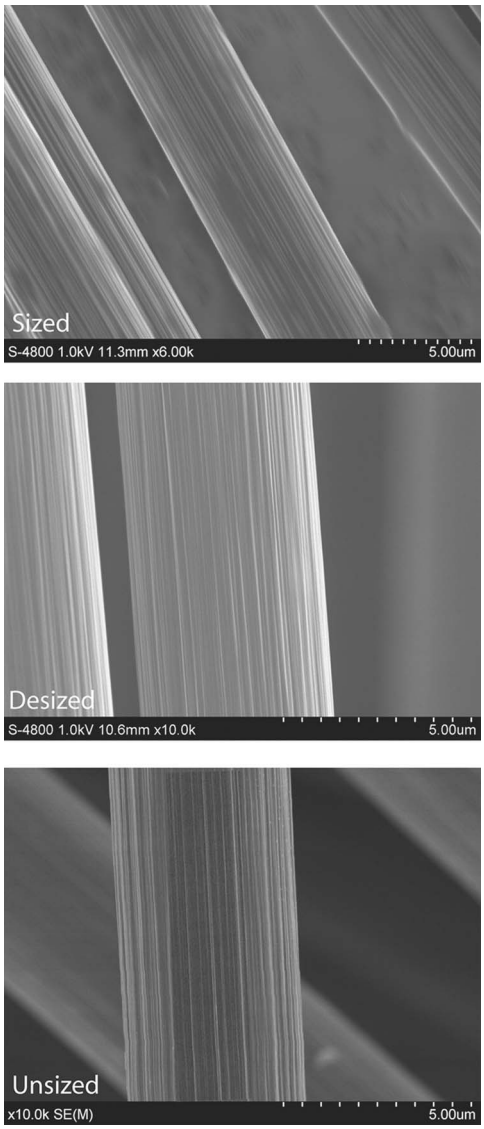

Figure 2. SEM images of sized, desized and unsized IMS65.

To investigate the impact of the amount of fiber filaments, cells with desized 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.[21] 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%,

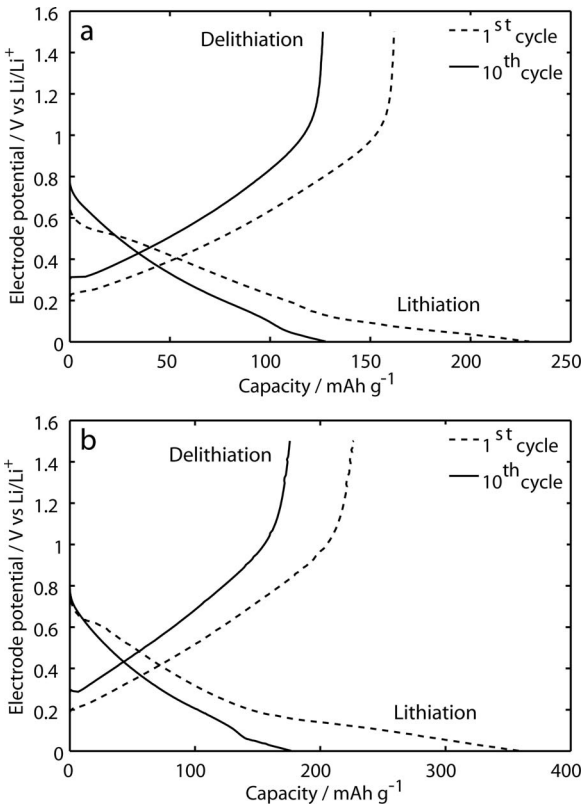

Figure 3. Lithiation/delithiation curves at 100 mA g^{-1} for the 1st and the 10th cycle for a) desized IMS65 and b) unsized IMS65.

