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„Novel Electrodes for Structural Batteries“

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Abstract

This work presents a technique to produce novel electrodes for structural composite batteries, which could reduce system weight by reducing the number of conventional batteries by realizing structural energy storage, which augment and/or supplement batteries. Among several applications, in electrical vehicles (EVs), for example, structural composite batteries would lead to significant reducing on weight/volume architecture, which would improve the performance of the car.

Electrophoretic deposition (EPD) was used to coat anodic and cathodic materials onto carbon fibers. Cathodes were produced by depositing lithium iron phosphate ($LiFePO_4$) onto the carbon fibers (CFs). Carbon black (CB) and polyvinylidene fluoride (PVDF) were added to improve electrical conductivity and adhesion of the coating respectively.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) showed that the materials were evenly dispersed on the fiber surface and uniform particle layers were produced. The electrical performance of $LiFePO_4$ coated fibers was evaluated by galvanostatic cycling tests. They showed that the functional coating performs well as a positive electrode with capacity around 60 – 110 $mAh.g^{-1}$.

Anodes were similarly produced by electrocoating germanium (Ge) nanocrystals onto carbon fibers. These nanoparticles have higher lithium ion storage capacity than unmodified carbon fibers. Preliminary results are very promising but the EDP-procedure still needs further optimization.

Zusammenfassung

Diese Arbeit stellt eine neuartige Technologie vor. Elektroden für strukturelle Verbundstoff Batterien wurden erzeugt und die Leistung eben jener verbessert. Durch den Teilweise Ersatz von herkömmlichen Strukturelementen durch Verbundstoff Batterien könnte die Abhängigkeit von herkömmlichen Batterien in vielen Anwendungsbereichen reduziert werden.

In vielen anderen Anwendungen, wie zum Beispiel in der Konstruktion elektrischer Fahrzeuge (EVs), würden Batterien mit Strukturverbundwerkstoffen zu einer erheblichen Verringerung des Gewichts/Volumens beitragen, was die Reichweite des Fahrzeugs verbessern würde.

Elektrophoretische Abscheidung (EDP) wurde verwendet, um anodische und kathodische Materialen auf Kohlenstofffasern aufzutragen. Kathoden wurden hergestellt, indem Lithiumeisenphosphat ($LiFePO_4$) auf Kohlenstofffasern (CFs) abgeschieden wurde. Carbon Black (CB) und Polyvinylidenfluorid (PVDF) wurden zugegeben, um die elektrische Leitfähigkeit bzw. die Haftung zu verbessern.

Raster-Elektronenmikroskopie (SEM) und energiedispersive Röntgenspektroskopie (EDX) zeigten, dass die Materialien gleichmäßig auf der Faseroberfläche verteilt waren und einheitliche Partikelschichten hergestellt werden konnten. Die Kapazität von mit $LiFePO_4$ beschichten Fasern wurde durch galvanostatische Tests bewertet. Diese bestätigt die guten Eigenschaften der funktionellen Beschichtung – die Positive Elektrode hat eine Kapazität von etwa 60 – 110 mAh/g.

Des Weiteren wurden Anoden durch Elektrotauchlackierung von Germanium (Ge) Nanokristallen auf Kohlenstofffasern hergestellt. Diese Nanopartikel haben eine höhere Lithiumionenspeicherkapazität als unmodifizierte Kohlenstofffasern. Vorläufige Ergebnisse sind vielversprechend aber das EPD Herstellungsverfahren muss optimiert werden.

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1. Introduction and Motivation

The ever-increasing demands for energy, the development of portable electronic devices, and electrical vehicles among others, have accentuated the need for more efficient and lighter energy storage systems. Literature points out that Lithium-ion batteries are the most rechargeable batteries available on market today. Since the 1990s, the energy density of lithium-ion batteries has increased 8-9% per year; however, a breakthrough in materials design is strongly desirable [1]. At the present, the lithium-ion battery consists of a cathode, which is a lithium metal oxide or phosphate, and an anode, usually graphite. Charge and discharge occurs by redox reactions, and the charge capacity depends on the amount of Li-ions incorporated into the electrode materials.

Some aspects of lithium-ion batteries can be improved such as reduction on size and weight, as well as the capacity for energy storage. In that sense, nanostructured electrode materials have the potential for much higher charge storage capacity [2;3].

This study is motivated by the need to lighter structures since batteries are heavy and structurally parasitic: structures carry load but is not able to provide energy storage capability.

1.1. Aim and Objective

The aim of this work is the development of a multifunctional material that combines structural and electric properties, that means, a multifunctional material that can carry load and simultaneously presents energy storage capability. The objective is the production of a structural electrode by means of electrophoretic deposition (EDP) and to demonstrate the feasibility of this technique as contribution to the realization of structural batteries.

2. Overview

2.1. Lithium-Ion Batteries

Lithium-ion batteries are very popular nowadays, mainly because they are the most common rechargeable batteries available [1-6]. They can be found in laptops, toys, tablets, cell phones and other electronic devices. The lithium-ion battery architecture consists of two electrodes and a separating membrane permeable for the electrolyte

(Figure 1). In general, the electrodes are graphite (anode) and lithium metal oxide ($LiMO_2$, M= metal) or phosphate. These electrodes have good reversibility for lithium intercalation/deintercalation. Widely known examples are lithium iron phosphate ($LiFePO_4$) and lithium cobalt oxide ($LiCoO_2$), which were developed and commercialized by Sony Inc. in 1991 [4].

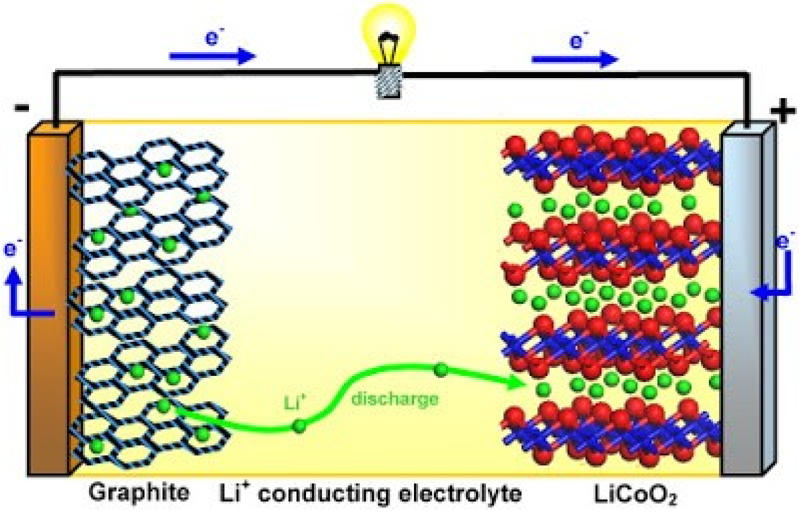


Figure 1. Schematic representation of a lithium-ion battery [5].

During charging, lithium ions are transported from the positive to the negative electrode, accepting one electron and bonding to the carbon. During a discharge the ions move back into the metal oxide/phosphate (cathode), creating a current that can perform work. General redox reactions are represented below [6]:

$6C + xLi^+ + xe^- \rightleftarrows Li_xC_6$ (negative electrode)

$LiMO_2 \rightleftarrows Li_{1-x}MO_2 + xLi^+ + xe^-$ (positive electrode)

$LiMO_2 + 6C \longleftrightarrow Li_{1-x}MO_2 + Li_xC_6$ (total reaction)

To ensure the workability of the cell additional lithium is added to electrolyte by dissolving a lithium salt, such as hexa-fluoro phosphate ($LiPF_6$) in the electrolyte. Common electrolytes used in lithium-ion batteries are liquids or semi-liquids, which are considered relatively unsafe because of their negative impact on people and/or the environment [7]. Moreover, they are quite harsh on the electrodes [8].

2.2. Multifunctional Materials and Structural Batteries

Multifunctional materials present characteristics that go beyond strength and stiffness, which guide science and engineering for structural materials [9]. These materials can be designed with the aim to integrate features such as electrical, magnetic, optical and power generative functionalities, among others, which work in synergy and lead to new features that go beyond those of the sum of their individual properties. Multifunctional materials can impact structural performance by reducing size, weight, cost, power consumption, and complexity while improving efficiency, safety and versatility.

Multifunctional structural materials combine at least one additional function that is capable of bearing mechanical loads and thus serves as a structural element [10]. In that sense, structural batteries are a prominent example of multifunctional materials since they combine structural and electric properties, reducing the weight/volume system and resulting in better performance.

The concept of structural or multi-functional batteries was introduced by Wetzel et al. in 2004 [11] and comes from the desire of lowering system weight by reducing or removing the battery weight form. This weight and volume reduction is associated to a better performance and thus of interest for a wide range of products, such as smartphones, laptops, and portable electronics and even electrical vehicles (EVs) and hybrid electrical vehicles (HEV).

2.3. Carbon Fibers

Carbon fiber (CF) is a thin-long strand of material composed mostly of carbon atoms, and with about 0.005-0.010 mm in diameter [12], which are bonded together and aligned parallel to the long axis of the fiber. This alignment makes the fiber incredibly strong.

