THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING
IN MATERIALS SCIENCE

Manufacture and characterisation of structural battery composite constituents

Ruben Tavano

Department of Industrial and Materials Science

Chalmers University of Technology

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Department of Industrial and Materials Science
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone + 46 (0)31-772 1000

Cover:
A carbon fibre used as the active material in the negative electrode of a structural battery has been left exposed to moisture and air. Lithium oxide dendrites have grown from the surface of the carbon fibre with a peculiar and fascinating conformation

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To my parents and Giulia

Abstract

Structural battery composites are a promising material that can help improve the efficiency of electric mobility. The possible efficiency gains come from the associated multifunctionality. A structural battery can store electric energy while also playing a structural role. This is made possible thanks to the careful choice of materials, particularly the active materials used for the negative electrode. Here, custom-made carbon fibres are manufactured to improve the multifunctionality in terms of mechanical and electrochemical properties. Different manufacturing processes are considered with three different carbonisation temperature profiles. A significant trade-off is found, with the elastic modulus and strength observed to decrease by up to 7%, while capacity increased by 15%. This suggests that by carefully selecting processing conditions in carbon fibre manufacturing, it is possible to tailor them for specific multifunctional applications within a constrained design space.

Carbon fibres are not the only crucial multifunctional constituent. The structural battery electrolyte also plays a key role, enabling load transfer and ionic transport between the layers. To date, no thorough characterisation of the mechanical properties has been performed. Here, we define a procedure to manufacture bulk samples and extensively characterise the mechanical behaviour of the structural battery electrolyte. The test campaign shows that the material has a very brittle behaviour, with moderate Young's modulus and low tensile strength. A significantly higher compressive strength is measured. Cure shrinkage is also investigated and found to be insignificant. These findings are essential for accurately predicting internal stress states in the structural battery electrolyte and guide future modelling efforts.

Keywords: Structural battery composites, carbon fibres, multifunctional performance, mechanical characterisation, electrochemical characterisation, structural battery electrolyte

List of publications

This thesis is based on the following publications:

[A] Ruben Tavano, Johanna Xu, Claudia Creighton, Fang Liu, Bhagya Dharmasiri, Luke C. Henderson, Leif E. Asp, “Influence of carbonisation temperatures on multifunctional properties of carbon fibres for structural battery applications”. *Batteries & Supercaps*, Volume 7, Issue 8, August 2024, *https://doi.org/10.1002/batt.202400110*

[B] Ruben Tavano, Michele Spagnol, Nawres Al-Ramahi, Roberts Joffe, Johanna Xu, Leif E. Asp, “Mechanical characterisation of a structural battery electrolyte”. Under review.

Preface

The work in this thesis was carried out between September 2022 and September 2024 at the Division of Material and Computational Mechanics, Department of Industrial and Materials Science, Chalmers University of Technology. The research was supported financially by the US Office of Naval Research through award number N62909-22-1-2037.

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Part I
Extended Summary

Chapter 1

Introduction

1.1. Background

Electric vehicles are growing in popularity due to the significant reduction in environmental impact associated with their use. These vehicles need to store the energy needed for their use in batteries, which are monofunctional and accompanied by a significant weight, contributing to up to 30% of the total vehicle mass[1]. A novel approach to increase the efficiency of electric mobility is offered by structural battery composites (SBCs), which may assist in significantly reducing the parasitic weight of conventional batteries, resulting in lighter vehicles[2–8]. In this case, the same system can fulfil two functions, such as storing and delivering energy (like a conventional battery) while at the same time carrying mechanical loads (like a structural component).

The multifunctionality associated with SBCs is made possible by a careful choice of constituents capable of playing multiple roles in the composite material. The desired architecture for SBCs consists of a thin-ply carbon fibre negative electrode stacked on a glass fibre separator and a positive electrode (usually lithium iron phosphate (LFP) coated on top of carbon fibres)[9,10]. The multiple layers are impregnated by a structural battery electrolyte (SBE), and the electrodes are attached to metallic tabs, which are then connected to an external circuit for powering the vehicle. This architecture, shown in Figure 1.1, resembles that of conventional batteries and, at the same time, the layered structure of composite structural panels.

