Title: Development of Novel Carbon Fiber based Electrodes for Lithium-ion Batteries for Proceedings of the American Society for Composites—Thirty-eighth Technical Conference

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ABSTRACT

Carbon fiber-based structural lithium-ion batteries are attracting significant attention in the automotive and aerospace industries due to their dual capability of energy storage and mechanical load-bearing, leading to weight reduction. These batteries utilize lightweight carbon fiber (CF) composites, which offer excellent stiffness, strength-toweight ratios, and electrical conductivity. Polyacrylonitrile-based CFs, comprising graphitic and amorphous carbon, are particularly suitable for Li-ion battery applications as they allow the storage of lithium ions. However, integrating lithium iron phosphate (LFP) into CFs poses challenges due to complex lab-scale processes and the use of toxic dispersants, hindering large-scale industrial compatibility. To address this, we investigate the development of water-based LFP-integrated CF structural Li-ion batteries. Homogeneous suspensions are created using cellulose nanocrystals (CNCs) to form hybrid structures. The battery system employs LFP-modified CF as the cathode, unsized CF as the anode, and a water-based electrolyte. The LFP-CNC-graphene nanoplatelet (GNP) hybrids are coated onto CFs through immersion coating. Scanning electron microscopy (SEM) images confirm the well-dispersed and well-adhered LFP-CNC-GNP structures on the CF surface, contributing to their mechanical interlocking and electrochemical performance. The batteries demonstrate a specific energy density of 62.67 Wh/kg and a specific capacity of 72.7 mAh/g. Furthermore, the cyclic voltammetry experiments reveal the stability of the LFP-CNC-GNP-coated CF batteries over 200 cycles without degradation. This research enables the engineering of hybrid nanostructured battery laminates using novel LFP-CNC-GNP-coated CFs, opening avenues for the development of innovative Li-ion structural batteries.

INTRODUCTION

The automotive and aerospace industries are increasingly focused on carbon fiber-based structural lithium-ion batteries, which offer the combined advantages of energy storage and mechanical load-bearing capabilities, leading to weight reduction. [1,2] These batteries utilize lightweight materials, predominantly carbon fiber (CF) composites, renowned for their exceptional stiffness, favorable strength-to-weight ratios, and excellent electrical conductivity. Specifically, polyacrylonitrile-based CFs, comprising both graphitic and amorphous carbon, exhibit the ability to store lithium ions, making them highly suitable for Li-ion battery applications. [3]

The architecture of these laminated batteries involves two distinct CF layers serving as the negative and positive electrodes, respectively, with an electrolyte in between. While various lithium sources such as LiCoO₂ and LiMn₂O exist, lithium iron phosphate (LiFePO₄ or LFP) is particularly desirable for positive electrodes due to its high theoretical specific capacity of 170 mAh/g, as well as its structural and chemical

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stability. [4] However, integrating LFPs into CFs poses challenges due to the complex lab-scale processes involved, and the use of toxic dispersants like N-Methyl-2-pyrrolidone (NMP) makes conventional processing methods incompatible with large-scale industrial applications. To address these concerns, integrating LFPs onto CFs through non-toxic suspensions, such as aqueous dispersion, not only ensures process safety but also facilitates scalability.

In this study, we investigate the development of water-based LFP-integrated CF structural Li-ion batteries. The modified CF serves as the cathode, while unsized CF acts as the anode, accompanied by an electrolyte. To achieve homogeneous and stable suspensions for coating, we utilize cellulose nanocrystals (CNCs) to create hybrid structures in water. By dissolving a 10 wt% mixture of LFP-CNC-graphene nanoplatelets (GNPs) with a ratio of 7.5:0.5:2 in water through probe ultrasonic treatment, we achieve the desired battery system. LFP functions as the active material for lithiation/delithiation, while CNC and GNP serve to bind LFPs and enhance conductivity, respectively. The hybrid LFP-CNC-GNP is transferred onto the CF surface using immersion coating. To evaluate the performance of these batteries, we fabricate a pouch cell setup in an argon-filled glove box environment. The LFP-CNC-GNP coated CF serves as the common counter and reference electrode, while the working electrode consists of uncoated CF, separated by twill woven glass fiber fabric. Scanning electron microscopy (SEM) images confirm the excellent dispersion of LFP-CNC-GNP on the CF surface, contributing to both the structural aspects, such as mechanical interlocking via surface roughness, and the electrochemical performance of the batteries. The electrochemical cycling experiments, employing cyclic voltammetry, reveal a specific energy density of 62.67 Wh/kg and a specific capacity of 72.7 mAh/g.

