

STRUCTURAL BATTERY MATERIALS

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Abstract

Since four years Swerea SICOMP has been leading a team of Swedish researchers developing structural battery materials from polymer composites. The research performed in the Swedish project KOMBATT (Lightweight structural energy storage materials) is funded by the Swedish foundation for strategic research (SSF). The research addresses two technical challenges in particular. Firstly, solid polymer electrolytes that efficiently transfer loads in the composite and simultaneously transports lithium ions, while being electrically insulating, must be developed. Secondly, the ability of the reinforcement, i.e. the carbon fibres, to intercalate lithium ions as part of the chemical redox reactions, while maintaining its mechanical properties must be assured. This paper is the first in a series of papers at this conference from the KOMBATT project team and presents background and overview of the project.

1 Introduction

Weight reduction is currently top priority for many applications in the transport industry. Use of lightweight materials has been identified as key for successful electrification of future road transport [1]. Reduced vehicle weight is required for increased range and energy efficiency of future electric cars [2]. In addition, reduced vehicle weight will allow reductions in battery volume and mass. Introduction of carbon fibre composites in electric vehicles is already taking place; see e.g. BMW i3 electric vehicle and Toyota Prius X/1. In addition efficient energy storage solutions are required. Current battery systems add significant weight to the vehicle, typically 300-350 kg. Traditional batteries do not contribute to the structural performance of a car. Components, which do not contribute to the load carrying capability are structurally parasitic. To address this issue development of multifunctional materials for combined structural and energy storage capabilities is desirable. Work in the US [3], UK [4] and Sweden [5] has demonstrated that such multifunctional materials can be synthesised from carbon fibre reinforced polymer composites.

The versatility of polymer composite materials offers an ideal opportunity to develop novel multifunctional lightweight materials for use in future cars. In 2009 an interdisciplinary team of Swedish researchers funded by SSF, led by the author, set out to develop structural batteries from polymer composite materials, i.e. a material which can simultaneously store electrical energy while meeting the demands of the mechanical loading [6]. The structural

batteries are developed with the ambition to further reduce system vehicle weight. The current paper presents an overview of results achieved over the last four years in KOMBATT project. Some of the work has also been conducted within the StorAGE project coordinated by Dr Greenhalgh at Imperial College London [7]. The European project StorAGE involves participation from Volvo Cars who wants to introduce these materials in their future cars.

The basic idea is to employ carbon fibres (CF) for mechanical performance and as electrode in a structural battery composite material, and to use a lithium-ion conductive polymer electrolyte, for mechanical load transfer between fibres and lithium-ion transport, as its matrix material. Carbon fibres are particularly attractive as graphitised carbon is commonly used as both electrodes, for their ability to intercalate and coordinate Li-ions and as high performance structural reinforcement, albeit the carbon is in different forms. The multifunctional capability provided by the structural batteries is expected to offer significant savings in system level mass and volume. The design approach, however, is relatively new and faces significant engineering, design, material and application challenges. To date research has focused on three of these; use of commercial carbon fibres as negative electrode, use of solid polymer electrolytes as composite matrix material and battery architecture. This paper provides an overview the carbon fibre electrodes and the solid polymer electrolyte matrix materials development and characterisation within the KOMBATT project.

2 Carbon fibres as structural electrodes

Different types of graphitised carbons have been used as the negative electrode in secondary, i.e. rechargeable, lithium-ion batteries [8]. The advantage of using carbon is its ability to intercalate lithium ions at a very low electrode potential, close to that of the metallic lithium electrode (-3.045V vs. standard hydrogen electrodes) [9]. Snyder et al. [10] performed the first in depth evaluation on commercial carbon fibres for use in structural battery electrodes. In their study Snyder et al. found carbon fibre electrodes from high and intermediate modulus polyacrylonitril (PAN)-based fibres to provide the best compromise for specific capacity and tensile strength.