Downloaded 23 Nov 2011 to 130.237.74.166. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

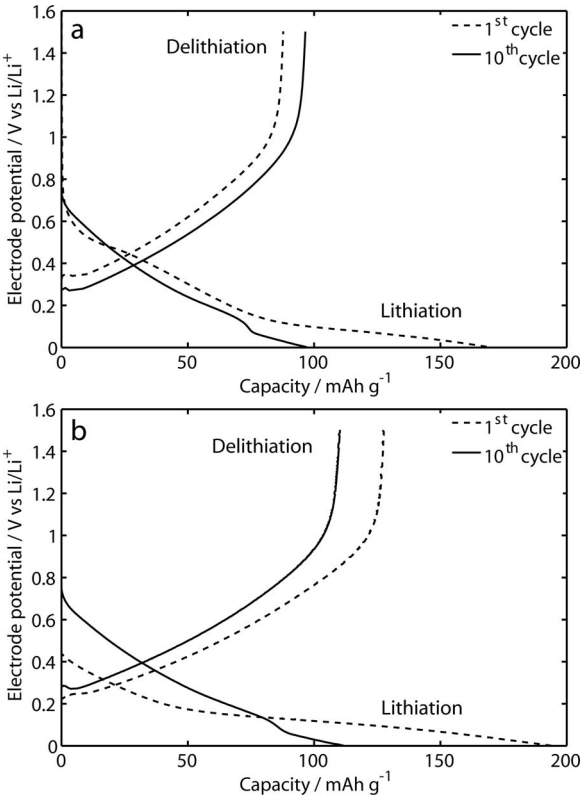

Figure 4. Lithiation/delithiation curves at 100 mA g^{-1} for the 1st and the 10th cycle for a) sized T800 and b) desized T800.

from 98 mAh g^{-1} to 136 mAh g^{-1}, for cells made with fewer fibers. The reason for this deviation is not known but since the T800 was more difficult to divide than IMS65 it might be a sign of non-uniform sizing.

Figure 5 shows the results from the analysis of T800, sized IMS65 and unsized IMS65 with different rates (currents based on the previously measured capacity in Table II). When the current is reduced by a tenth, the capacity is more or less doubled; this trend can be seen for all the tested fibers. Figure 6 shows all the lithiation curves for unsized IMS65. The large variation in capacity shows that the design of a structural battery using PAN-fibers as the negative electrode will need to be specifically designed to achieve optimal energy storage and

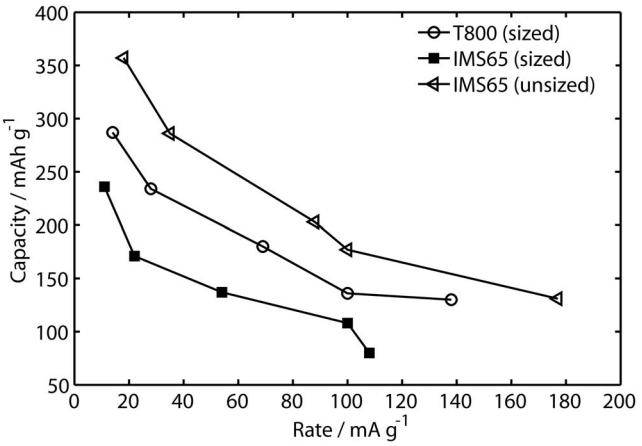

Figure 5. Capacity at different lithiation rates for T800, sized IMS65 and unsized IMS65 (the rates are based on the values in Table II).

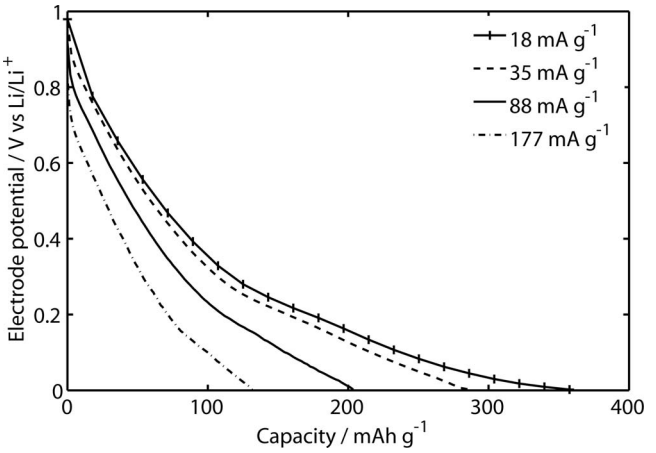

Figure 6. Lithiation curves at different rates for unsized IMS65 (the charging rates are equal to 0.1, 0.2, 0.5, and 1.0C based on $C_s = 177$ mA g^{-1}).