Carbon fibers are made by carbonization of precursor materials, mainly rayon, petroleum pitch and polyacrylonitrile (PAN) [12]. In this work, PAN-based carbon fibers were used because PAN polymer is the main precursor to produce high performance carbon fibers: PAN-based CFs have high tensile strength (HTS), up to 6000 MPa, their density is about 1.8 g/cm3, and they exhibit good electrical conductivity in their length direction [15]. The combination of these features made PAN-based carbon fibers ideal to produce electrodes for structural batteries.

Carbon fibers (CFs) are attractive for structural applications because of their high performance as reinforcement material and because their good electrical conductivity [12]. In addition, the graphitic structure of carbon fibers allows for reversible intercalation of lithium ion [13].

Structural battery composite can be produced by combining carbon fibers with a solid polymer electrolyte [14], and designed in any shape or size. For that, a tow of spread carbon fiber coated with cathodic material and that coated with anodic material would be covered by a solid polymer electrolyte (SPE), which also forms the matrix of the structural composite. A solid polymer electrolyte is a crosslinked poly-methacrylates containing a lithium salt as, for example, lithium triflate (CF_3LiO_3S) [15]. An illustration of an ideal designed carbon fiber composite battery is showed in Figure 2.

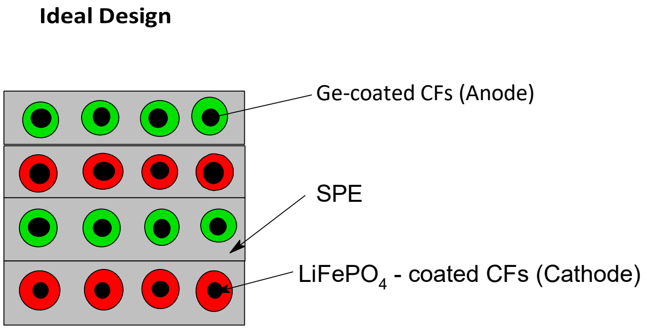


Figure 2. Schematic ideal design of a carbon fiber composite battery.

2.4. $LiFePO_4$ and Ge

Lithium-iron phosphate ($LiFePO_4$) and germanium (Ge) are prominent candidates to cathodic and anodic material, respectively, in reason of their high theoretical capacity among other properties.

Lithium-iron phosphate can be found in nature as the mineral triphylite [16]. However, impurities present in the crystalline body affect its electrochemical properties [17]. With a general formula $LiMPO_4$, $LiFePO_4$ belongs to the group of olivine structure, where M includes also Co, Mn and Ti [18]. $LiFePO_4$ was first mentioned as a cathodic material for lithium-ion batteries in 1996 by Goodenough et al. [19; 20]. Because of the low electrical conductivity of $LiFePO_4$, all $LiFePO_4$ cathodes under consideration are actually a composite cathode $LiFePO_4$/Carbon [21]. During charge/discharge, lithium ions are extracted concomitantly with Fe oxidation:

$$LiFe^{II}PO_4 \rightleftarrows Fe^{III}PO_4 + Li^+ + e^-$$

Lithium-iron phosphate caught the market attention in reason of its low cost, non-toxicity, the natural abundance of iron, as well as its excellent thermal stability, safety characteristics, electrochemical performance, and specific capacity (170 mA·h/g, or 610 C/g) [22]. $LiFePO_4$ can be produced by heating a variety of iron and lithium salts with phosphates or phosphoric acid. Many synthesis routes to produce $LiFePO_4$ have been reported, including hydrothermal synthesis [23].

Graphite has been used as anode for lithium-ion batteries (LIBs). However, its theoretical capacity is relatively low (372 mAh/g) [24], which limits its energy storage capacity. In order to achieve higher energy storage capacity some group-IV elements, such as Ge, Si and Sn, are being considered as substitute for graphite because of their higher theoretical capacities [25].

Germanium has been received less attention compared to silicon probably because of its higher price [26]. However, Ge presents excellent properties as a promising anode material such as high electronic conductivity (Ge band gap, E_g=0.66 eV, is smaller than Si, whose Eg = 1.12 eV, at 300K) [27]; and high lithium-ion diffusivity (Li-ion in Ge is about two times higher than that of Si at room temperature) [28]. With these favorable properties, Ge will likely have better rate capability and faster electrons transport. A greater disadvantage of high-capacity electrodes is that they present a much bigger volume change during full lithiation/delithiation. This can cause pulverization of the electrode and consequently lead to capacity loss of the LIBs [29]. A battery design, such as structural battery, could balance optimal energy and power densities through a Ge-structural anode.

Nowadays, in an attempt to meet the high demand for energy storage, researchers and technology industries have been paying attention to Ge and Ge-based materials for applications on LIBs [30] such as Prof. Brian A. Korgel's Group (Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, USA – see reference 44), who works on silicon and germanium anodes for lithium-ion batteries, as well as a cooperative work of the Center for Integrated Technologies (CINT-Albuquerque, New Mexico, USA) with Pennsylvania State University (USA) and the Georgia Institute of Technology (USA), who develop a work on Ge-based electrode materials for LIBs (see reference 24). Ge is present in the Earth's soil at about 1.6 ppm [31]. It usually occurs only as a trace element in ores and carbonaceous materials [32]. It can be assumed that the development and refinement of techniques for large scale production of Ge might lower its price in the future.

Taking in account the properties of these materials, the aim of this work is the construction of structural electrodes, both cathode and anode, using $LiFePO_4$ as a cathodic material and Ge as anodic material. The objective in this study, is to reach the construction of these electrodes through electrophoretic deposition (EDP) of these materials onto carbon fibers' surface.

3. Experimental

3.1. Materials

Nanocrystalline $LiFePO_4$ powder (Life Power P2/100-300 nm particle size) and Super P carbon black - CB - (Imerys Graphite & Carbon /10-100 nm particle size) - were both provided by our collaborators from the Royal Institute of Technology - KTH, in Sweden. Ge nanocrystals were supplied by Mr. Michael Haag (Quickhatch Corporation, Boulder, Colorado, USA). Carbon fibers, used as working electrode (WE), consisted of commercial AS4 unsized polyacrylonitrile (PAN)-based carbon fibers (Hextow). Polyvinylidene fluoride (Kynar® PVDF family), acetone (purity ≥ 99%, Sigma-Aldrich Co.), iodine ($I_2 \geq 99.8\%$ from Sigma-Aldrich Co.) and a non-ionic surfactant, 4-(1,1,3,3-Tetramethylbutyl) phenyl-polyethylene glycol (Sigma-Aldrich Co.), also known as Triton X-100, were all used without further purification.

3.2. Electrophoretic Deposition of $LiFePO_4$ onto Carbon Fibers

Electrophoretic deposition (EDP) is a colloidal process in which materials are deposited directly from a stable suspension by a DC electric field [33]. The suspension was produced by dispersing different amounts of $LiFePO_4$ and carbon black (CB) in 300mL acetone, containing 1.2 mL of Triton X-100 and 0.1819 g of iodine (I_2). Thereafter, by means of an ultrasonic processor (UP100H, Hielscher Ultrasonics GmbH,Teldow, Germany), the suspensions were homogenized for at least 20 min. The composition of the suspensions is listed on Table 1.

EDP is a two-step process: in a first step, fine particles suspended in a liquid move towards an electrode under application of an electrical field; in a second step, the particles are deposited on the surface of the electrode [34]. Electrophoretic deposition of lithium iron phosphate ($LiFePO_4$) onto carbon fibers was performed. The working electrode (WE) consisted of a bundle of carbon fibers (approximately 25 cm long) pulled over a purpose-built glass tube framework. Two platinum rods (length = 10 cm, diameter = 0.2 cm) served as counter electrodes (CEs) were fixed parallel to the carbon fibers at a distance of 3.5 cm. A silicone pot holder was attached onto the top of the beaker to fix the electrodes. A diagram of the setup is shown in Figure 3, and pictures of the EPD setup are shown in Figure 4 and 5.

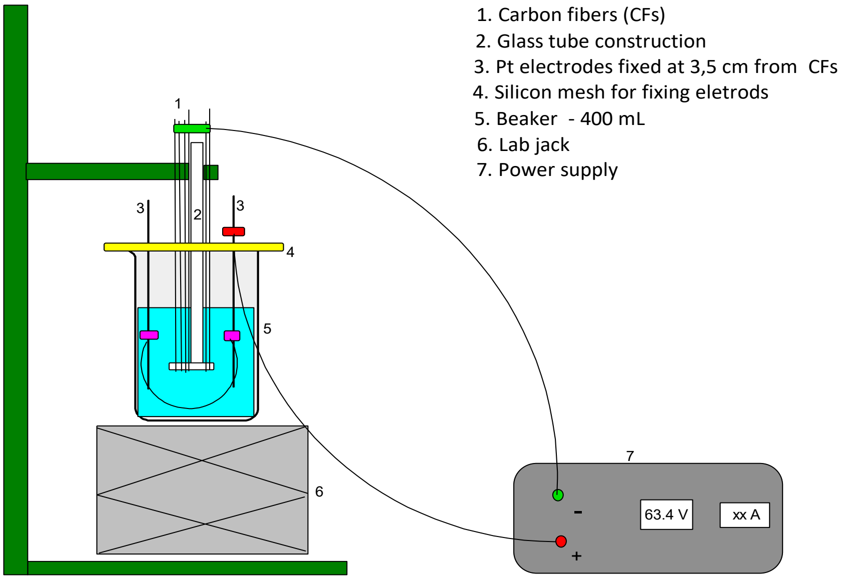


Figure 3. Illustration of the EDP set up for coating carbon fibers with $LiFePO_4$

Figure 4. Electrodes fixed by a silicon mesh

Figure 5. Setup for coating fibers

The WE (cathode - CFs) was connected to the negative output of the power supply (Elektro-Automatik EA-PS 3065-05 B, Viersen, Germany - able to deliver at least 60 V) as the $LiFePO_4$ particles are positively charged. Thus, the CE (anode – Pt rods) was connected into the positive output of the power supply.

