STRUCTURAL POSITIVE ELECTRODES FOR MULTIFUNCTIONAL COMPOSITE MATERIALS.

Karl Bouton[1], Brian Chen[2], Dan Zenkert[3] and Göran Lindbergh[4]

[1] Department of Aeronautical and Vehicle Engineering, Lightweight Structures, KTH Royal Institute of Technology, Stockholm SE-10044, Sweden, bouton@kth.se

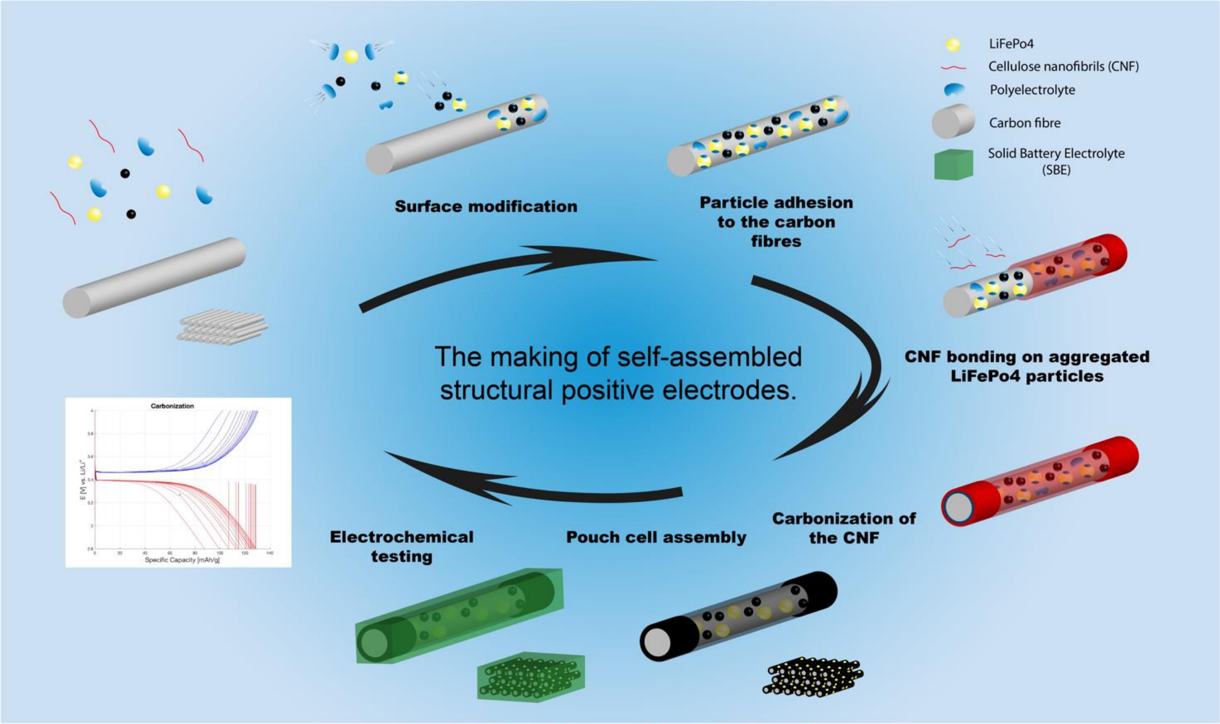
[2] Department of Chemical Engineering, The City College of New York, New York, NY, USA, bchen004@citymail.cuny.edu

[3] Department of Aeronautical and Vehicle Engineering, Lightweight Structures, KTH Royal Institute of Technology, Stockholm SE-10044, Sweden, danz@kth.se

[4] Department of Chemical Engineering, Applied Electrochemistry, KTH Royal Institute of Technology, Stockholm SE-10044, Sweden, gnli@kth.se