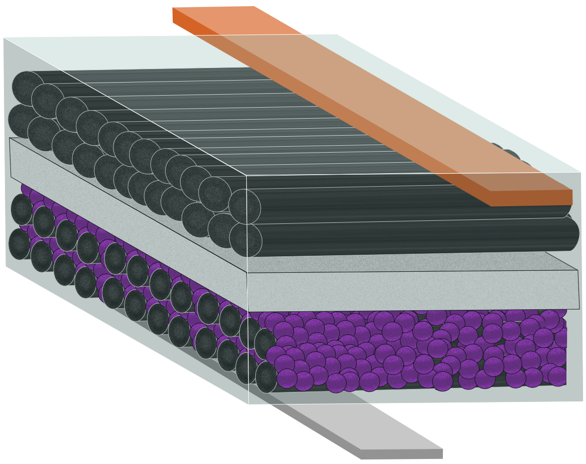

Figure 1.1 Schematic illustration of the architecture of an all-carbon fibre structural battery composite. From bottom to top: positive electrode current connector, positive electrode made with coated carbon fibres, glass fibre separator, negative electrode made with carbon fibres, negative electrode current connector. All the layers are impregnated with the SBE.

1.2. Carbon fibres

The most important constituent which makes energy storing and structural support possible is the carbon fibre negative electrode. Carbon fibres are made starting from a polymeric precursor (usually polyacrylonitrile (PAN)), which is then subjected to a series of heating steps combined with mechanical tension, leading to a progressive microstructural evolution and the elimination of any non-carbonaceous element until a carbon content of around 95-99% by weight is reached. Excellent specific mechanical properties are achieved afterwards, making carbon fibres traditionally used for composite materials manufacturing. As mentioned, carbon fibres have a microstructure made almost entirely of carbon atoms, a feature shared with graphite, one of the most commonly used materials in conventional lithium-ion battery negative electrodes. However, the arrangement of the carbon atoms in graphite and carbon fibre is different: carbon fibres have a peculiar microstructural organisation called turbostratic graphite, where graphitic areas are folded upon themselves, and multiple defects such as voids and amorphous domains are also introduced. Furthermore, a certain amount of heteroatoms (e.g. nitrogen, oxygen) are kept from the initial precursor.

Extensive studies have been performed in the past to determine the effects of different carbon fibre manufacturing processes on the microstructure and, consequently, on the mechanical properties since the only use for carbon fibres has traditionally been in structural components[11–13]. On the other hand, only a small number of studies have investigated the effects of different carbon fibre microstructures on the electrochemical properties, which are crucially important for SBCs. Additionally, almost the entirety of the studies have looked at commercially available carbon fibres, where little is known about the manufacturing process and which are optimised for mechanical performance only. Nonetheless, important findings have been obtained in terms of what type of microstructural features are desirable for this type of application. Kjell et al. and Hagberg et al. investigated the electrochemical behaviour of a series of commercially available carbon fibres to identify the most promising types [14,15]. They found that intermediate modulus (IM) carbon fibres are a good candidate for this application. Starting from this, several studies by Fredi et al. and Johansen et al. looked at the reasons for the better performances, showing that the presence of a higher percentage of amorphous domains, smaller crystalline domains, as well as specific chemical states for nitrogen heteroatoms are beneficial for lithium-ion insertion[16,17]. Additionally, Johansen et al. studied the mechanism of lithium-ion insertion to identify zones where the ions can be preferentially inserted and remain trapped[18,19].

As mentioned above, commercial carbon fibres are designed with mechanical performance in mind and therefore, energy storing capabilities are present only as a side effect. To achieve better multifunctionally performing carbon fibres, Xu et al. manufactured different carbon fibres starting from the same PAN-based precursor, varying the applied mechanical tension during the first step of the carbon fibre production, the oxidation/stabilisation step[20]. Three distinct tension forces were applied: low tension at 720 cN, medium tension at 2300 cN, and high tension at 3025 cN. The electrochemical capacity, elastic modulus, and tensile strength of the fibres were assessed. It was observed that applying lower tension during the stabilisation phase enhanced electrochemical capacity but decreased the tensile strength and modulus of the final carbon fibre. In contrast, higher tension improved mechanical properties but significantly diminished the fibres' lithium-ion storing capacity. These variations in behaviour were attributed to inherent differences in d-spacing, crystallite orientation, size, and content. The carbon fibre produced under medium tension demonstrated the best multifunctional performance. This study highlighted how process-induced microstructural variations enable the development of carbon fibres with tailored multifunctional properties for use in structural battery negative electrodes.