In the KOMBATT project carbon fibres are analysed at the Royal Institute of Technology (KTH), Sweden, for their potential use as negative electrodes in structural batteries [11,12]. This work is lead by Professors Lindbergh and Zenkert. The research is based on the assumption that a battery with good mechanical properties can be achieved by employing continuous carbon fibre yarns acting as negative electrode. Carbon fibres have reasonably good electrical conductivity in the axial direction of the fibre. Values up to $2 \cdot 10^4$ 1/Ωcm have been reported for carbon fibres [13]. For this reason, the negative electrode in a structural battery may be designed so that no current collectors or conductive additives are needed. Kjell et al. [14] recently published a study of the electrochemical properties of several different grades of commercially available PAN-based fibres. They particularly investigated effects of lithiation rates on electrochemical capacity. In total seven types of CFs were analysed at different charging rates. The best electrochemically performing fibre was the IMS65, by Toho Tenax (a fibre with a stiffness and strength of 290 GPa and 6000 MPa respectively [14]). The reversible capacity for the IMS65 fibre was 177 mAh/g at 1C charge rate and as high as 350 mAh/g at 0.1C. The latter is close to the theoretical maximum for graphite, which is 372 mAh/g.

Effects of electrical charging and discharging (i.e. lithiation and delithiation of the CF) on the mechanical performance of carbon fibres were studied by Jacques et al. [15]. IMS65 and

T800 carbon fibres, by Toho Tenax and Soficar respectively, were tested in tension after 1, 10, 100 and 1000 charging cycles. The tensile stiffness was found unaffected by both lithium-ion intercalation and electrochemical cycling. This is very inspiring as most structures are designed with respect to stiffness in a car application. The fibre tensile strength was found to be reduced by about 20% by the first lithiations but was partly recovered during delithiation. Effects of mechanical loading on the electrochemical performance have also been studied [12]. The graphite structure deforms when an external mechanical load is applied. Thus, mechanical loading may affect the lithium ion intercalation in the graphite structure of the carbon fibre. Jacques et al. [12] have investigated the effect of mechanical loading on the electrochemical capacity of a T800 fibre electrode. Tests were done prior and during charging as well as after discharging, see Fig.1. It was found that the applied strain did not affect the specific capacity of the CF. Axial swelling and shrinkage was also measured in these tests. Swelling and shrinkage of approximately 0.3% in the axial direction of the fibre were recorded. These results are very encouraging for the development of structural energy storage composite materials as these require reasonable fibre dimensional stability during electric cycling. Swelling of the carbon fibres and the solid polymer electrolyte matrix is being modelled by Prof Varna and co-workers [16].

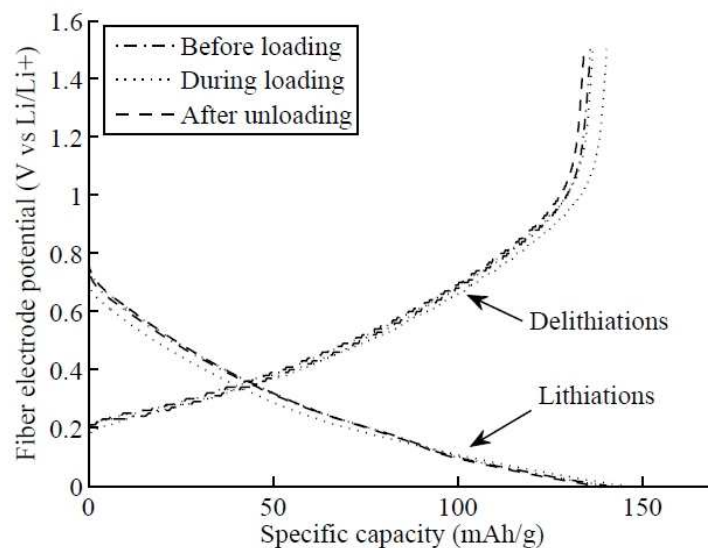


Figure 1. Lithiation and delithiation curves for T800 fibre electrode, before and during loading and after unloading [12].