Keywords: structural positive electrode, structural battery

GRAPHICAL ABSTRACT



1 INTRODUCTION

The growing interest of the automotive and aeronautical industries for electric vehicles has motivated the development of new structural composite materials with inherent energy storage capability. These multifunctional composite materials are expected to have a battery function and to carry a mechanical load at the same time. Thus, this kind of multifunctional material could lead to lighter vehicles and aircrafts. Batteries consist of cells in which a negative electrode, a positive electrode and a liquid electrolyte enable electrochemical reactions. In the same way, structural batteries are solid-state batteries made of carbon fibre-based electrodes separated by a solid battery electrolyte (SBE). While ordinary carbon fibre tows are used for the negative electrode [1], the carbon fibres used for the positive side have to be grafted with lithium oxide particles, in order to enable electrochemical reactions. This study aims at filling the lack of research on structural positive electrodes, i.e. long continuous carbon fibres coated with lithium oxide particles. A previous attempt to make structural positive electrodes has been made by Hagberg et al. [2]. Here, to coat the carbon fibres with the lithium oxide particles (LiFePo4 or LFP), a dip coating process consisting in a Layer-by-Layer (LbL) assembly of LFP particles has been chosen. While LbL usually enables the growth of nanometre thick layers (few nanometres), thicker layers were grown here due to the size of the LFP particles (few hundreds of nanometres). Several questions were addressed. Firstly, the microstructure of the coating is studied. Secondly, the coating has to show good electrochemical properties. Thirdly, the lithium oxide particles have to be electrically connected in order for the current to flow through the electrodes without restriction. To solve this last point, we chose to carbonise the coating. Carbonisation is often used to create carbon substrate from organic ones. This carbonisation has two objectives: to turn the organic and insulating binders used in the coating process into an electrically conductive network. The second objective is to get rid of these organic binders as it could induce chemical side reactions with the electrolyte. Side reactions would interfere with lithium ions transport and even prevent it, leading to instabilities in the electrode's electrochemical performances. The use of a carbonisation technique to make the coating electrically conductive is quite unconventional and the use of conductive additives like carbon black is often preferred. In this respect, we investigated the optimal carbonisation temperature, the one that gives optimal electrochemical properties. Finally, the impact of the experimental method on the final performances was investigated too. As a result, the optimal carbonisation temperature was found to be about 450°C. At this temperature, the positive electrodes show a specific capacity of more than 100mAh/g at a C-rate of C/10. In addition, the preparation technique of the LFP have an impact on the electrode's performances.

2 EXPERIMENTAL DETAILS

2.1 Materials

The structural positive electrodes are based on 24K carbon fibres spread tows of the IMS65 kind, originally manufactured by Toho Tenax and spread by Oxeon AB. For the Layer-by-Layer assembly, Polyethylene(imine) (PEI Mw=750 000, 50% in water) have been provided by Sigma-Aldrich and Carbon-coated LiFePo4 particles by Phostech Lithium (LFP, 3.6 g.cm-3). The Carboxymethylated cellulose nanofibrils (CNF) have been prepared according to the following procedure [3]. The battery grade liquid electrolyte system (LP40), also purchased from Sigma Aldrich, is composed of ethylene carbonate (EC), dimethyl carbonate (DMC) at a ratio of 1:1 and contains 1M of Lithium hexafluorophosphate ($LiPF_6$).

2.2 Preparation of the CNF dispersion

A Cellulose Nanofibrils gel was prepared according to the procedure described by Wågberg and al. [3]. The resulting gel was then added to some MQ water and mechanically stirred in order to achieve a CNF solution with a concentration of $1 g.L^{-1}$. Next, the fibrils were dispersed by sonication, at 40% amplitude, during 10min using a one probe sonicator (Sonics Vibra-cell). To remove any impurities, the dispersed nanofibrils were centrifuged for 1h at 3500RPM using a compact benchtop centrifuge (Rotina 420) and sonicated again.

2.3 Preparation of the PEI-LFP solution

The aim of the PEI-LFP combination is to modify the LFP particles by grafting positive charges on their surface. Indeed, PEI is a positively charged polymer (cationic polyelectrolyte) containing amino groups and commonly used for its cationic character in surface modification applications. Thus, the PEI-LFP solution consists of $LiFePo_4$ particles dispersed in a solution of Polyethyleneimine (PEI). For the preparation of this solution, PEI and $LiFePo_4$ particles were firstly added to MQ water, to the concentrations of, respectively, $1g.L^{-1}$ and $10g.L^{-1}$. The solution containing the two species was then mechanically stirred for one hour to ensure a rough dispersion of the components and sonicated at 40% of amplitude for 10min using the one probe sonicator (Sonics Vibra-cell). In order to refine this PEI-LFP solution, the PEI-LFP solution was centrifuged at 3500 RPM for 1h. After centrifugation, the LFP particles agglomerated at the bottom of the centrifuge's tubes were taken off and re-dispersed by sonication. This refining step allows the removal of the excess of PEI. Therefore, by lowering the PEI concentration and solution ionic strength, one increases the positive charge's activity of the PEI-grafted LFP particles. In the next paragraphs, the initial non-refined solution is named "Solution 1" (Sol1) while the refined one is named "Solution 2" (Sol2).

