

INITIAL STUDY OF THE MICROSTRUCTURE OF CARBON FIBRES ACTING AS NEGATIVE ELECTRODES IN STRUCTURAL BATTERY COMPOSITES

Fang Liu¹, Masoud Rashidi² and Leif Asp³

¹ Department of Physics, Chalmers University of Technology, 41296 Göteborg, Sweden
Email: fang.liu@chalmers.se

¹ Department of Physics, Chalmers University of Technology, 41296 Göteborg, Sweden
Email: masoud.rashidi@chalmers.se

³ Department of Applied Mechanics, Chalmers University of Technology, 41296 Göteborg, Sweden
Email: leif.asp@chalmers.se

Keywords: structural batteries, carbon fibres, microstructure, SEM, TEM,

Abstract

Structural composite batteries are a novel type of multifunctional devices, which have a great potential to remarkably reduce the mass of electric vehicles, and thus increase their energy efficiency. In these batteries, carbon fibres (Carbon fibres) play dual roles: reinforcements (as in CARBON FIBRE composites) and negative electrodes (as in batteries). However, the relationship between the microstructure and the electrochemical property of the Carbon fibres is not well understood. In this study, the microstructure of two Carbon fibres, M60J and IMS65, were studied by using scanning electron microscopy and transmission electron microscopy. Detailed microstructural features were revealed, and correlated to the electrochemical properties of the Carbon fibres. The more disordered microstructure, and rather large pores are the reasons for the better electrochemical properties of IMS65 compared to M60J.

1. Introduction

Imagine the polymeric composite frame of a car simultaneously stores electrochemical energy. This can be realized by a multifunctional device called structural composite battery. Multifunctionality is more efficient in realizing substantial weight/volume savings, compared to the conventional approach by optimising the individual subsystems, i.e. in this case the load-bearing structure and the power storage component. A Swedish interdisciplinary team of scientists formed in 2009 is now one of the leading teams in the new research field of structural composite batteries. In 2012 we proposed a radically novel concept for structural battery [1]: using the individual carbon fibres as battery electrodes. We have demonstrated such a battery with an energy density of 10 Wh/kg. By optimizing different components of the battery an energy density of 200 Wh/kg and a shear modulus of 1 GPa can be realized [2].

The most crucial component for a structural composite battery is carbon fibres, which provide mechanical strengthening and simultaneously function as negative electrodes, thanks to their capability of intercalating lithium ion at very low electrode potential. Under the same condition, electrochemical capacity of different carbon fibres (i.e. the capacity of lithiation and delithiation) can vary up to nearly eight times [3]. The reason lies in the microstructure of carbon fibres. Breaking the microstructure of a carbon fibre down to the most basic level, it contains turbostratic (or disordered) graphite – graphene layers with relatively large distances (~ 0.3 nm) in between. Twisted graphite

domains form fibrils, which further align along the fibre axis and finally form carbon fibres with a diameter $\sim 5 \mu\text{m}$. In the fibres there are always some structural defects, such as pores. The porosity rate can sometimes reach up to 20%. How the microstructure of carbon fibres governs lithium intercalation remains largely unknown.

In this paper we present the initial findings of fibre microstructure of two commercially available carbon fibres and compare these with their measured electrochemical properties. Here, only pristine fibres are studied using a high-resolution scanning electron microscope (SEM) and transmission electron microscopes (TEM).

2. Materials and experiment

Two commercially available polyacrylonitrile (PAN)-based carbon fibres were studied: M60J (Toray), and IMS65 (Toho Tenax). The strength and modulus are 3920 MPa and 588 GPa for M60J, and 6000 MPa and 290 GPa for IMS65.

A Leo Ultra 55 SEM with a field emission gun was used. The SEM was operated at a low voltage range 1–10 kV. An in-lens secondary electron detector was used to acquire SEM micrographs. In order to investigate the transverse cross-sections of the carbon fibres using SEM, the fibres were broken, while merged in liquid nitrogen, using a pair of tweezers.

A Titan 80-300 TEM, operated at 300 kV, was used to analyse the axial cross-sections of carbon fibres. Both bright field and dark field images were acquired. Convergent beam electron diffraction was performed to study ordering of the microstructure in carbon fibres. In order to prepare TEM specimens with a thickness of $\sim 100 \text{ nm}$, the in-situ lift-out technique was employed using an FEI Versa 3D workstation, a combined focused ion beam microscope and SEM (FIB/SEM), equipped with an Omniprobe micromanipulator. To protect the very surface of the carbon fibre from ion damaging during the specimen preparation procedure, a layer of Pt was deposited with the aid of the gas injection system in the workstation. Figure 1 (a) shows a carbon fibre with a deposited Pt layer. After this step, a small piece was cut out using the FIB; then lifted out from its surrounding; transferred to a 3 mm TEM grid using the micromanipulator; and finally ion polished down to 100 nm thick with the FIB. Thus, a TEM specimen was obtained. Figure 1 (b) shows the TEM specimen with axial cross-section of the carbon fibre. A detailed description of this sample preparation process technique was reported elsewhere [4].