Before the carbon fibers were submerged into the suspension, a check for short circuit was performed by applying the maximum possible voltage (65.3 V). If this value could be reached without any current, no short circuits were present. After immersing the carbon fibers into the coating suspension, the voltage dropped immediately.

To reach the potential required for deposition, the lowest possible current had to be applied (0.05 - 0.1 A). Deposition was performed for 300 s at a constant potential between 61 and 65 V. The coated fiber tow was then removed from the coating suspension and dried overnight in the fume hood at room temperature. Pictures of coated carbon fibers are shown in Figure 6.

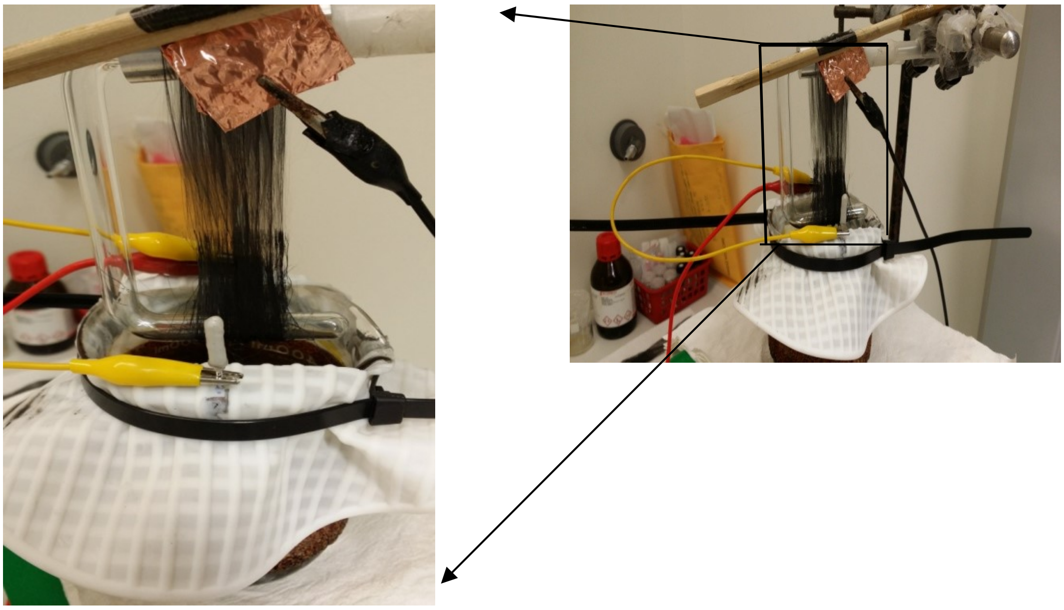


Figure 6. $LiFePO_4$-coated carbon fibers.

In order to investigate the effects of different functional-fiber-coating compositions, the suspension's composition was varied. Percental compositions of the coatings are summarized in Table 1 and their corresponding amounts are shown in Table 2.

Table 1. Summary of the composition of the coating suspensions

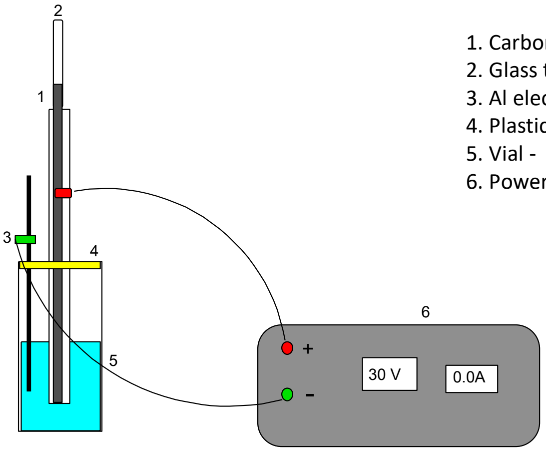
$LiFePO_4$ [%]	**CB [%]**	**PVDF [%]**	**$\sum$ (LiFePO4+CB+PVDF) [mg]**
90	6	4	293.1
92	4	4	293.1
88	8	4	293.1
88	6	6	293.1
86	6	8	293.1

Table 2. Average of parameters for composition of suspensions and EDP

$m_{LiFePO4}$ [g]	**m_{CB} [g]**	**m_{PVDF} [g]**	**m I_2 [g]**	**V_{Triton}[mL]**	**$V_{Acetone}$[mL]**	**P [V]**	**i [A]**
0.2637	0.0176	0.0119	0.1821	1.2	300	63.4	0.04
0.2695	0.0117	0.0117	0.1819	1.2	300	63.4	0.04
0.2579	0.0234	0.0117	0.1816	1.2	300	63.4	0.05
0.2578	0.0176	0.0176	0.1819	1.2	300	63.4	0.05
0.2521	0.0176	0.0234	0.1819	1.2	300	63.4	0.05

3.3. Deposition of Ge onto Carbon Fibers

Electrophoretic deposition of Ge nano-crystals onto the PAN-based carbon fibers was performed in a smaller scale compared to the $LiFePO_4$ coating. The EDP-setup was then adapted to accommodate a small volume of Ge suspension (app. 9 mL). The preparation of suspensions was similar to the suspension of $LiFePO_4$, except for iodine (I_2), which was not necessary in this case. The setup for coating carbon fibers with Ge is shown in Figure 7.



1. Carbon fibers (CFs)
2. Glass tube construction
3. Al electrode fixed at 1,5 cm from CFs
4. Plastic cap
5. Vial - 20 mL
6. Power Supply

Figure 7. Setup for deposition of nc-Ge onto carbon fibers

A vial (20mL) was employed instead of a beaker because we had only a small amount of Ge available. The glass cap was pierced at the end to pin the aluminum electrode, used now by suggestion of our Ge supplier. The WE (cathode - CFs) was connected to the positive output of the power supply (Elektro-Automatik EA-PS 3065-05 B, Viersen, Germany) as the Ge particles are negatively charged. The cable connecting the CE (anode – Al rod) to the power supply was plugged into the negative output. This electrocoating method was based on a procedure provided by Mr. Michael Haag (Quickhatch Corporation, Boulder, Colorado, USA), who successfully performed the coating of nc-Ge and nc-Si onto ITO (indium tin oxide coated glass) by means of EDP [35].

The suitable amounts of nc-Ge, PVDF and CB in the suspension were determined empirically. Main parameter varied was PVDF because it may influence the adhesion of the nc-Ge onto the carbon fibers' surface since PVDF was used as binder. In the case of nc-Ge EDP, a potential of 30 V was applied for 10 min and no current was observed during the coating process. A summary of the compositions of the EDP suspensions is shown in Table 3.

Table 3. Average of parameters for composition of suspensions and EDP

m_{Ge} [g]	m_{CB} [g]	m_{PVDF} [g]	V_{Triton} [mL]	$V_{Acetone}$ [mL]	P [V]	i [A]
0.0310	0.0097	0.0049	1,2	7.0	30	0.0
0.0303	0.0103	0.0026	1,2	7.0	30	0.0
0.0302	0.0101	0.0012	1,2	7.0	30	0.0

4. Characterization

4.1. SEM and EDX

The samples produced in this study were analyzed by means of Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX). SEM provides detailed surface information by tracing a sample in a raster pattern with an electron beam.

Energy Dispersive X-Ray Analysis (EDX), which is an X-ray technique used to identify the elemental composition [36], was also used to analyze samples. The EDX system was attached to the Scanning Electron Microscope (SEM). The data generated by the EDX consist of X-ray spectra emissions corresponding to the chemical elements present on the sample surface that allow obtaining an elemental mapping of the sample.

Two different Scanning Electron Microscopes (SEMs) were used to take images of the various samples and starting products: the first was a JCM-6000 Neoscope Benchtop SEM (produced by Jeol Ltda, USA) that was initially used to characterize the quality of the coating. Images were captured in the secondary electron imaging (SEI) mode at an acceleration voltage of 15 kV. The second was a Zeiss Supra 55 VP FESEM (produced by Carl Zeiss SMT AG Company, Oberkochen, Germany), in which a scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) with elemental mapping were performed. An in-lense detector and a current of 5 kV was used for capturing SEM-images. For EDX measurements, an acceleration voltage of 20 kV was applied, the aperture size was changed and the EDX-detector was selected. The compositions of a few selected samples were measured at different locations and the results averaged. Additionally, their elemental maps were also recorded.