structural performance. 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 double-layer capacitance can be used as a measure of the electrochemically assessable surface area, assuming that the specific capacitance is not affected by the sizing. Table III shows the double-layer capacitance for sized, desized, unsized IMS65 and T800, both divided and full tows. The results from the CV scan, at potentials above the intercalation region, demonstrate that the electrochemical surface area is affected by the presence of sizing but not by the tow size for IMS65. The desized IMS65 have a surface area in between those obtained for the sized and unsized samples, which suggests that the desizing is not perfect. The surface area of sized T800, unlike IMS65, is affected by tow size. These results agree with the deviation seen in capacity for different tow sizes of sized T800 and confirm that a divided tow has an increased specific surface area. Figure 7 shows the CV curves of sized, desized and unsized IMS65, with a mesocarbon microbeads (MCMB) composite electrode as reference. A slight shift to the right of the anodic peak can be seen for the desized and sized IMS65 compared to that of the unsized IMS65, indicating that the sizing affects the kinetics in a negative way. Figure 8 displays the effect of fiber grade on the intercalation kinetics for sized T800 and sized IMS65. The effect can be seen as an anodic peak-shift to the right for IMS65, corresponding to slower intercalation kinetics, which confirms the results seen in Figure 5 that sized T800 perform better than sized IMS65 at moderate lithiation rates.

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

Table III. Double-layer capacitance measured with CV (sweep rate 10 mV s^{-1}).

Grade	Capacitance (F g^{-1})
IMS65 unsized full tow	0.14
IMS65 unsized divided	0.17
IMS65 desized divided	0.12
IMS65 sized full tow	0.08
IMS65 sized divided	0.07
T800 sized full tow	0.07
T800 sized divided	0.21
MCMB	2.77

Downloaded 23 Nov 2011 to 130.237.74.166. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

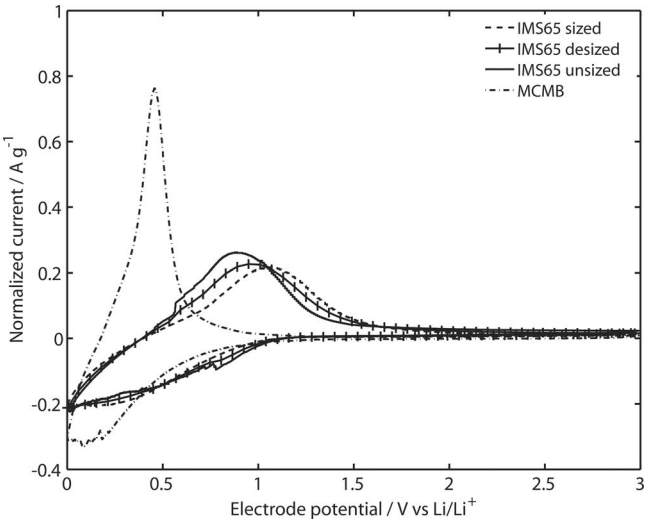

Figure 7. Cyclic voltammograms of sized IMS65, desized IMS65, unsized IMS65 and MCMB composite electrode (sweep rate 1 mV s^{-1}).

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

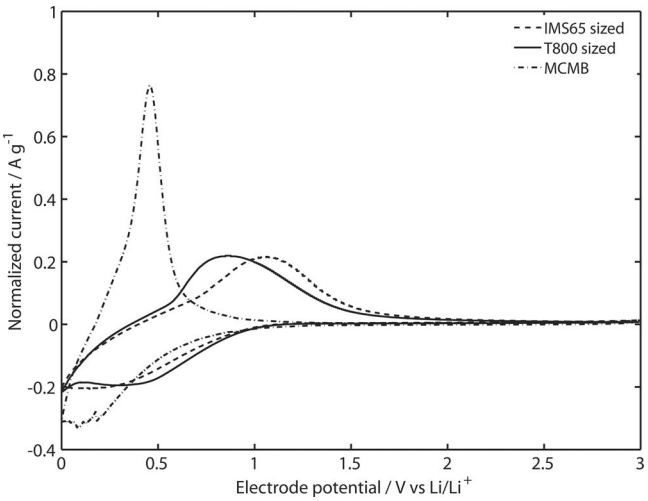

Figure 8. Cyclic voltammograms of sized IMS65, sized T800, and MCMB composite electrode (sweep rate 1 mV s^{-1}).

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.