3 METHOD

A Layer-by-Layer assembly process has been used to coat the carbon fibre substrate with LFP particles, using CNF as a binder. The resulting slurry made of LFP particles bonded by the CNF were then dried at air and ambient temperature for 24h to form a film. In order to make this film electrically conductive, the coated carbon fibres were carbonised under Argon for 1h. This carbonisation process aims at turning the insulating CNF into some electrically conductive carbon material. Another interest of the carbonisation is to get rid of the organic molecules, i.e. CNF and PEI, which could induce side reactions with the battery electrolyte. For electrochemical characterisation, the samples were assembled into pouch cells, using Lithium metal as a counter electrode.

3.1 Dip coating

To begin with, the samples were dipped into a solution of PEI ($1g.L^{-1}$) in order to prepare the carbon fibres' surface for the LbL deposition. The positively charged PEI adsorbed on the carbon fibres' surface provides an anchoring layer for the negatively charged CNF and promotes electrostatic interactions. The carbon fibres were then dipped in the PEI- LFP dispersions. On the same principle, PEI-grafted LFP particles formed electrostatic interactions with the previously laid CNF layer. Each step is followed by the washing of the substrate in a bath of MQ water, for 5 min. This washing step allows the removal of any unattached molecule. Each dipping cycle led to the formation of a bilayer, i.e., the combination of a layer of the anionic CNF binder and a layer of the modified cationic LFP particles. The dipping cycles were repeated several times in order to form a coating made of several bilayers. By increasing the number of bilayers, one increases the electrode's LFP content and its electrochemical capacity. In this study, the dipping process was repeated 6 times, leading to 6 bilayers. This choice was motivated by the need to minimize the manufacturing time and by the fact that the 6 bilayers contained enough LFP particles to run electrochemical testing. Since the spread tows used in this study are delicate to handle, especially when dipped into an aqueous solution, a custom-made sample holder has been manufactured (Figure 1). The dipping operation was performed by a compact industrial robotic arm (Kuka Robotics KR C4 compact, Figure 1). This set-up enables the automated coating of 10cm-long continuous spread tows.

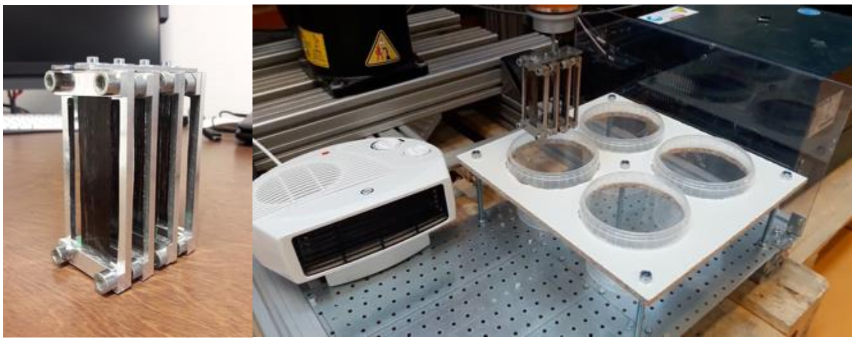


Figure 1: (left) custom-made sample holder; (right) automated LbL setup.

3.2 Carbonisation

The carbonisation has been carried out with a tube furnace (Carbolite, Eurotherm 2048), under nitrogen flow, until the different final target temperatures were reached. The target temperature was held for 1h. For each carbonisation experiment, the heating rate was set to 5°C/min, and a 1 hour-long isotherm was done at 300°C. This isotherm is meant to occur when the CNF undergo their carbonisation. The influence of the target temperature has been studied and the different carbonisations were achieved either at 350°C or at 450°C. These target temperatures were chosen after a thermogravimetric analysis (TGA, Figure 2) under Argon of both the PEI and the CNF. The TGA shows CNF losing 67% and 75% of their mass at, respectively, 350°C and 450°C while PEI is fully decomposed at 400°C. Thus, by carrying out the carbonisation at 350°C and 450°C, one can observe the impact of the PEI degradation on the electrode's properties. Low carbonisation temperature is also preferred to avoid undesirable phenomena like an evolution of the LFP crystalline structure. In the same time, one wants to keep enough CNF to insure the coating's mechanical integrity and effective electrons transport.