4.2. Electrochemical characterization

In order to check the capacity of the electrodes to storage energy, cycling tests were performed by our collaborators at KTH – Royal Institute of Technology, in Sweden.

* “For electrochemical cycling experiments, a pouch cell design was used. The EDP-coated carbon fibers were dried in a vacuum oven overnight at 60 °C prior to cell assembly in a glove box with argon atmosphere (< 1 ppm H_2O and O_2). To ensure electrical contact, an aluminum current collector was attached to the end of the carbon fiber tows on an uncoated part with silver glue, and then sealed inside the pouch to ensure that the electrolyte was not contaminated. A half-cell setup was used with lithium foil as the common counter and reference electrode, a 250 µm Whatman glass microfiber filter was used as separator and BASF 1.0 M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by weight) was used as electrolyte. Galvanostatic cycling at different rates was carried out using a Biologic VMP3 potentiostat. High precision coulometry was performed with an in-house constructed cycling setup, similar to the one used by Dahn et al. [37] utilizing Keithley 220 current sources and high precision resistors connected to a Keitley 2700/2701 multimeter to measure the current. The cells were placed in temperature controlled chambers at 25±0.1°C. This setup allowed for the determination of the columbic efficiency (CE) with an accuracy of

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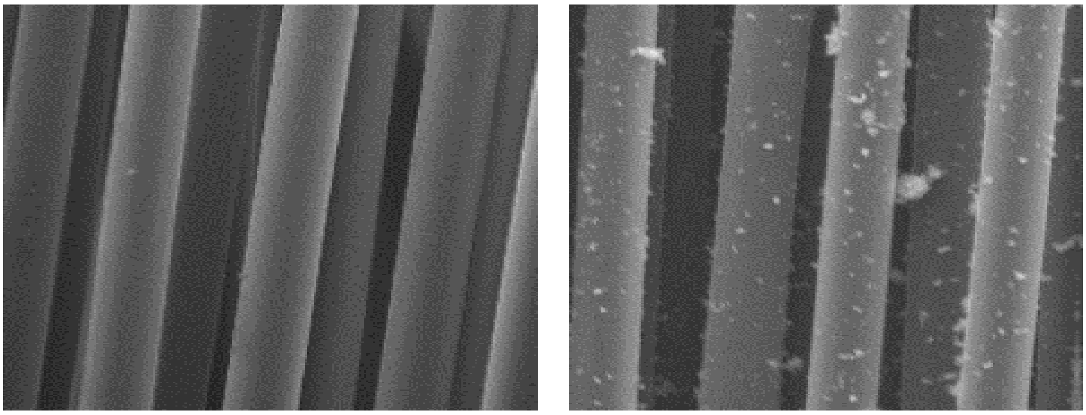
* Text from the article: “Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries” by Johan Hagberg, Henry Maples, Kayne S.P. Alvim, Johanna Xu, Wilhelm Johannisson, Alexander Bismarck, Dan Zenkert, Göran Lindbergh. Composites Science and Technology. Available online 3 May 2018.

±0.02 % for C-rates below 0.1C. All cycling was carried out between 2.8 and 3.8 V vs. Li/Li+. The C-rate was defined according to the specified specific capacity of the LFP of 150 mAh/g, 1C = 150 mA/g, fully charged in one hour.”

5. Results and Discussion

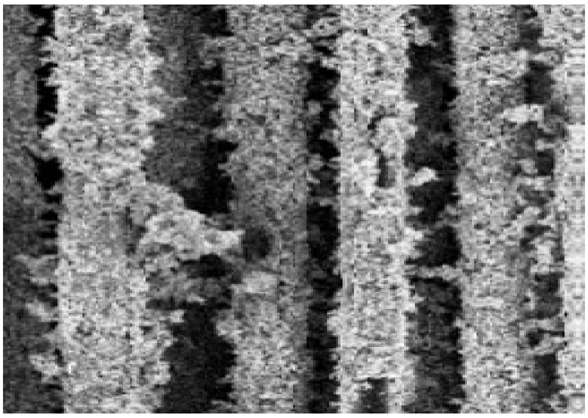
5.1. $LiFePO_4$ – coated fibers

All the $LiFePO_4$- coated samples presented a deposition of a material. Scanning Electron Microscopy (SEM) was employed to verify the quality of coating on carbon fibers. The abundance of the coating can be illustrated by taking a bunch of unsized carbon fibers as a standard for comparison (Figure 8).



(a) Carbon fibers without coating

(b) Carbon fibers poorly coated



(c) Carbon fibers well coated

Figure 8. Illustrative comparison for carbon fiber coatings.

SEM confirmed that coated carbon fibers samples produced for this work presented deposition of a material on the surface, which is assumed to be LiFePO4 mixed with nanocrystalline carbon black, was successfully deposited onto the carbon fibers. Some samples presented a very patchy coating and large agglomerates rather than a thin homogeneous coating, varying with the concentration of $LiFePO_4$, carbon black and PVDF. SEM showed that carbon fibers were well coated, although some samples presented bigger agglomerates. The quality of the coatings of some samples can be observed in Figures 9 and 10. Further pictures can be seen in Annex I.

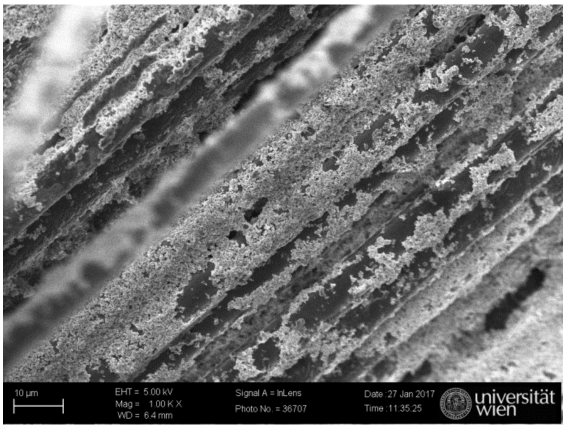


Figure 9. Sample (90:6:4) %w/w

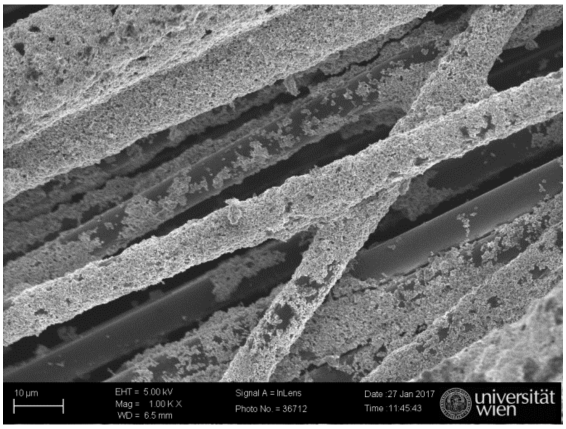
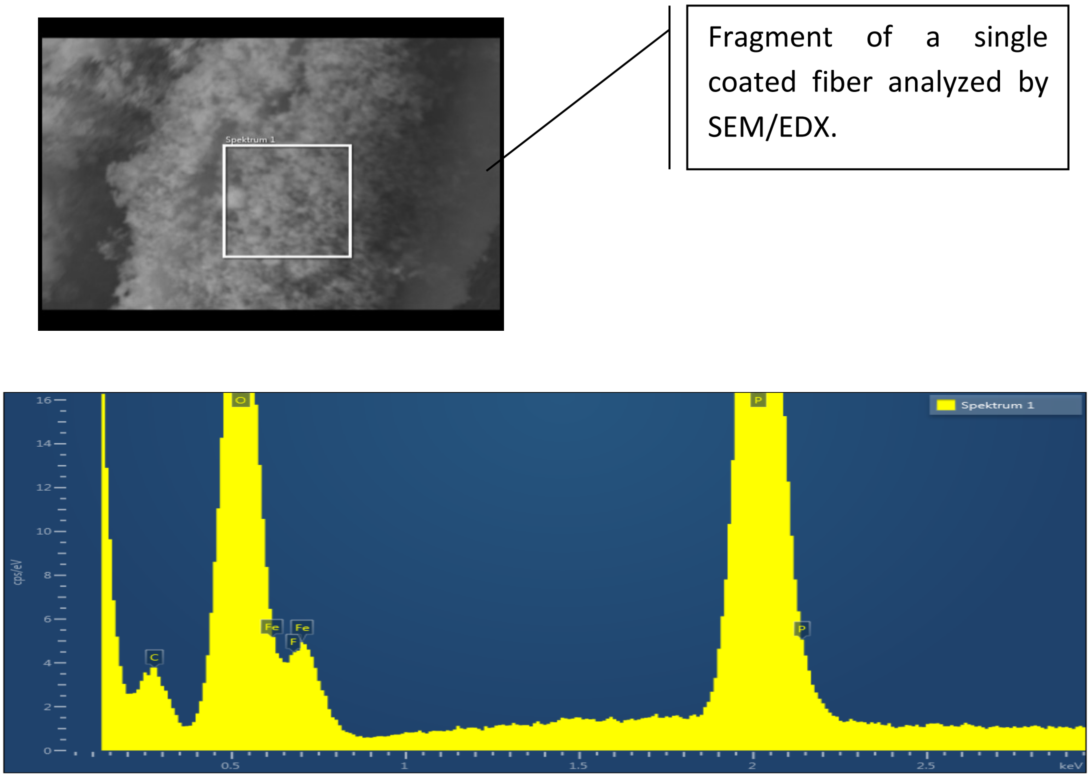