3 Solid polymer electrolytes (SPE)

The electrolyte is essential in a lithium-ion battery. Its function is to transport lithium ions at a certain rate to produce a current. During discharge lithium ions are transported from the negative to the positive electrode. This transport is restricted if the electrolyte is a solid polymer electrolyte. The challenge is thus to allow sufficient mobility of the lithium ions whilst retaining mechanical performance of the structural battery. Current solid polymer electrolytes hold conductivities up to 10^{-5} S/cm, whereas contemporary liquid electrolytes exhibit conductivities as high as 10^{-2} S/cm [17]. However, a liquid electrolyte cannot carry any mechanical load. Consequently, in the structural battery application one has to accept the lower lithium-ion conductivity. The relationship between lithium-ion conductivity and stiffness is schematically illustrated in Fig. 2. In the figure a shaded area has been included to

indicate desired properties of the polymer electrolytes for realization of structural battery composite materials. Ongoing research on multifunctional SPE is described below.

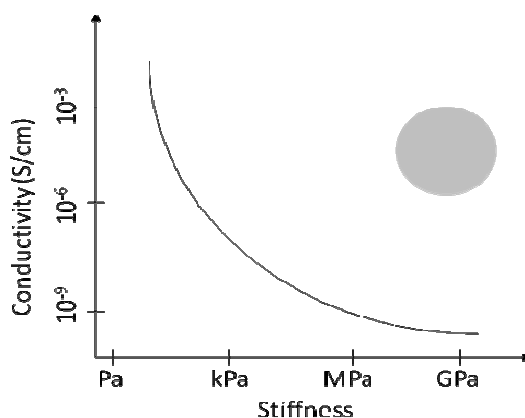


Figure 2. Schematic of the lithium ion conductivity vs. stiffness for SPEs.

One route to create solid polymer electrolytes is to employ polymers containing ethylene oxide (EO) groups [18]. The polymer ethylene oxide (PEO) chains can be formulated to cross-link in order to form a polymer network. The cross-linking density in relation to EO groups will decide the stiffness to conductivity ratio, and hence the multifunctionality, of the structural polymer electrolyte. Snyder et al. [17,19] were first to try to improve the multifunctional behaviour of structural electrolytes by co-polymerization of cross-linking and conductive monomers. Solid polymer electrolytes were made by co-polymerisation of two types of monomers for multifunctionality. The first monomer is a highly lithium-ion conductive monomer, containing long chains of ethylene oxide (EO). The second monomer is a difunctional methacrylate, which provides the cross-linked network. By mixing these monomers in different mixing ratios a variation in cross-linking density and chain mobility can be achieved. By this approach they were able to move the performance of the structural electrolyte towards the grey area in Fig. 2. Inspired by the work of Snyder et al. the KOMBATT team has developed SPEs from similar co-polymers for cure in the presence of a lithium salt (lithium triflate) [20, 21, 22]. This is beneficiary as no post-cure swelling of the SPE to introduce the salt is needed. Two different approaches have been taken in KOMBATT. In a first study Wysocki et al. [20] employed thermal curing of co-polymerised methacrylate monomers to investigate influence of mixing ratios on the multifunctionality of polymer electrolytes. In a second approach, Willgert et al. [21,22] employed UV-induced polymerisation of similar monomers and investigated the influence of cross-linking and lithium salt content on the multifunctionality of the polymer electrolytes. Use of a UV-cure technique is beneficial as thermal cure can be avoided, limiting gas-emissions during cure that may cause voids in the SPE. Study of the effect of lithium salt content revealed that the conductivity in the SPE is constant at salt levels above 4 wt% [21]. Fairly good conductivity (1.5×10^{-6} S/cm) and stiffness (1.5 GPa) has been demonstrated for the co-polymer SPE [20,22] investigating the influence of cross-linking on the multifunctionality of these polymer electrolytes.

More recently, another SPE option has been explored by our team – thiol-ene based SPE. In reference [23], the team led by Prof. Johansson at KTH has demonstrated that addition of small amounts thiol (an organosulfur compound) increases the lithium conductivity of the SPE without compromising its stiffness. This concept is based on the fact that thioether

groups allow lithium ions to be dissolved in the SPE without too strong coordination to the polymer as compared to EO-based systems.