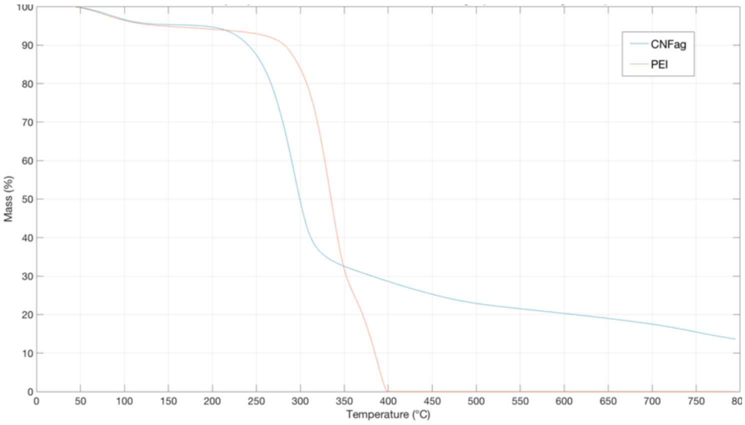


Figure 2: Thermogravimetric Analysis of Polyethylenimine (PEI) and Cellulose Nanofibrils (CNF) under Argon.

3.3 Pouch cells manufacturing

For the electrochemical testing, the samples were tested in pouch cells. The pouch cells consist in the LbL-made positive electrode, a piece of Lithium metal used as a counter electrode and a Whatman glass fibres- based separator to separate the two electrodes and avoid short circuits. The positive electrode and counter electrode are put in contact with aluminium and nickel current collectors, respectively. The whole assembly was then enclosed in a pouch providing a good barrier to moisture and oxygen. The making of the pouch cells was carried out in a glovebox, under argon atmosphere.

4 CHARACTERIZATION

4.1 Scanning electron microscopy

The coating’s microstructure was observed using a Hitachi S-4800 Scanning Electron Microscope (SEM) at an accelerating voltage of 2kV. The samples were cut and coated with a 3nm-thick layer of Pt/Pd using an Agar HR sputter coater. No other preparation was done on the samples prior to observation.

4.2 LFP mass assessment

Knowing the mass of LFP is essential to measure the specific capacity of the structural positive electrodes. On the other hand, the deposition of active material is driven by the self-assembly of the LFP particles on the carbon fibres substrate. For this reason, the amount of LFP particles is not known. In order to assess the mass of LFP, the samples were weighted before carbonisation. This value included the mass of carbon fibres, LFP, CNF and PEI. The samples were weighted a second time after carbonisation, during which the PEI is burned off and the CNF get carbonised. The initial mass of PEI was considered negligible compared to the other components. Therefore, the weight difference was attributed to the weight loss of CNF assuming that the LFP particles and carbon fibres didn’t lose mass during the carbonisation process. From this observation, and knowing the initial mass of carbon fibres, it was possible to estimate the mass of LFP.

4.3 Electrochemical characterization

Galvanostatic cycling was carried out between 2.8V and 4.0V using a VMP3 Biologic potentiostat. A first set of experiments consisted in charging and discharging the electrodes at the same charging rate of 10 hours, the current density being determined by the measured mass of LFP. Another set of experiments consisted in cycling the electrodes at the same current density of 15μA in order to observe the differences in charging rates and specific capacities.

5 RESULTS

5.1 Coating’s microstructure

Figure 3 shows the SEM images of the coated carbon fibres. On these pictures, one can see how the coating is formed on the outer surface of the carbon fibres tow. The layer-by-layer process enables the aggregation of LFP particles, bonded by the CNF, around the carbon fibres. Incidentally, one can observe the carbon fibres’ imprint as well as the top CNF layer covering the LFP aggregates. After carbonisation, this top layer turns into an electrically conductive graphitic sheet, connecting the particles all together and insuring electrons transport to the electrode’s current collector.