Figure 10. Sample (92:4:4) %w/w

Energy Dispersive X-Ray Analysis (EDX) was used to determine the composition of the sample (90:6:4) %w/w (equivalent to LFP:CB:PVDF) as a whole, as well as the composition of individual components. Elemental map and statistical data for sample (90:60:4) %w/w is shown in Figure 11. Statistical data confirmed the deposition of the elements present in the solution, although these numbers are not very accurate (since samples were not physically homogeneous). EDX mapping showed that C, O, F, P and Fe were distributed in accordance to their concentration in the suspension for all samples. Further elemental maps and statistical data can be found in Annex II.



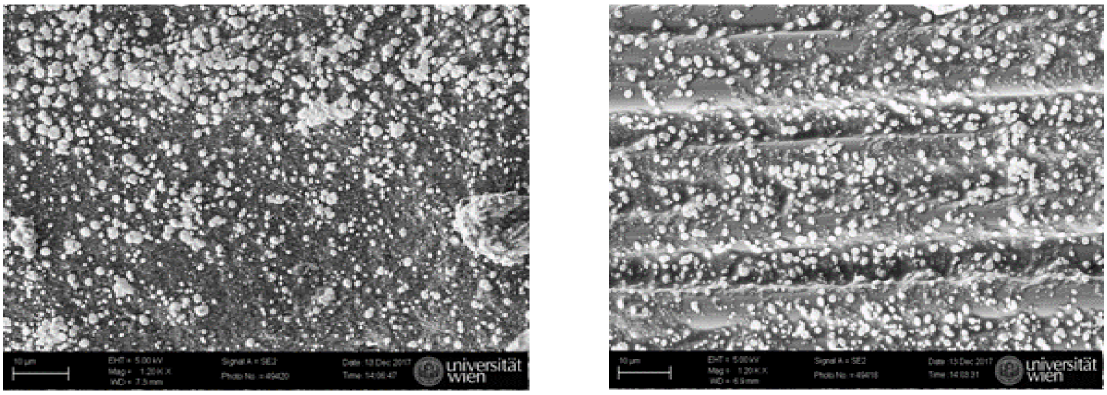
Fragment of a single coated fiber analyzed by SEM/EDX.

Statistics	C	O	F	P	Fe
Max	37.79	41.92	0.00	9.70	10.60
Min	37.79	41.92	0.00	9.70	10.60
Average	37.79	41.92	0.00	9.70	10.60
Standard deviation	0.00	0.00	0.00	0.00	0.00

Figure 11. Elemental map of sample (90:6:4) %w/w

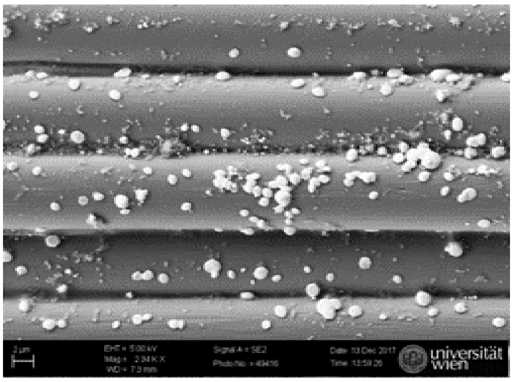
5.2. Ge – coated fibers

Similarly to $LiFePO_4$ –coated carbon fibers, SEM images showed the deposition of a material, that we assume to be Ge, onto the carbon fibers' surface. In this case, the amount of coating is lower in comparison to the lithium phosphate coating since in suspensions were much lower amount of materials. PVDF was used as binder, and was the main component to be seen. Thus, suspensions were prepared with 0.005 g; 0.0025 g and 0.00125 g of PVDF. The amount of deposited material seemed to be related to the PVDF concentration as it can be seen in Figure 12.



(a) Ge coating with 0.005 g of PVDF

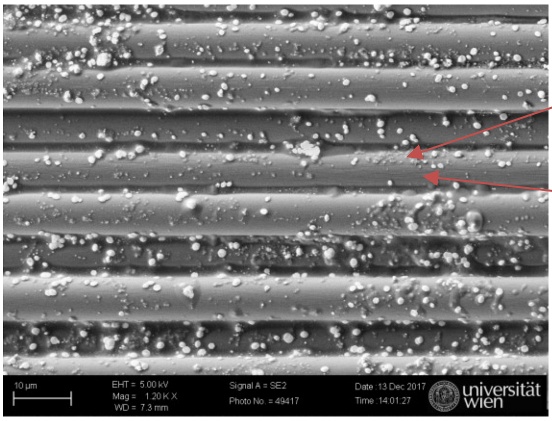
(b) Ge coating with 0.0025 g of PVDF



(c) Ge coating with 0.00125g of PVDF

Figure 12. Amount of coated material according to PVDF concentration.

Similarly to $LiFePO_4$ coated CFs, an EDX mapping was conducted to investigate whether Ge was deposited on the CFs' surface and how it was distributed. The exact amount of elements present on coated fibers cannot be determined since samples are not homogeneous. However, the identification and distribution of elements is possible. It can be assumed that all materials presented in the suspension are deposited on the carbon fiber surfaces. Figure 13 shows an EDX image for sample with lower amount of PVDF (0.00125 g) of Ge coated CF. Oxygen was present for all performed EDX mapping on Ge coated CFs. It was noticed, through EDX, that oxygen looks surround Ge particles. One can be deduced that the O present is probably a result of oxidation of the germanium surface since germanium, like silicon, naturally reacts and forms complexes with oxygen in nature.



Element	Line Type	Apparent Concentration	k Ratio	Wt%
C	K series	81.01	0.81014	96.78
Cu	K series	0.04	0.00042	0.05
Ge	K series	2.32	0.02323	3.17
Total:				100.00

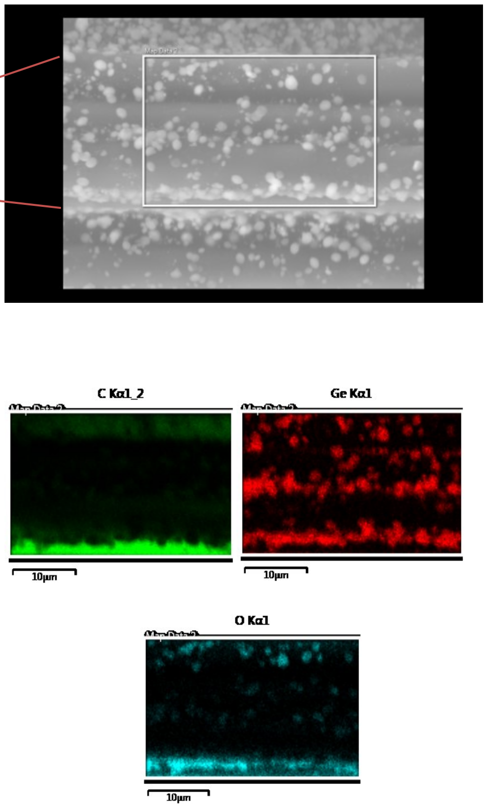


Figure 13. Elemental identification and distribution for Ge-coated CF

5.3. Electrochemical characterization of $LiFePO_4$ –coated CFs

* "A typical charging/discharging voltage profile for different C-rates for an electrode coated with the composition 92:4:4 % w/w for $LiFePO_4$, CB and PVDF, respectively, is shown in Figure 14. The charging/discharging voltage profiles looked similar for all tested coating compositions. Voltage profiles with a plateau around 3.4 V vs. Li/Li^+ are typical for LFP [38]. The polarization is low; the charge/discharge overpotential is 39 mV at 0.1C, 51 mV at 0.2C, 94 mV at 1C and 142 mV at 2C. The capacity retention is also high at around 0.85 at 1C and 0.75 at 2C compared to the 0.1C capacity.

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* Text from the article: "Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries" by Johan Hagberg, Henry Maples, Kayne S.P. Alvim, Johanna Xu, Wilhelm Johannisson, Alexander Bismarck, Dan Zenkert, Göran Lindbergh. Composites Science and Technology. Available online 3 May 2018.

This is attributed to the short electronic diffusion distance from the carbon fiber current collectors to the active particles and due to the coating of individual fibers. This also shows that the conductivity of the carbon fibers is high enough even for high power applications. Conductivity of the carbon fibers used in this study is 588 S cm^{-1}, which is typical for PAN-based carbon fibers [39]. The low polarization also indicates a homogenous distribution of the CB particles (conductive additive) throughout the coating providing a conducting pathway between the carbon fibers and dispersed LFP particles. According to the manufacturer, the specified capacity for the carbon coated LFP used was 150 mAh/g. For the presented sample (Figure 14), the capacity reached was 123 mAh/g, which means that around 82 % of the active material was utilized. This is attributed to loss of electrical contact between a fraction of LFP particles and the CFs in areas of excessive coating thickness.

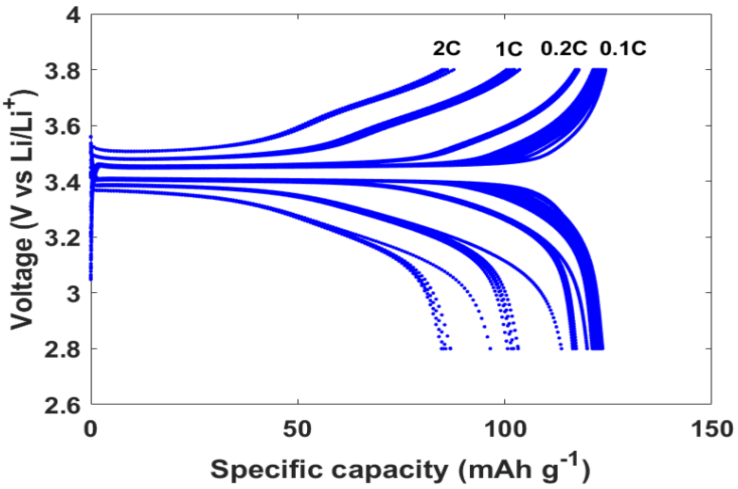

Figure *14*. Voltage profile for different charging rates for the sample composition 92:4:4%w/w

Table 4 shows the average specific capacities of the coated carbon fibers for the different tested compositions cycled at 0.1C. There are no clear trends and the values vary between around 60 and 110 mAh/g. The amount of coating varies between 30 to 50 wt.%. This is relatively low compared to commercial batteries since a low current collector weight is better for a higher energy density. However, here the carbon fibers should perform multiple functions simultaneously: they should carry mechanical load and act as current collectors. An excessive amount of active coating would lower the fiber volume fraction in a structural composite battery, which is detrimental in terms of its mechanical properties. Balancing the mechanical properties and the energy storage capabilities is an optimization question, i.e. a higher coating weight fraction would lead to a higher energy density but a much worse mechanical performance, and vice versa. Interesting to note is that the highest capacity was reached for the composition with the lowest amount of additive (4 wt% CB and PVDF). This is attributed to the short electrical contact distance between the carbon fibers and the network of LFP particles dispersed throughout the coating and indicates that as little as 4 wt.% of additive is sufficient to bind the LFP particles to the carbon fibers while guaranteeing sufficient electrical contact. This is beneficial in terms of gravimetric energy density since a high loading of active material can be incorporated into the coating, counterbalancing the relatively high carbon fiber/coating ratio.

Table 4. Average specific capacities of the coated CF electrodes based on the weight of the LFP for the different compositions and the coating wt.% of total electrode weight. ¥Not enough samples for standard deviation

Composition	Average specific capacity at 0.1C (mAh.g^{-1})	Coating wt.%
92:4:4	108 ± 20.5	32
90:6:4	62 ± 6.8	31
88:8:4	90 ± 5.7	45
88:6:6	66¥	50
86:6:8	75 ± 8.5	41

The rate performance for different compositions is shown in Figure 15. Varying the amount of CB from 6 and 8 wt.% in the coating - Figure 15 (a) - does not result in large differences in rate performance. The retention is around 0.85 at 1C and 0.75 at 2C. For a very low amount (4 wt.%) of CB, the rate performance is slightly worse with a retention of around 0.7 at 2C, but this is still acceptable since 2C is a very high current. At 0.1C all coated carbon fiber electrodes have retention close to 1, here the 90:6:4%w/w composition have a slightly better retention. This indicates that the internal resistance in the electrodes is low, even for amounts as low as 4 wt% CB, which provides the electrically conducting network in the coating. This can be compared to commercial electrodes where a CB content of more than 10 wt.% is often needed for full utilization of the active material [40]. This is so because the electrical conductivity of LFP is inherently low and, especially for sub-micron sized particles; a substantial amount of conductive additive is needed, even when the LFP is carbon coated.

Figure 15 (b) shows the rate performance of coated CF electrodes when varying the amount of PVDF binder in the coating. Increasing the amount of PVDF to more than 4 wt.% had a detrimental effect on the rate performance. At 2C the retention is around 0.75 for the sample with 4 wt.% PVDF, around 0.70 for 6 wt.% and around 0.65 for 8 wt.%. When reapplying 0.1C, the retention was close to 1 for the fibers coated with compositions 90.6:4 % w/w and 88:6:8 % w/w, but declined quickly for the fiber coated with the 86:6:8 composition, indicating that the cycling is not stable for a high PVDF content in the coating. The reasons for the decreased rate performance for functional fiber coatings containing a PVDF binder content lower than 4 wt.% could possibly be: Li-ion diffusion pathways in the porous coating are blocked or LFP particles are isolated from electrically conductive paths. In terms of the electrochemical performance, there is no benefit in increasing the PVDF above 4 wt.%. The functional carbon fiber coating with a composition of 90:6:4 %w/w had the best rate performance. This is a relatively low additive content, which is beneficial in terms of gravimetric energy density. The differences in rate performance, however, are not large and since the fibers coated in a composition of 92:4:4 %w/w exhibited a higher capacity (Table 4) that could be a better composition in terms of overall electrochemical performance. The big advantage of the EPD process to coat carbon fibers is that every fiber is individually coated and, therefore, only a rather low amount of PVDF is required to bind the LPF particles to the fibers. A 3D network electrode with additional benefits compared to traditional layer by layer designs is achieved, such as short electrical contact distances between active particles and current collector and the possibility for the electrodes to be used in a carbon fiber reinforced composite.

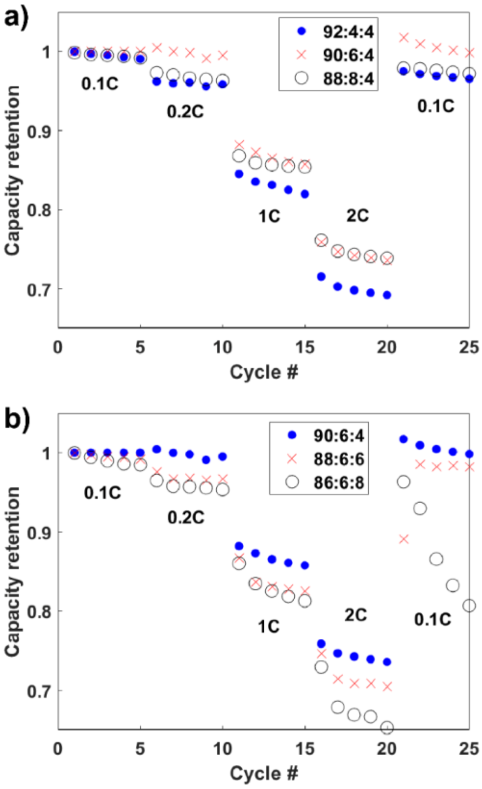

Figure 15. Rate performance for the different coated compositions: a) Varying the amount of CB and b) that of PVDF binder in the functional carbon fiber coating

The long-term cycling performance, 1000 cycles at 1C for an electrode with the coating composition 90:6:4 %w/w, is shown in Figure 16. The capacity is steadily declining and the capacity retention for this coating was 62 % after 500 cycles and 47 % after 1000 cycles when compared to the first cycle. The observed degradation is higher than for commercial cells but could be an effect of the pouch cells used. One of the reasons for the capacity decline could be the slow ingress of air/moisture in to the pouch, for high C-rates the thick separator used (a 250 µm thick glass microfiber filter compared to around 30 µm thick polymer separator in commercial cells) could also affect the performance. Another reason could be electrolyte degradation or dendrite formation on the lithium foil counter electrode, leading to an increased cell resistance. The latter is a known problem for half-cells when cycling at higher rates [41]. The few points with lower capacity at around 700 and 820 cycles could be measurement error since the channel was switched around that time. Overall, the cycling seems stable over 1000 cycles, indicating that the functional coating maintains electrical contact with the carbon fiber current collectors.

The coulombic efficiency (CE) of the carbon fiber battery electrode coated with the composition of 90:6:4 %w/w, determined by high precision coulometry, is shown in Figure 17. The CE remained stable at around 99.8 % which is comparable to commercial LFP/graphite batteries [42], indicating that a few side reactions occur (because of impurities, reactions with solvent, etc), which is beneficial for the battery lifetime.”

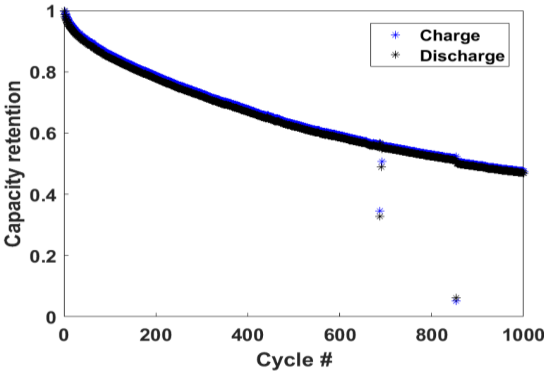

Figure 16. Long term cycling at 1C for a carbon fiber electrode with the composition 90:6:4

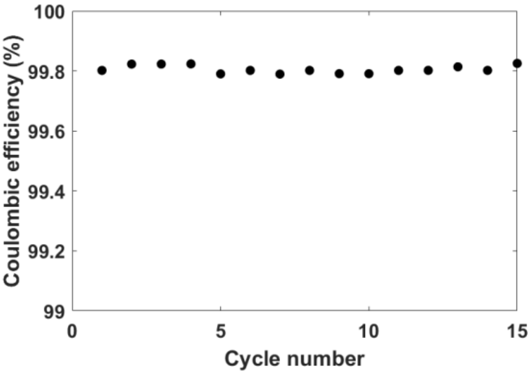

Figure 17. CE for a 90:6:4 sample cycled at 0.1C

5.4. Electrochemical characterization of Ge –coated CFs

Although the EDP-coating of Ge onto CFs seemed to be successful, cycling tests were not performed since optimization of coatings is necessary as well as a further investigation on Ge surface oxidation. All these parameters may be subject of investigation in a future study on this topic.

6. Conclusion

Electrophoretic deposition (EDP) proved to be an efficient method for producing structural electrodes. SEM and EDX showed that carbon fibers were homogenously coated with $LiFePO_4$. This means that PVDF provided a good adhesion of particles onto the carbon fiber surface, and carbon black (CB) is a suitable electrical conductor for the preparation of functional coatings on structural fibers to be used as electrodes by means of EDP. Electrochemical evaluation of $LiFePO_4$-coated CFs showed that the functional coating presents good performance as positive electrode, with capacity around 60 – 110 mAh/g and high Coulombic efficiency (app. 99.8%). Moreover, the quality of coatings was not affected by continuous cycling. The production of an anode by means of EDP also seems to be promising since the coating of Ge onto carbon fiber surfaces was obtained.

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Annex I

SEM images for different compositions of $LiFePO_4$/CFs coatings.

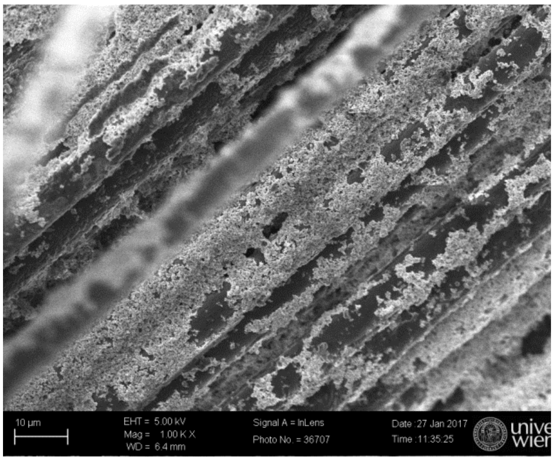


Figure AI_1. Sample (90:6: 4) %w/w

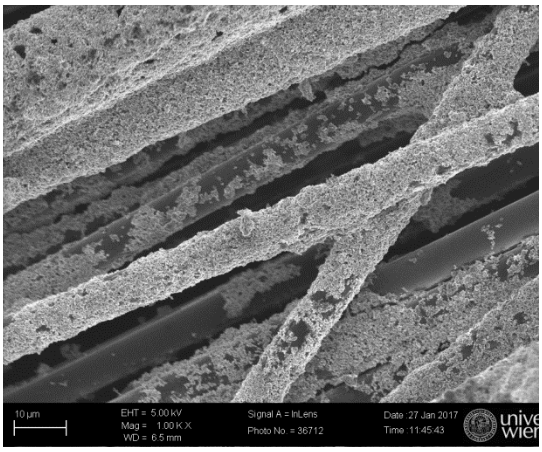


Figure AI_2. Sample (92:4: 4) %w/w

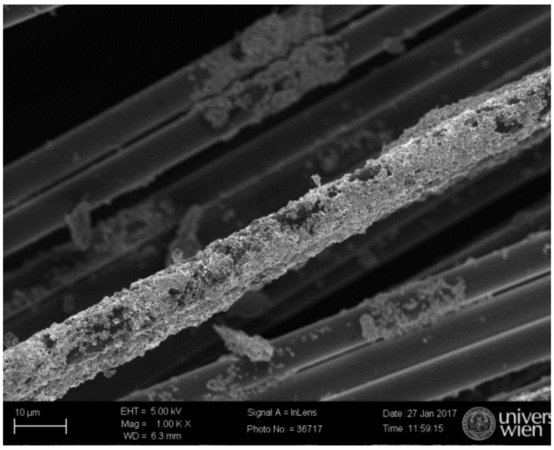


Figure AI_3. Sample (88:8: 4) %w/w

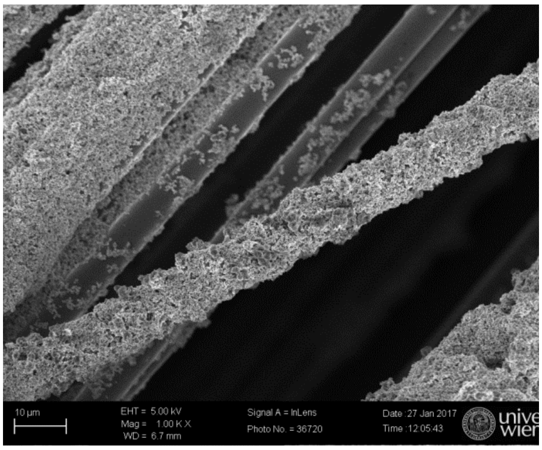


Figure AI_4. Sample (88:6: 6) %w/w

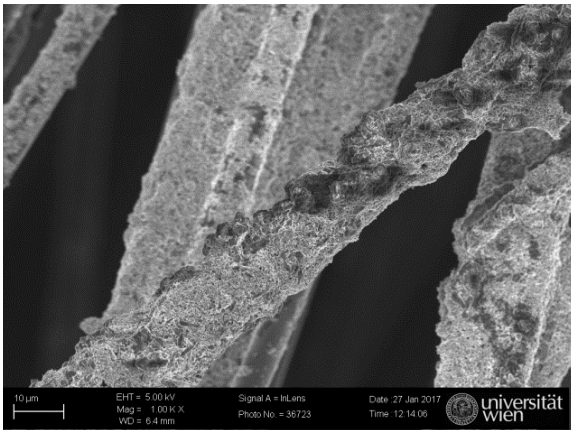
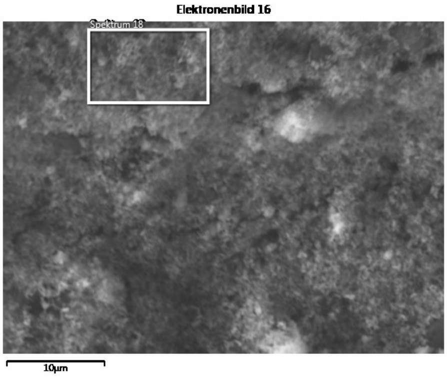


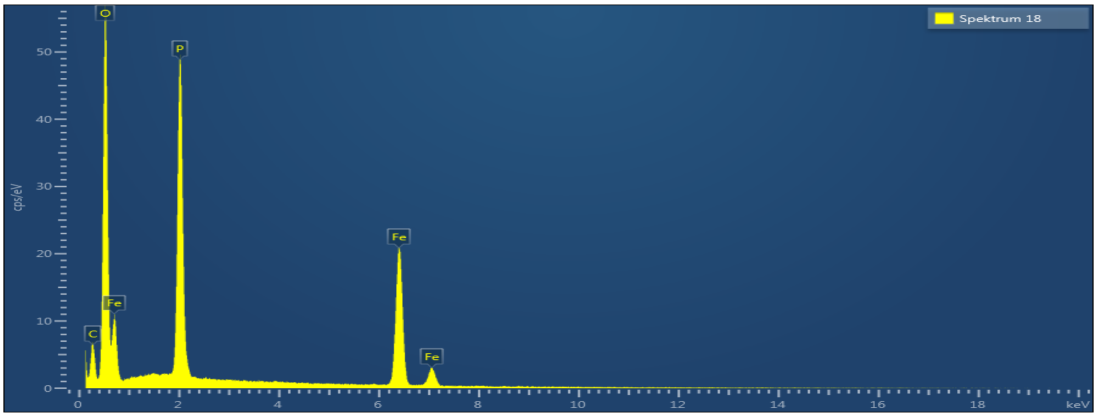
Figure AI_5. Sample (86:6: 8) %w/

Annex II

EDX mapping for different compositions of $LiFePO_4$/CFs coatings.