Acknowledgments

Funding by the Swedish Foundation for Strategic Research (SSF), framework grant RMA08-0002 is gratefully acknowledged.

References

1. K. Zaghib and K. Kinoshita, in *New Trends in Intercalation Compounds for Energy Storage*, C. Julien, J. P. PereiraRamos and A. Momchilov Editors, p. 27 (2002).
2. W. Schalkwijk, B. Scrosati, Z. Ogumi, and M. Inaba, in *Advances in Lithium-Ion Batteries*, p. 79, Springer US (2002).
3. S. H. Yoon, C. W. Park, H. J. Yang, Y. Korai, I. Mochida, R. T. K. Baker, and N. M. Rodriguez, *Carbon*, **42**, 21 (2004).
4. T. K. Zhao, Y. N. Liu, T. H. Li, and X. Zhao, *Journal of Nanoscience and Nanotechnology*, **10**, 3873 (2010).
5. Y. C. Chang, H. J. Sohn, C. H. Ku, Y. G. Wang, Y. Korai, and I. Mochida, *Carbon*, **37**, 1285 (1999).
6. T. Iijima, K. Suzuki, and Y. Matsuda, *Synthetic Metals*, **73**, 9 (1995).
7. M. Lu, Y. Y. Tian, and Y. Yang, *Electrochimica Acta*, **54**, 6792 (2009).
8. S. Ekstedt, M. Wysocki, and L. E. Asp, *Plastics, Rubber and Composites*, **39**, 148 (2010).
9. J. P. Thomas and M. A. Qidwai, *Jom*, **57**, 18 (2005).
10. P. Liu, E. Sherman, and A. Jacobsen, *Journal of Power Sources*, **189**, 646 (2009).
11. J. F. Snyder, R. H. Carter, E. L. Wong, P.-A. Nguyen, E. H. Ngo, and E. D. Wetzel, *Proceedings of the 25th Army Science Conference* (2006).
12. E. L. Wong, D. M. Baechle, K. Xu, R. H. Carter, J. F. Snyder, and E. D. Wetzel, *Proceedings of Society for the Advancement of Materiel and Process Engineering (SAMPE)* (2007).
13. J. B. Donnet and R. C. Bansal, in *Carbon fibers*, M. Dekker (1990).
14. D. D. Edie, J. J. McHugh, and D. B. Timothy, in *Carbon Materials for Advanced Technologies*, p. 119, Elsevier Science Ltd, Oxford (1999).
15. K. Suzuki, T. Iijima, and M. Wakihara, *Electrochimica Acta*, **44**, 2185 (1999).
16. N. Imanishi, H. Kashiwagi, T. Ichikawa, Y. Takeda, O. Yamamoto, and M. Inagaki, *Journal of the Electrochemical Society*, **140**, 315 (1993).
17. J. F. Snyder, E. L. Wong, and C. W. Hubbard, *Journal of the Electrochemical Society*, **156**, A215 (2009).

Downloaded 23 Nov 2011 to 130.237.74.166. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

18. Y. J. Kim, H. J. Lee, S. W. Lee, B. W. Cho, and C. R. Park, *Carbon*, **43**, 163 (2005).
19. J. K. Lee, K. W. An, J. B. Ju, B. W. Cho, W. I. Cho, D. Park, and K. S. Yun, *Carbon*, **39**, 1299 (2001).
20. R. Kanno, Y. Kawamoto, Y. Takeda, S. Ohashi, N. Imanishi, and O. Yamamoto, *Journal of the Electrochemical Society*, **139**, 3397 (1992).
21. E. Jacques, M. H. Kjell, D. Zenkert, M. Willgert, G. Lindbergh, M. Behm, and M. Johansson, Manuscript to be submitted to *Composites Science and Technology*.
22. J. S. Kim, W. Y. Yoon, K. S. Yoo, G. S. Park, C. W. Lee, Y. Murakami, and D. Shindo, *Journal of Power Sources*, **104**, 175 (2002).
23. Q. M. Pan, K. K. Guo, L. Z. Wang, and S. B. Fangz, *Electrochemical and Solid State Letters*, **6**, A265 (2003).
24. X. Huang, *Materials*, **2**, 2369 (2009).
25. M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novak, *Advanced Materials*, **10**, 725 (1998).

Downloaded 23 Nov 2011 to 130.237.74.166. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp