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Energimyndighetens titel på projektet – svenska Inverkan av mekaniska och elektrokemiska processer på kolfibrer i strukturella kompositbatterier
Energimyndighetens titel på projektet – engelska Towards multifunctional batteries – insights into carbon fibres in dynamic electrochemical and mechanical processes

Universitet/högskola/företag	Avdelning/institution
Chalmers Tekniska Högskola	Materials and Manufacture

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Nyckelord: 5-7 st multifunctional composite materials, structrual battery, carbon fibres, microstructure charaterization, lithiation, atom probe tomography, Auger spectroscopy

Förord

This project has been financially supported by the Swedish Energy Agency and Chalmers University of Technology. The success of the project largely relies on the close collaboration between the Swedish structural battery research team, including Profs Fang Liu, Johanna Xu, Leif Asp at Chalmers, and Profs. Mats Johansson, Dan Zenkert, and Göran Lindbergh at KTH.

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Sammanfattning

Föreställ dig att panelerna på en elbil också fungerar som energilagringsenheter! Denna vision kan realiseras genom en multifunktionell lösning kallad strukturellt kompositbatteri, som har stor potential att minska vikten på elfordon och därmed förbättra deras energieffektivitet. I dessa innovativa batterier fyller kolfibrer en dubbel funktion: de fungerar både som förstärkningselement (som i kolfiberkompositer) och som anoder (som i batterier). Dock är sambandet mellan kolfibrernas mikrostruktur och deras elektrokemiska egenskaper ännu inte fullt förstått, vilket begränsar den fortsatta utvecklingen av dessa batterier.

I detta projekt har vi för första gången undersökt lithierade kolfibrer med hjälp av avancerade mikroskopitekniker, särskilt atomsondstomografi, för att kartlägga fördelning av litium ända ner på atomnivå. Våra resultat visar att pyridiniska och pyrroliska N-heteroatomer kan förbättra kolfibrernas elektrokemiska prestandan; under laddning sker initial litiuminlagring i amorfa domäner, medan högre lithieringsnivåer sker i kristallina domäner. Genom atomupplösta analyser av enskilda atomer i lithierade kolfibrer fann vi att litiumens fördelning är oberoende av N-heteroatomernas fördelning. Litium fördelas jämnt över alla domäner, men aggregerar vid högre lithieringsnivåer.

Summary

Imagine that the panels of an electric car also store electrochemical energy! This vision can be realized by a multifunctional device called structural composite battery, which has a great potential to remarkably reduce the mass of electric vehicles, and thus increase their energy efficiency. In these novel batteries, carbon fibres play dual roles: reinforcements (as in carbon fibre composites) and anodes (as in batteries). However, the relationship between the microstructure and the electrochemical property of the carbon fibres is not fully understood. This knowledge gap severely hinders further development of the battery. In this project we have, for the first time, studied lithiated carbon fibres by using a combination of state-of-the-art microscopy techniques, particularly atom probe tomography to map Li distribution down to the atomic level.

We have revealed that pyridinic and pyrrolic type of N heteroatoms can enhance electrochemical performance of carbon fibres; during charging, Li is initially inserted in amorphous domains and with increased states of lithiation in crystalline domains; by analysing individual atoms inside lithiated carbon fibre with atomic resolution, we found that the distribution of Li is independent of the distribution of N heteroatoms; trapped Li is distributed rather uniformly in all domains; and Li agglomerates at elevated states of lithiation.

Inledning/Bakgrund

Reducing the weight of batteries – a key challenge

Sweden has committed to cutting net greenhouse gas emissions to zero by 2045 [1], which requires radical changes in various sectors. Although representing a large source of greenhouse gas emissions today (~25% in Sweden [2] and >20% globally [3]), the transport sector has a great potential to dramatically reduce greenhouse gas emissions through particularly electrification of vehicles, especially given the rapid growth of renewable electricity generation. However, a primary obstacle that hinders the wide adoption of electric vehicles is the short driving range, which is partially attributed to the weight of the batteries. The dilemma here is: in order to have a longer driving range, an electric vehicle needs more/heavier batteries, which means extra energy is needed just to carry the extra batteries around.

Imagine that the panels of an electric car also store energy (Fig. 1)! This vision can be realized by a multifunctional device called structural composite battery [4], which can simultaneously carry mechanical loads and store energy. Compared to the conventional approach that optimises the individual subsystems, multi-functionalization provides a more efficient way to realize substantial weight savings on the system level. It was estimated that replacing the outer panels of an electric car with structural composite batteries can cut ~ 15% of the overall mass of the car, and thus increasing its energy efficiency by 6–10% [5,6].

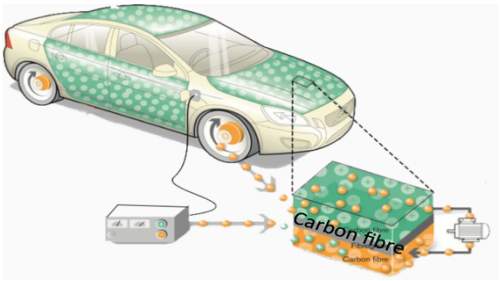

Fig. 1 *The concept of structural composite batteries. Carbon fibre composite material builds up the panels, and simultaneously stores electrical energy in a personal vehicle.*

Structural composite batteries

There are two major approaches to realize the concept of structural composite batteries: battery safe inside the structure, and structure acting as battery. The former is based on embedding conventional lithium-ion battery cells in carbon fibre reinforced composites [7]; while the latter integrating energy storage function into carbon fibre reinforced composites [8,9], by making use of the intrinsic electrochemical nature of carbon fibres and solid electrolyte matrix. The second approach attracts considerable scientific and technological interest, since it realizes truly multifunctional from the level of base materials. The proposed project focuses only on this approach.

A structural composite battery is rechargeable. Carbon fibres play dual roles here, reinforcements (as in carbon fibre composites) and negative electrodes (as in batteries); and the polymer matrix is also multifunctional, bonding the fibres together and transferring loads between them (as in carbon fibre composites), and also functioning as electrolytes (as in batteries). Huge progress has been made in i) demonstrating that carbon fibres are viable as an electrode material – some fibre grades exhibit an electrochemical capacity on a par with commercial graphite

based electrode materials, and a coulombic efficiency (an indication of the lifetime of a battery) even higher than commercial graphite based electrode materials [10,11]; ii) improving the ion conductivity, while maintaining the stiffness of solid polymer electrolytes in these batteries[12,13]. For instance, via using reaction induced phase separation, a sub-micron interconnected two phase system forms, where one phase provides ionic conductivity and the other mechanical integrity; and iii) proving the concept of structural composite batteries [14]. However, in order to further improve the performance of these multifunctional batteries, several scientific challenges closely related to carbon fibres need to be addressed: i) What microstructure features facilitate electrochemical performance of carbon fibres? ii) How Li atoms interact with the microstructure features of carbon fibres?

Genomförande

In this project, we focused on

i) revealing the chemical states of N-heteroatoms in carbon fibres and correlating it with the electrochemical properties of the fibres with synchrotron hard X-ray photoelectron spectroscopy (HEXPES);
ii) revealing the interaction between the Li atoms and amorphous and crystalline domains in intermediate strength carbon fibres using Auger Spectroscopy;
iii) developing the methodology of analysing carbon fibres and lithiated carbon fibres using atom probe tomography (APT);
iv) mapping Li distribution in carbon fibres using APT;

This project was mainly conducted by PhD student Marcus Johansen and me. We collaborated with Prof Leif Asp and Dr Johanna Xu to manufacture structural composite battery cells to obtain carbon fibres with various states of lithiation. Additionally, we collaborated with Dr Christoph Schlueter at Desy (Deutsches Elektronen-Synchrotron, Hamburg, Germany) for HAXPES analysis and Prof Dr Baptise Gault from Max Planck Institute of Sustainable Materials in Düsseldorf for APT of lithiated carbon fibres.

Resultat

1. Pyridinic and pyrrolic type of N heteroatoms can enhance electrochemical performance of carbon fibres. (Publication: “Mapping nitrogen heteroatoms in carbon fibres using atom probe tomography and photoelectron spectroscopy”, *Carbon*, 2021. https://doi.org/10.1016/j.carbon.2021.03.061)

Our previous transmission electron microscopy studies have shown that carbon fibres’ crystallinity play an important role in determining their energy capacity. High-modulus (HM) carbon fibre M60J (Toray) exhibits high crystallinity but low energy capacity (159 mAh/g), while the intermediate-modulus (IM) carbon fibre T800 (Toray) and IMS65 (Teijin) exhibit low crystallinity and higher energy capacity (265 and 358 mAh/g). With similar crystallinity as IMS65, T800 however, has 35% lower capacity.

In order to understand the reason behind the difference in the capacity of IMS65 and T800, we used APT and synchrotron HAXPES. We found that the average N concentration varies between the fibres and APT specimens: T800 1.6–2.9 at%, IMS65 1.3–2.9 at%, and M60J virtually 0 at%. In order to shed light on the chemical states of N, we analysed the fibres using synchrotron HAXPES. In IMS65, a higher level of N has the pyridinic- and pyrrolic-N configuration (~20% in total) compared to T800 (~14%). As a result, with comparable N concentration, IMS65 has more N induced defects working as active sites and consequently higher capacity than T800.

2. Auger electron spectroscopy can distinguish chemical configurations of lithium. (Publication: "Lithiated Carbon Fibres for Structural Batteries Characterised with Auger Electron Spectroscopy", *Applied Surface Science*, 2023, https://doi.org/10.1016/j.apsusc.2023.157323)

Intermediate-modulus carbon fibre T800 and IMS65 have a relatively high energy capacity, 265 and 358 mAh/g, respectively (compared to 372 mAh/g for graphite). However, their lithiation mechanisms are not clear. We have shown that Auger electron spectroscopy (AES) is a powerful tool to analyse lithiated carbon fibres. It possesses a spatial resolution down to the nano-metre level, and capability to study both the surface and depth information. Additionally, it can distinguish chemical configurations of lithium, for instance Li-O, Li-C, Li metal, and intercalated Li with antibonding π^*. We revealed that lithium is first inserted into disordered domains of carbon fibres, then ordered. The thickness and chemical composition of solid electrolyte interphase varies between carbon fibres in the same carbon fibre tow. AES analysis across the cross-section of fully lithiated carbon fibres reveals that the Li/C intensity ratio is rather uniform across the transverse direction of the fibre and no preferential Li enriched region is observed. We also found the concentration of remaining Li in fully discharged carbon fibres depends on the discharge rate. When fully discharged down to 0 % of the electrochemical potential at a low discharge rate of C/20, the Li signal drops below the detection limit for AES. However, for the fully discharged fibres at a more rapid discharge rate of C/5, detectable quantities of Li remain in the fibres. Additionally, at increased discharge rates the remaining Li is preferentially located at the inner part of the fibre.

3. The distribution and agglomeration of Li in lithiated carbon fibres have been successfully revealed by atom probe tomography. (Publication: "Unravelling lithium distribution in carbon fibre electrodes for structural batteries with atom probe tomography", *Carbon*, Vol, 225, 119091, 2024. https://doi.org/10.1016/j.carbon.2024.119091)

We have demonstrated the important role of N heteroatoms in determining the electrochemical properties of carbon fibres. An interesting follow-up question is "How do N heteroatoms interact with Li atoms?". Using the high spatial resolution of APT in lithiated carbon fibres, we discovered that: Firstly, the distribution of Li is independent of the distribution of N heteroatoms; Secondly, trapped Li atoms are distributed rather uniformly in all domains; and finally, Li

agglomerate preferably in the amorphous domains at elevated states of lithiation, and the turbostratic crystalline domain is less accessible to Li.

4. This project has paved the way for using atom probe tomography to analyse both carbon fibers and lithiated carbon fibers. (Publications: “Best practices for analysing carbon fibres by atom probe tomography”, *Microscopy and microanalysis*, 2022. https://doi.org/10.1017/S1431927621012812, “Suppressing lithium migration in carbon fiber negative electrode during atom probe tomography analysis”, *Microscopy and microanalysis*, 2024. https://doi.org/10.1093/mam/ozae058)

APT of carbon fibers was still unexplored when we started this project. Based on our previous work on carbon fibres’ microstructure and correlated physical properties, we developed methods to interpret the complex mass spectra of carbon fibers, enhance the mass resolution of mass spectra, and increase the obtained analysis volume. For the first time, a guidance for future APT studies on carbon fibers has been provided.

Analysing lithiated carbon fibers is extremely challenging since lithiated carbon fibers experience massive Li migration once exposed to the electric field in the APT instrument. Consequently, the original positions of individual atoms are lost, along with critical information about the interactions between Li atoms and the carbon fiber. We demonstrated that a few nanometers of a chromium (Cr) coating on APT specimens can shield the electric field and suppress the massive Li migration.

Diskussion

The results of this project are significant in at least the following two aspects:

i) Tailor design carbon fibres for structural composite batteries with optimised multifunctional properties–both mechanical and electrochemical. The majority of carbon fibres are manufactured from the precursor polyacrylonitrile (PAN) with chemical formula $(C_3H_3N)n$. During manufacture, PAN precursor fibres undergo multiple steps of thermal treatment that alter their chemical composition and structure. Depending on the treatment, the obtained carbon fibres contain from 90 to > 99 wt% C, the rest being mainly O and N. We have found that pyridinic and pyrrolic type of N heteroatoms can enhance electrochemical performance of carbon fibres. It is worth noting that N are intrinsically abundant in the PAN precursor, hence it provides a convenient “in-situ” route to produce N-doped carbon fibres. Additionally, with the detailed information on the interaction of Li atoms with carbon fibres revealed by APT and AES, Hence, we identify key for enhancing the electrochemical capacity of carbon fibres to be modification of the crystalline domains–changing the graphene stacking to be less turbostratic and more ordered

towards graphitic. Thus, controlling heteroatoms and crystalline domains in carbon fibres can enable enhanced electrochemical properties.

ii) The methodologies developed for APT and AES of pristine and lithiated carbon fibres provide power tools to probe the microstructure and reveal the fundamental processing-structure-properties relationship. These methods can also be used in other carbon based materials for energy storage.

Publication list

1. M. Johansen, C. Schlueter, P. L. Tam, L. E. Asp, **F. Liu**. "Mapping nitrogen heteroatoms in carbon fibres using atom probe tomography and photoelectron spectroscopy". *Carbon*, Vol. 179, p 20–27, 2021. https://doi.org/10.1016/j.carbon.2021.03.061
2. M. Johansen, J. Xu, P. L. Tam, L. E. Asp, **F. Liu**, "Lithiated Carbon Fibres for Structural Batteries Characterised with Auger Electron Spectroscopy", *Applied Surface Science*, Vol. 627, 157323, 2023, https://doi.org/10.1016/j.apsusc.2023.157323
3. M. Johansen, M. Singh, J. Xu, L. E. Asp, B. Gault, **F. Liu**, "Unravelling lithium distribution in carbon fibre electrodes for structural batteries with atom probe tomography", *Carbon*, Vol, 225, 119091, 2024. https://doi.org/10.1016/j.carbon.2024.119091
4. M. Johansen, M. Singh, B. Gault, **F. Liu**, "Suppressing lithium migration in carbon fiber negative electrode during atom probe tomography analysis", *Microscopy and microanalysis*, 2024. https://doi.org/10.1093/mam/ozae058
5. M. Johansen, **F. Liu**. "Best practices for analysing carbon fibres by atom probe tomography", *Microscopy and microanalysis*, Vol 28, p 1092–1101, 2022. https://doi.org/10.1017/S1431927621012812

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- R. Tavano, J. Xu, C. Creighton, **F. Liu**, B. Dharmasiri, L. C. Henderson, L. E. Asp "Influence of carbonisation temperatures on multifunctional properties of carbon fibres for structural battery applications", *Batteries & Supercaps*, 2024. https://doi.org/10.1002/batt.202400110
- J. Xu, C. Creighton, M. Johansen, **F. Liu**, S. Duan, D. Carlstedt, P. Mota-Santiago, P. Lynch, L. E. Asp, "Effect of tension during stabilization on carbon fiber multifunctionality for structural battery composites", *Carbon*, Vol 209, 117982, 2023. https://doi.org/10.1016/j.carbon.2023.03.057
- S. Duan, M. Cattaruzza , V. Tu , R. M. Auenhammer, R. Jänicke, M. K. G. Johansson, **F. Liu** and L. E. Asp, "Three-dimensional reconstruction and computational analysis of a structural battery composite electrolyte", Vol. 4,

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2. Vetenskapliga artiklar

- M. Johansen, M. Singh, J. Xu, L. E. Asp, B. Gault, **F. Liu**, "Unravelling lithium distribution in carbon fibre electrodes for structural batteries with atom probe tomography", *Carbon*, Vol, 225, 119091, 2024. https://doi.org/10.1016/j.carbon.2024.119091
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3. Avhandling av Marcus Johansen