1.3. Structural battery electrolyte (SBE)

Another key component of SBCs is the SBE, which is also multifunctional, having to transfer mechanical loads between every layer of the system and to move ions from one electrode to the other.

The most used SBE consists of a solid/liquid bi-phasic structure, as shown in Figure 1.2. The liquid electrolyte is dispersed in the interconnected network of pores, enabling the ion transfer upon charging and discharging. The solid part is responsible for the mechanical properties. This configuration with a heterogeneous SBE is achieved via a polymerisation induced phase separation (PIPS) reaction and was first proposed by Ihrner et al. and later improved by Schneider et al.[21,22]. Overall, a good multifunctional material with moderate mechanical performance and ionic conductivities was achieved.

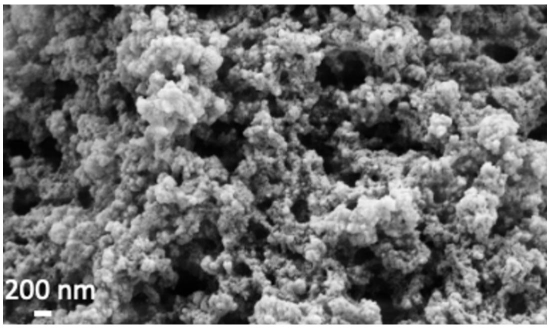

Figure 1.2 Scanning electron microscopy image of the SBE microstructure at x20k magnification

Although stiffness data for the mechanical behaviour of the SBE have been reported, the data available was measured using dynamic mechanical analysis (DMA). The storage modulus E' obtained with this technique provides an indication of the elastic modulus but cannot be directly translated into Young's modulus. Young's modulus must be known to accurately predict the internal stress state in the SBE in SBCs. Such predictions are vital to ensure that structural integrity is maintained during the electrochemical cycling of the structural battery[23]. In fact, the active materials in both electrodes are subjected to a significant swelling when lithium-ions are inserted, meaning that the SBE situated between two or more carbon fibres in the negative electrode (or two or more LFP particles in the positive electrode) will be subjected to high mechanical loads. Additionally, other properties such as Poisson's ratio, strengths and strains to failure, both in compression and tension, and the overall behaviour of stress-strain curves are also required.

1.4. Research scope

This thesis is divided into two main research topics related to two distinct constituents of SBCs: the carbon fibre negative electrode and the SBE.

We first investigate the effects of different manufacturing processes, particularly different carbonisation temperatures, on the multifunctionality of carbon fibres aimed for use in the negative electrode. Information about which temperatures are preferable and how these translate into different microstructural features is crucial in guiding the development of custom-made carbon fibres for improved performance in SBCs.

The research scopes can be summarised in the following points for paper A:

- To investigate how the manufacturing process of carbon fibres affects the microstructure of the turbostratic graphitic structure in carbon fibres;
- To understand how different microstructures relate to the mechanical and electrochemical performance, i.e. multifunctional performance, of the carbon fibres;
- To identify what relation there is between mechanical properties and electrochemical properties and what design window can be achieved;

- To identify possible routes to further improve the multifunctional performance of future carbon fibres.

Secondly, we develop a method to manufacture bulk SBE samples for mechanical testing and improve our understanding of the mechanical behaviour of the SBE. Extensive information about the mechanical properties is key to the development of reliable models that can look at the microscale level (SBE confined between two or more carbon fibres or LFP particles) as well as on a macroscale level for the full SBC system.

The research scopes can be summarised in the following points for paper B:

- To develop a technique to characterise the mechanical properties, such as Young's modulus, Poisson's ratio, and mechanical strengths, of the SBE in bulk samples;
- To determine the mechanical response of the SBE subjected to tensile and compressive loads;
- To provide useful and reliable material parameters for future modelling of SBCs.

Chapter 2

Summary of the appended papers

2.1. Paper A

Ruben Tavano, Johanna Xu, Claudia Creighton, Fang Liu, Bhagya Dharmasiri,
Luke C. Henderson, Leif E. Asp
Influence of carbonisation temperatures on multifunctional properties of carbon fibres for structural battery applications
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In this paper, the effects of different carbonisation temperatures on the multifunctional performance of carbon fibres are investigated. The mechanical and electrochemical properties are governed by the carbonaceous microstructure of the carbon fibres. For this reason, knowing how the processing parameters affect the multifunctionality is crucial for the future of structural batteries. Custom-made carbon fibres are manufactured considering different temperature profiles for the last step of the manufacturing, the carbonisation. A lower temperature profile (284-1300 °C), intermediate temperature profile (350-1400 °C) and higher temperature profile (450-1500 °C) are considered, while all the other parameters are kept unchanged among all the fibre types. Carbon fibres are extensively characterised in terms of physical properties (density, fibre diameter, electrical conductivity, and surface area), microstructure (wide-angle x-ray scattering, and transmission electron microscopy), mechanical properties and electrochemical properties. A moderate trade-off between mechanical and electrochemical performance is identified, with an increase in elastic modulus and strength, which corresponds to a decrease in the lithium-ion storing capacity and vice versa. For the considered temperatures, the mechanical properties can vary by up to 7%, while the electrochemical capacity can vary by up to 15%. This shows that specific designs can be achieved by a careful choice of how the carbon fibres are processed, even though the multifunctionality window achieved until now is narrow.

2.2. Paper B

Ruben Tavano, Michele Spagnol, Nawres Al-Ramahi, Roberts Joffe, Johanna Xu,
Leif E. Asp
Mechanical characterisation of a structural battery electrolyte
Under review

In this paper, the bi-phasic structural battery electrolyte is extensively characterised to determine its mechanical behaviour. Knowing the mechanical properties is of fundamental importance for structural battery applications since it allows for reliable modelling of the electrolyte behaviour when constrained in the electrodes, as well as determining the macroscopic response of the structural battery composite. Due to the criticality of bulk sample manufacturing, a procedure is detailed for the production of tensile dog bone-shaped and compressive cylindrical samples. The samples are then tested in tension to determine Young's modulus, tensile strength, tensile strain to failure, and Poisson's ratio. The samples are also tested in compression to measure the compressive strength and strain to failure. Furthermore, the mechanical response from the complete stress-strain curves (tensile and compressive curves) is obtained. Finally, the cure shrinkage is assessed. Overall, the tests show that the structural battery electrolyte is a brittle material with a low tensile strength and an order of magnitude higher compressive strength. The Poisson's ratio is equal to 0.34, and the cure shrinkage is found to be insignificant. This study enables us to repeatably and consistently test bulk samples made of materials sensitive to oxygen and moisture. Additionally, this work helps us obtain an almost complete picture of the material behaviour, which will be very useful for modelling structural battery composites. This will show how critical the load cases are upon battery cycling and will make it possible to guide the development of further improved structural battery electrolyte formulations.

Chapter 3

Concluding remarks and outlook

This thesis covers extensive work performed on two of the main constituents of structural battery composites. We investigated how we can affect the multifunctionality of carbon fibres by employing different processing parameters. We identified a clear trade-off between mechanical and electrochemical performance and we showed that the design window for conventional carbon fibres (e.g. intermediate and standard modulus carbon fibres, such as the ones produced in this study) is rather limited but still allows for a choice of what processing parameters one should apply for a more specific type of application (e.g. preferentially structural or energy storing application). We also extensively characterised the mechanical behaviour of the structural battery electrolyte so that accurate modelling of the in-operando stress states and reliable predictions on mechanical failure can be performed.

In the future, we will focus on expanding the achievable lithium-ion storing capabilities by manufacturing carbon fibres with unconventional microstructures, significantly expanding the multifunctionality design window. Furthermore, we will assess the interfacial adhesion strength between carbon fibres and the currently used structural battery electrolyte, and we will identify possible routes to improve the performance of structural battery composites by modifying the surface chemistry of carbon fibres. Finally, the upscaling of the manufacturing process for structural battery composites will be studied to achieve even more reliable and repeatable performance.

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