4 Structural battery designs

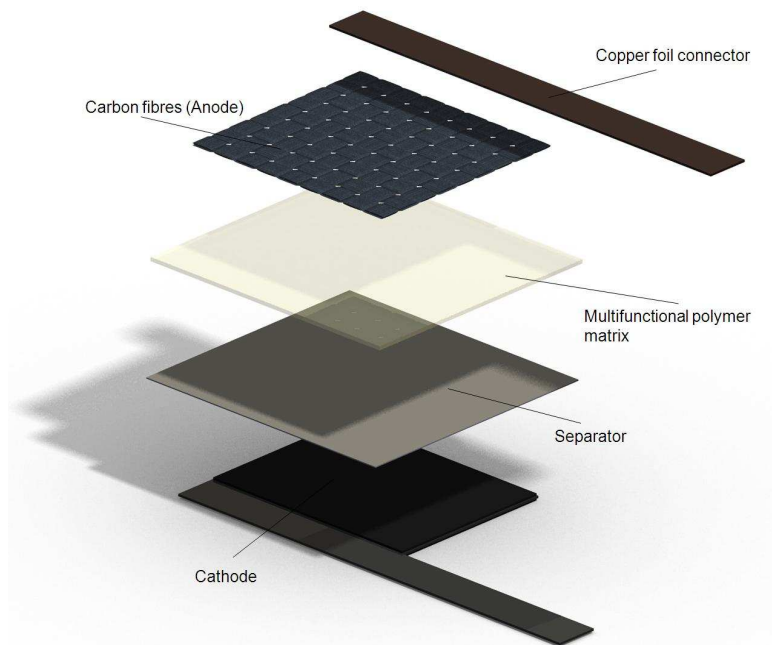


Figure 3. The CFRP battery laminate design developed in KOMBATT and StorAGE.

To date all functioning structural battery lay-outs have exploited the architectural resemblance between laminated composites and batteries [5], see Fig. 3. As mentioned above, such battery designs rely on SPEs with high conductivity and stiffness (as the matrix dominates the composite's charge rate and out-of-plane mechanical properties). Other battery designs have been developed in the KOMBATT project. However, these cannot be discussed in this paper due to IPR issues.

All batteries made and tested in the KOMBATT and StorAGE projects have been assembled and processed in a glove box with dry argon atmosphere (<1 ppm H₂O) at a temperature of 80°C for 12 hours. For operation outside the glove box the structural battery was bagged and sealed as illustrated in Fig. 4.

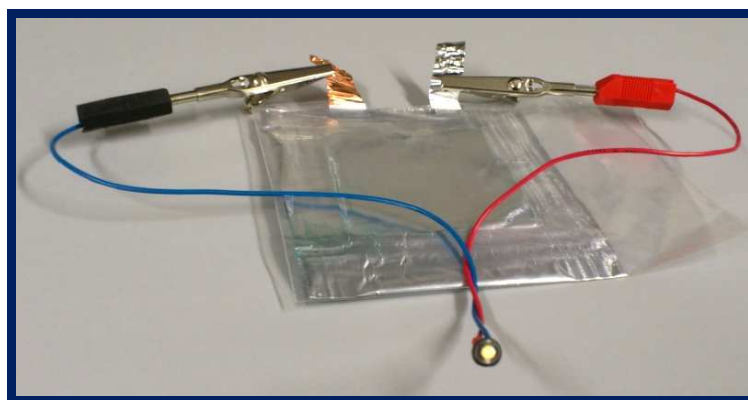


Figure 4. The CFRP battery laminate sealed in a metallized PP-bag.

5 Summary

This paper presents an overview of the current status of research performed to facilitate structural batteries within the Swedish research project *Lightweight structural energy storage materials (KOMBATT)*. Realisation of structural batteries from polymer composites relies on solutions to a number of engineering challenges. Two of these challenges are addressed in this paper – applicability of commercial grades of carbon fibre as negative electrode in a battery exposed to high mechanical loads and use of solid polymer electrolytes as composite matrix material.

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