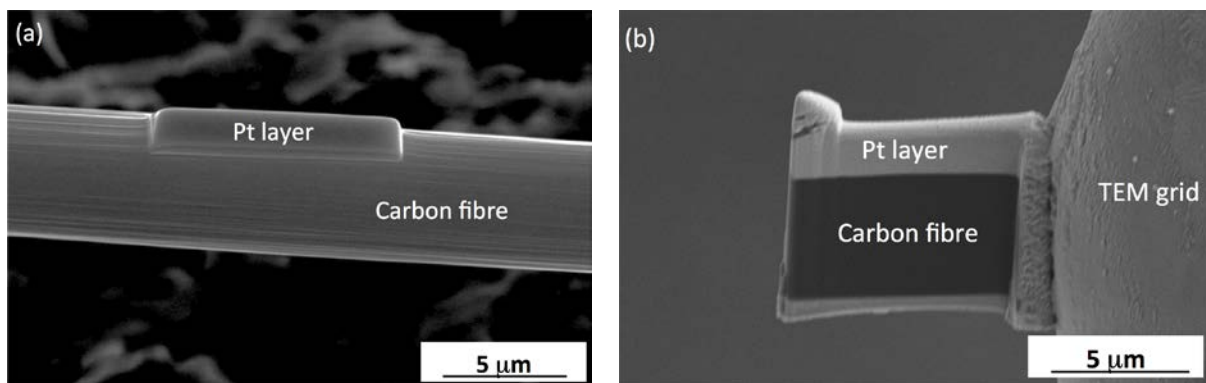


Figure 1. SEM micrographs showing the TEM specimen preparation procedures. (a) A carbon fibre with a Pt layer on top to protect the surface. (b) A TEM specimen with axial cross-section of the carbon fibre.

3. Results and discussion

The fractured surfaces are very rough (Figure 2 (a) and (c)). The topography of the surface varies remarkably especially for IMS65, probably due to the poorly controlled fracture procedure. However, it reflects the difference in the microstructure. Both amorphous and crystalline areas were observed in the transverse cross-sections of M60J and IMS65. The amorphous areas appear very smooth, while the crystalline areas with small granules appear rough in the high resolution SEM micrographs (Figure 2(b) and (d)). Dozens of cross-sections were investigated; the proportion of amorphous areas varies quite a lot even for the same grade of fibre. In the crystalline areas of M60J, the granules appear spherical and have a rather smooth surface, with a size around 100 nm. In the crystalline areas of IMS65, the granules are much smaller, under 20 nm. Therefore, it yields a very rough surface. Another striking difference between these two fibres is that in M60J almost no pores were observed using SEM, while in IMS65 the voids are ubiquitous, and the size of the pores is about 20 nm.

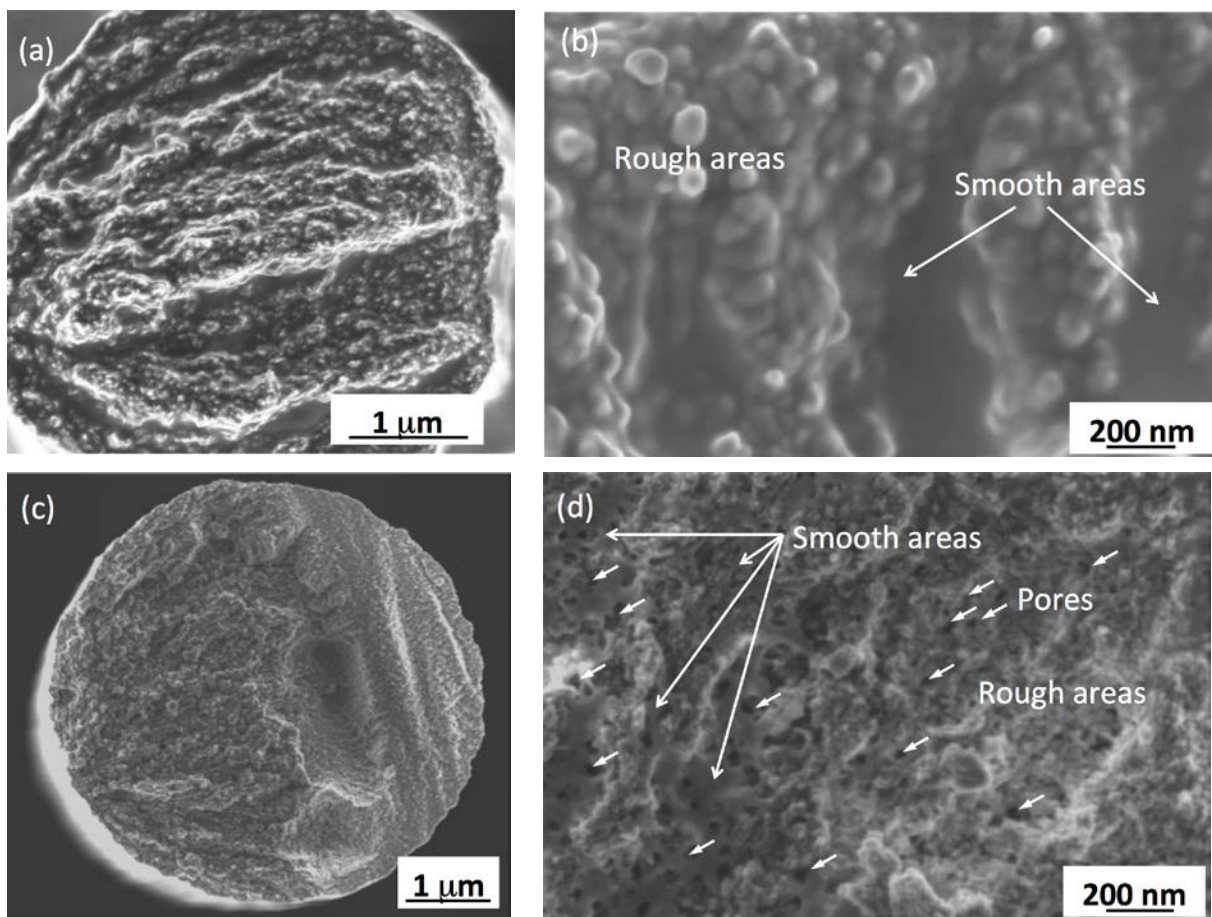


Figure 2. SEM micrographs showing detailed microstructure of the fractured transverse cross-sections of M60J and IMS65. (a) Overview of the surface of M60J. (b) Detailed microstructure in M60J showing smooth areas and rough granular areas. The granules are spherical shape, the size is rather big, around 100 nm, and their surface is rather smooth. There are no visible voids. (c) Overview of the surface of IMS65. (d) Detailed microstructure in IMS65 showing the smooth areas, rough granular areas, and voids. The size of granules is much smaller, under 20 nm. The size of the voids is about 20 nm.

TEM was used to determine the degree of microstructural ordering in the carbon fibres in much detail. Figure 3 (a) shows a dark field TEM micrograph of the axial cross-section of M60J, using the (002)

diffraction spot. The inset is a typical convergent beam electron diffraction pattern taken from M60J. The size of the electron beam is barely a few nanometres, which means that these patterns reflect the local crystallographic information from a volume a few nanometres in width and 100 nm in depth. The (002) diffraction patterns are sharp, small, and round disks. Hence the grapheme layers (with the (002) index) are well aligned in this material. In addition, there are many elongated needle-shaped pores, appearing dark in contrast. Their sizes are a few nanometres wide and more than 10 nm long. Although the dark field micrographs of IMS65 appear similar to those of M60J, convergent beam electron diffraction patterns reveal significant difference (Figure 3 (b) inset). Instead of round disks, the (002) diffraction patterns appear as sections of an arc, which means that in the small volume of a few nanometres in width and 100 nm in depth, the orientation of the grapheme layers varies. The high resolution TEM micrograph of IMS65 also showed highly disordered structure (Figure 3 (b)).

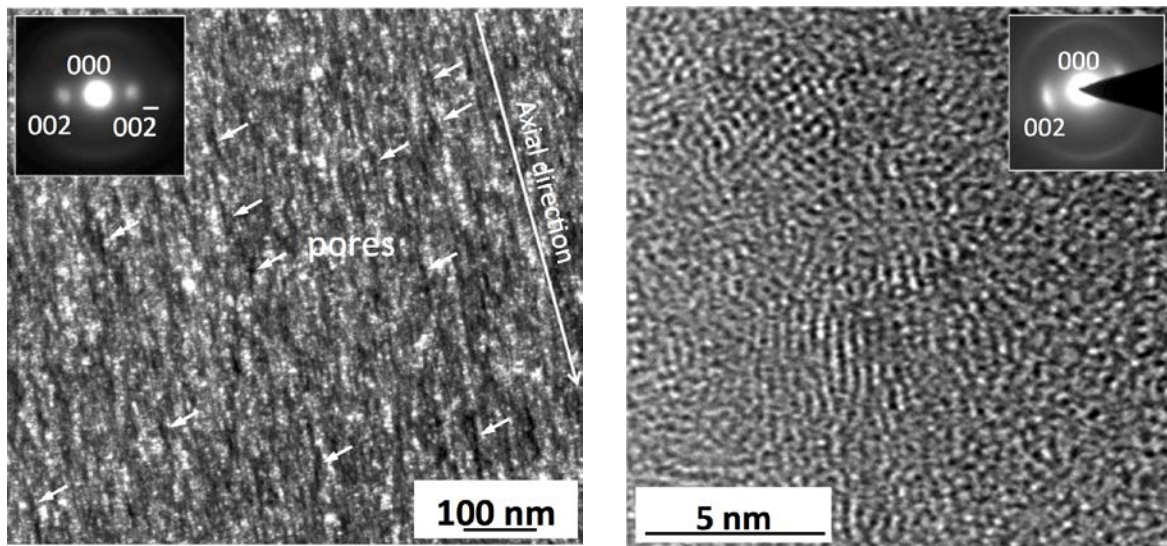


Figure 3. TEM micrographs showing the microstructure of the carbon fibres along the axial direction. (a) A dark field micrograph of M60J, using the (002) diffraction. Note that there are many pores with dark contrast, and a few of them are highlighted by arrows. The pores are elongated (> 10 nm in length, and a few nanometres in width) and aligned along the axial direction. (b) HRTEM micrograph of IMS65. The structure is highly disordered. The inset is a typical convergent beam diffraction pattern. Note that the (002) patterns are sections of an arc.

IMS65 have demonstrated promising electrochemical properties for applications in structural composite batteries [3,5]. The initial and cycling capacity of lithiation and delithiation of IMS65 is better than many other grades of carbon fibres, approaching 370 mAh g^{-1} . This value is comparable with the maximum value for perfect graphitic carbons 372 mAh g^{-1} . In addition, IMS65 have many other advantageous electrochemical properties such as mass transport, exchange current density, and electronic conductivity [5]. Interestingly, amorphous carbon with small dimensional graphite crystallites exhibits a much higher capacity than perfect graphite carbon – up to 900 mAh/g and more [6]. The present study shows that indeed IMS65 have a more disordered microstructure, which explains their better electrochemical properties. In addition, the pores may also play important roles in accommodating Li ions. However, detailed electrochemical processes and mechanisms, for instance how lithium ions intercalate into the carbon fibres, needs further investigation.

4. Conclusions

The detailed microstructure of M60J and IMS65 was studied using SEM and TEM. M60J has a much

more ordered microstructure with many small needle-shaped pores. IMS65 has a much more disordered microstructure, with many relatively large pores. The highly disordered microstructure, and rather large pores may explain the better electrochemical properties of IMS65 compared to M60J.

Acknowledgements

Funding from the strategic innovation programme LIGHTer provided by VINNOVA and Chalmers AoA Energy is gratefully acknowledged.

References

- [1] L. E. Asp, et al., PCT Intl Appl No. PCT/EP2013/068024. 2012.
- [2] L. E. Asp, and E. S. Greenhalgh, *Comp Sci Technol*, Vol. 101, 2014, pp. 41-61.
- [3] M. H. Kjell, E. Jacques, D. Zenkert, M. Behm, G. Lindbergh, PAN-Based Carbon fibre Negative Electrodes for Structural Lithium-Ion Batteries, *Journal of the Electrochemical Society*, Vol. 158(12), 1455-60, 2011.
- [4] F. Liu, H. Götlind, J.-E. Svensson, L.-G. Johansson, M. Halvarsson, TEM Investigation of the Microstructure of the Scale Formed on a FeCrAlRE alloy at 900°C – the Effect of Y-rich RE Particles, *Oxidation of metals*, Vol. 74, 11-32, 2010.
- [5] M. H. Kjell, T. G. Zavalis, M. Behm, G. Lindbergh, Electrochemical Characterization of Lithium Intercalation Processes of PAN-Based Carbon Fibres in a Microelectrode System Batteries and Energy Storage, *Journal of the Electrochemical Society*, Vol. 160(9), 1473-81, 2013.
- [6] Lijun Fu et al. *Negative Electrode materials based on carbon*. in: Wu Yuping (Ed.), *Lithium Ion Batteries, Fundamentals and Applications*, CRC Press, 161-224 2015.