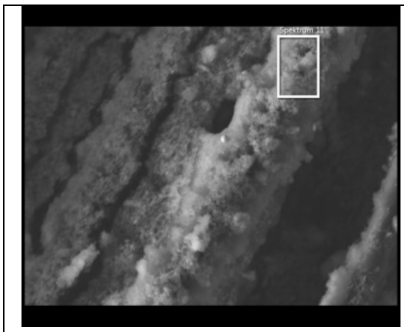


Element Spectrum	Spectrum 18
C	30.40
O	52.76
P	8.69
Fe	8.15
Sum	100.00

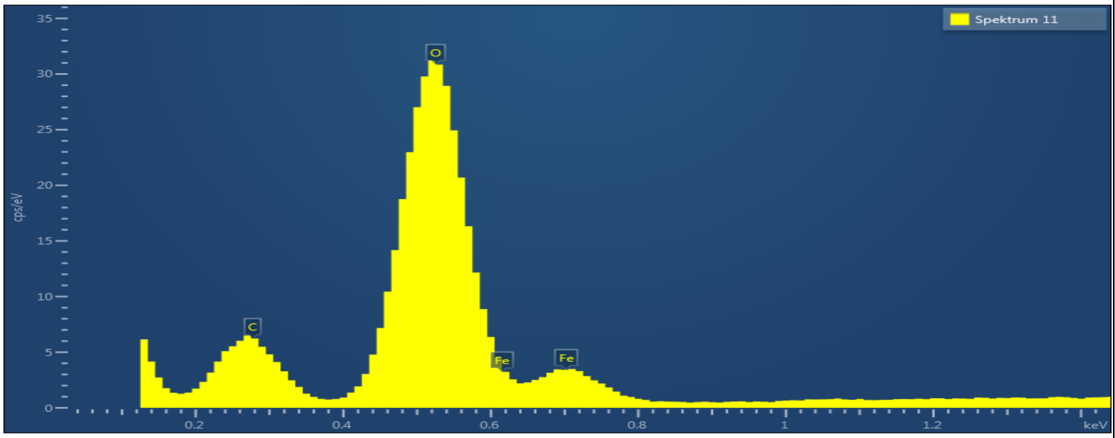


Statistcs	C	O	P	Fe
Max	30.40	52.76	8.69	8.15
Min	30.40	52.76	8.69	8.15
Average	30.40	52.76	8.69	8.15
Standard deviation	0.00	0.00	0.00	0.00

Figure AII_1. EDX for sample (92:4:4) % w/w

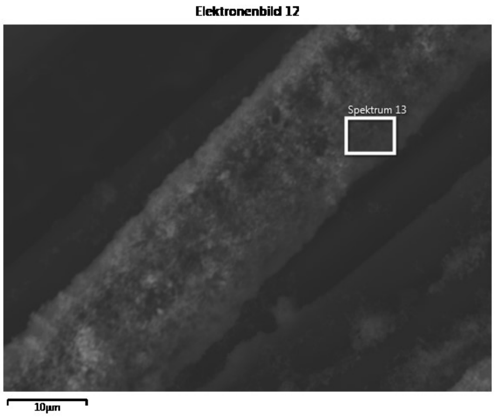


Element Spectrum	Spectrum 11
C	38.45
O	51.31
P	4.73
Fe	5.51
Sum	100.00

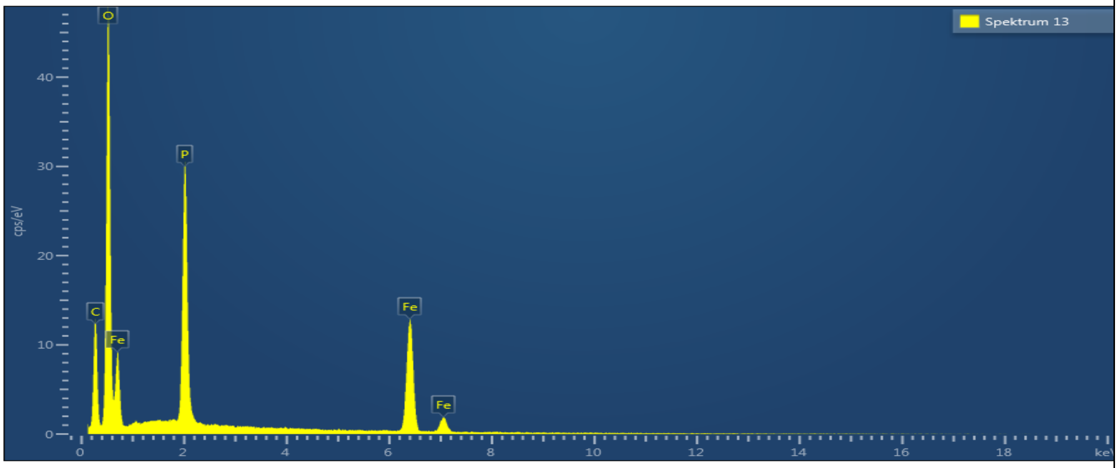


Multiple Spectra Statistics	C	O	P	Fe
Max	38.45	51.31	4.73	5.51
Min	38.45	51.31	4.73	5.51
Average	38.45	51.31	4.73	5.51
Standard deviation	0.00	0.00	0.00	0.00

Figure AII_2. EDX for sample (88:8:4) % w/w

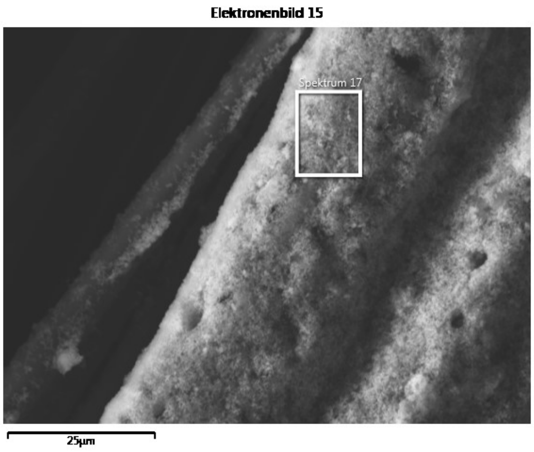


Element Spectrum	Spectrum 13
C	40.92
O	48.62
P	5.17
Fe	5.29
Sum	100.00

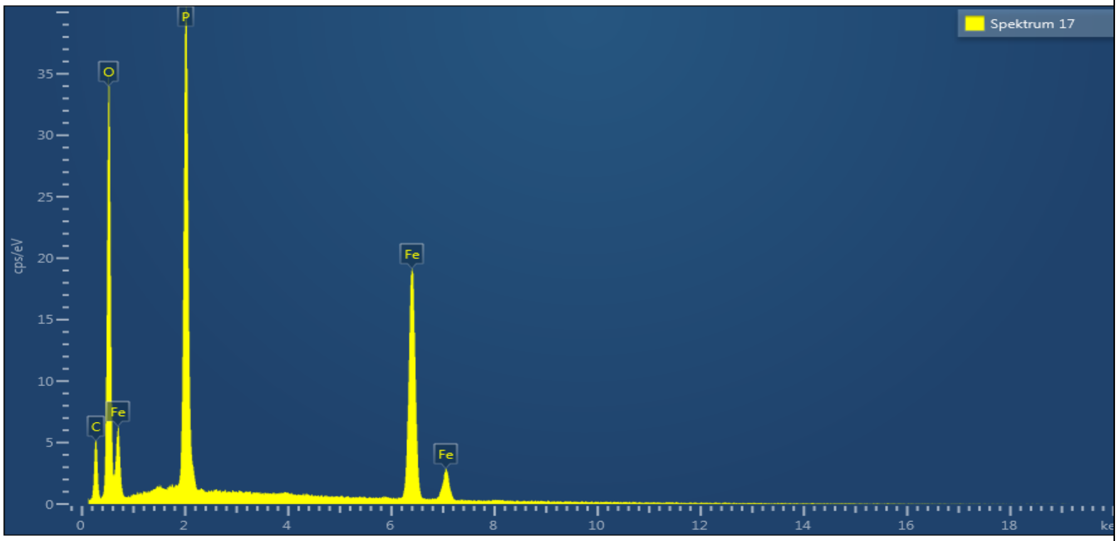


Multiple Spectra Statistics	C	O	P	Fe
Max	40.92	48.62	5.17	5.29
Min	40.92	48.62	5.17	5.29
Average	40.92	48.62	5.17	5.29
Standard deviation	0.00	0.00	0.00	0.00

Figure AII_3. EDX for sample (88:6: 6) % w/w



Element Spectrum	Spectrum 17
C	32.34
O	45.84
P	10.41
Fe	11.41
Sum	100.00



Multiple Spectra Statistics	C	O	P	Fe
Max	32.34	45.84	10.41	11.41
Min	32.34	45.84	10.41	11.41
Average	32.34	45.84	10.41	11.41
Standard deviation	0.00	0.00	0.00	0.00

Figure AII_4. EDX for sample (86:6: 8) % w/w