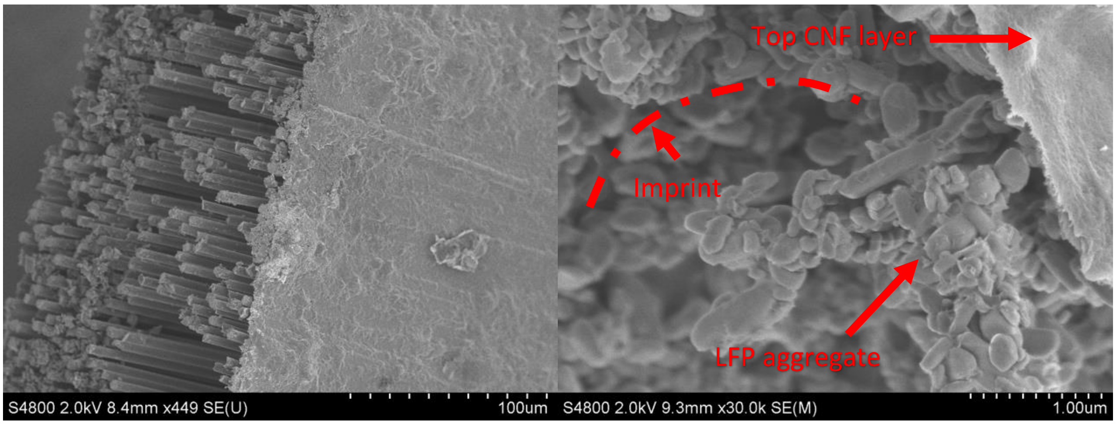


Figure 3: (left) Overview of the coated carbon fibres; (right) cross-section view of the carbon fibre’s coating.

5.2 Electrode's specific capacity

After carbonisation, the electrodes were tested electrochemically. The carbonised coating proved to be a good cathode material as galvanostatic cycling, i.e. charge and discharge under a constant current density, were successfully performed. The electrodes prepared according to different techniques and carbonised at different carbonisation temperatures were first cycled at a fixed charging rate of 10 hours and their specific capacity compared. In this study, the specific capacity tended to increase slightly during the first charge-discharge cycles and showed stable values from the 5th cycle. Thus, Figure 4 compares the different electrodes' specific capacity during their 5th charge and discharge. The results show that the specific capacities vary from 35mAh/g to 107mAh/g. The benefits of both the PEI-LFP solution's refinement and a high carbonisation temperature are demonstrated here. Indeed, these two criteria tend to increase the specific capacity of the LbL-made electrodes. On one hand, refining the PEI-LFP solution increases the PEI's positive charges activity and their ability to bond efficiently with the CNF. When the CNF get carbonised, this improved bonding induces a better contact between the carbon network and the LFP particles. As a consequence, the electron transport is enhanced and one takes more advantage of the LFP particles contained in the coating. On the other hand, increasing the carbonisation temperature promotes the complete removal of the PEI and reduces the CNF content, offering access to more Lithium oxide particles. Indeed, at 350°C CNF just finish their carbonisation and not all the PEI is burned off. As a consequence, the remaining PEI could trap the Lithium ions as PEI is known to bond easily with metal ions. At 450°C, all the PEI is burned off and the CNF is completely carbonised. The CNF is believed to fuse around the LFP particles, creating good electrical contact without the need of PEI.

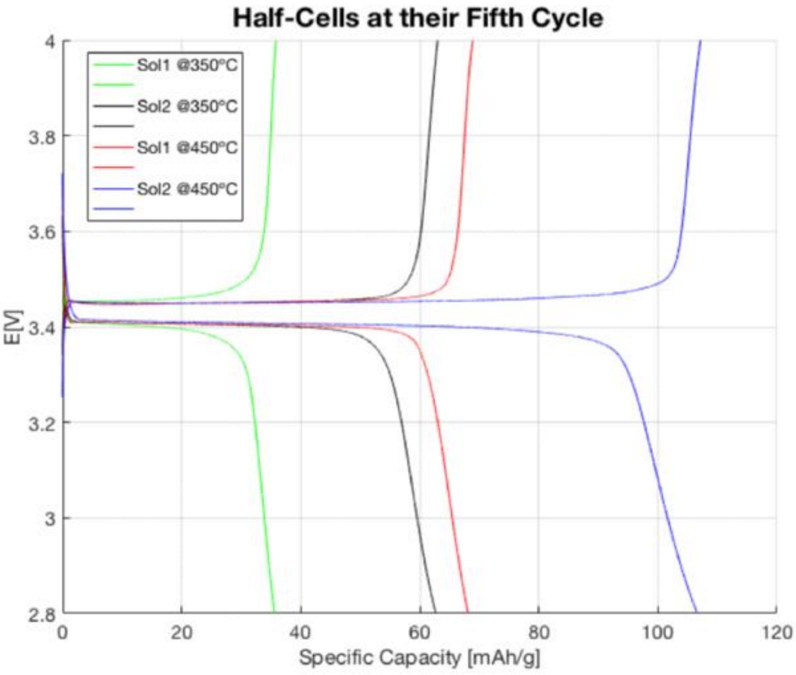


Figure 4: Maximum specific capacity for the different positive electrodes after 5 cycles for the same charging/discharging time of 10 hours.

From a different perspective, the different electrodes were cycled 10 times at the same current density of 15µA (Figure 5) in order to investigate the influence of the preparation method and carbonisation temperature on the average charge-discharge cycle duration and specific capacities. Similar conclusions can be drawn here. The fine tuning of the PEI-LFP solution and the high carbonisation temperature led to higher specific capacities and longer cycle duration. These two phenomena are linked and show that more LFP is playing an active role in the redox reaction happening at the electrode.

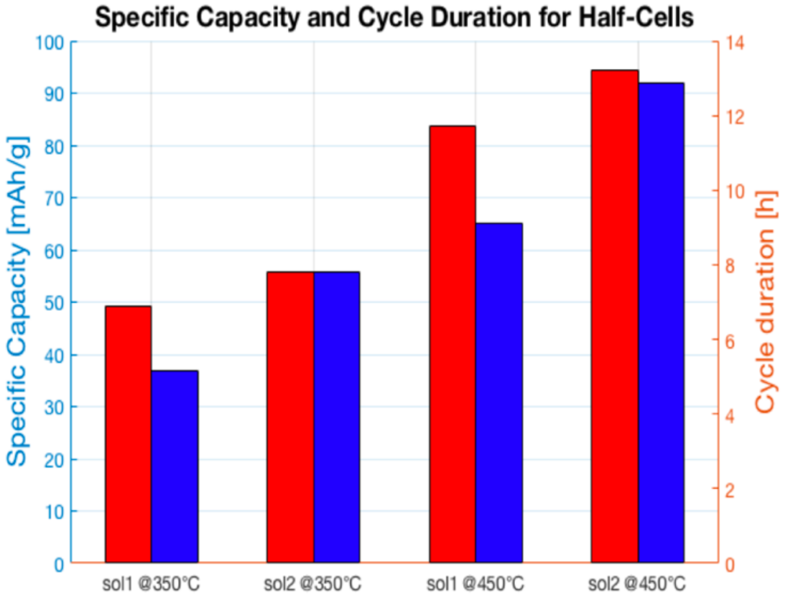


Figure 5: Average specific capacities and cycle duration of positive electrodes for the same current density of 15 µA.

6 CONCLUSIONS

This study proposes an innovative way to manufacture structural positive electrodes which are meant to be used in structural batteries. The success of the electrode's manufacturing lies on a fine tuning of the composition of the chemical bath used during the dip coating. However, the carbonisation process used to turn the initial coating into a usable cathode material is important too. Indeed, the setting of a suitable carbonisation temperature offers optimal electrochemical performances. With a specific capacity approaching 100mAh/g, these performances were not far from what one can expect from LFP-coated aluminium foils, commonly used as commercial positive electrodes in battery cells. In contrast, the theoretical specific capacity of these commercial positive electrodes is about 150mAh/g. Future work will focus on the study of the electrode's mechanical properties when infused with a Solid Battery Electrolyte and a further improvement of the electrode's performance.

ACKNOWLEDGMENTS

This project is part of the ”Sorcerer” project funded by the European Union through “Clean Sky 2” and the “Horizon 2020” Research and innovation program. The authors acknowledge the different partners participating in this project for the fruitful discussions and collaboration. The Swedish research group KOMBATT is also acknowledged for the teamwork and support.

REFERENCES

[1] J. Hagberg, H.A. Maples, K.S.P. Alvim, J. Xu, W. Johannisson, A. Bismarck, D. Zenkert, and G. Lindbergh, Lithium Iron Phosphate Coated Carbon Fiber Electrodes for Structural Lithium Ion Batteries, *Composites Science and Technology*, 162, 2018, pp. 235–43, (https://doi:10.1016/j.compscitech.2018.04.041).

[2] W. Johannisson, N. Ihrner, D. Zenkert, M. Johansson, D. Carlstedt, L.E. Asp, and F. Sieland, Multifunctional Performance of a Carbon Fiber UD Lamina Electrode for Structural Batteries,*Composites Science and Technology*, 168, 2018, pp.81–87 (https://doi:10.1016/j.compscitech.2018.08.044).

[3] L. Wågberg, G. Decher, M. Norgren, T. Lindström, M. Ankerfors, and K. Axnäs, The Build-Up of Polyelectrolyte Multilayers of Microfibrillated Cellulose and Cationic Polyelectrolytes, *Langmuir*, 24, 2008, pp. 784–95 (https://doi.org/10.1021/la702481v).