MATERIALS and METHODS

The suspension for coating of carbon fiber cathode is prepared using 10 wt % lithium iron phosphate (LFP) – cellulose nanocrystal (CNC) – graphene nanoplatelet (GNP) 7.5:0.5:2 ratio using ultrasonic treatment. LFP is carbon coated that is purchased from MTI Corporation, and GNP and CNC are provided from CheapTubes and CelluForce, respectively. The carbon fiber $(1 \times 1 \text{ cm}^2)$ is by the immersion technique. The immersion-coated carbon fibers are dried in a vacuum oven for 48 hours at 60 °C prior to cell assembly (pouch cell design) in a glove box (MBRAUN Model LABstar Pro Glovebox) with argon atmosphere (>1 ppm O₂ and >1 ppm H₂O). To ensure electrical contact, aluminum, and copper current collectors are attached to the end of the uncoated and coated carbon fiber mat, respectively, with silver paste, and then sealed inside the pouch outside of the active cell volume to ensure the electrolyte is not contaminated. A full-cell setup is fabricated with coated CF as the common counter and reference electrode and uncoated CF as the working electrode, which is separated with twill woven glass fiber fabric. Sigma Aldrich 1.0M LiPF6 in ethylene carbonate (EC): diethyl carbonate (DEC) (1:1 by weight) is used as an electrolyte with an ion conductivity of 1.12 x 10 -2 S/cm [1]. Cyclic voltammetry at different rates is carried out using a potentiostat (BioLogic Model SP-200) for 500 cycles. The cells are placed in temperature-controlled chambers at 25 ± 0.1 °C. All cycling is carried out between -1.2 V and 1.2 V vs. Li/Li+. To find the relatively suitable equivalent circuit for analyzing Electrochemical impedance spectroscopy (EIS) plots, Gamry Alchemist software is used. The fundamental of the software is based on the least square principle to acquire the minimum value of the least square coefficient between the fitting and the original data.

RESULTS AND DISCUSSION

SEM images of carbon fibers dip-coated with composition LFP-CNC-GNP 7.5:0.5:2 before and after cycling are presented in Figure 1. Well-dispersed sub-micrometer-sized LFP particles can be seen throughout the coating. Homogeneous LFP-CNC-GNP dispersion indicates well adhesion between the nanomaterials and carbon fiber surface (Figures 1 a and 1 b). No apparent difference is seen before and after electrochemical cycling (Figure 1 a-d), which suggests that the adhesion of the coating to the carbon fibers is sufficiently high even when inserting/extracting lithium in the LFP. One drawback of electrochemical cycling on carbon fiber unidirectional fabric is that cycling results in changing the fiber orientation. Compared to the morphology in pre-cycled carbon fiber fabric presented in Figure 1 a, which is unidirectional, a bundle of fibers oriented about $\pm 20-30^{\circ}$. This might affect the mechanical performance since the fiber direction becomes uneven and randomly oriented. However, a thin, even coating can compensate for the trade-off caused by the misorientation of fibers. As a result, a thin and even coating of LFP-CNC-GNP guarantees consistent interfacial properties between the coated carbon fibers and the polymer matrix due to the presence of stiff GNPs and polar groups containing CNCs [5] once combined with solid-state polymer electrolyte.

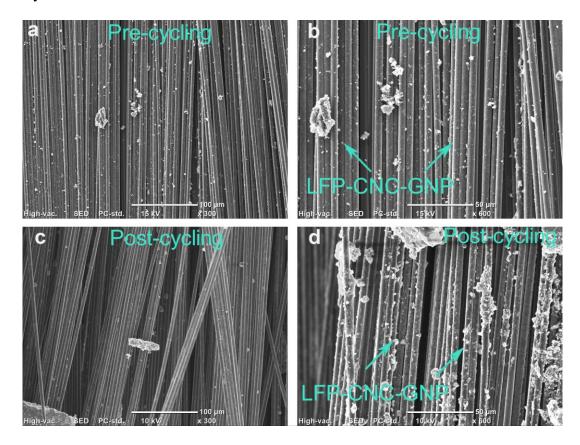


Figure 2 and Table I present the EDS map of a carbon fiber coated with LFP-CNC-GNP with the composition 7.5:0.5:2. The phosphor (P) and iron (Fe) EDS map for both preand post-cycling pf carbon fibers indicates a homogenous distribution of LFP across the coating. The oxygen (O), stemming from both CNC and LFP, is mainly present around the particles, which is expected for a binder. The distribution of GNP was not able to be determined because of the overlapping signal from the carbon fiber substrate. According to Table I, the mass percent of C reduces from 90.12 % to 75.19 % whereas that of O increases from 6.75 % to 21.01 % in pre-cycled and post-cycled CF, respectively. This indicates that Li ions traveling between neat carbon fiber (e.g., anode) and LFP-CNC-GNP coated carbon fiber (e.g., cathode) encounters reacts with surface contamination of either electrode and creates Li-metal oxide compounds, which result in an increase in O mass percent on the cathode electrode.

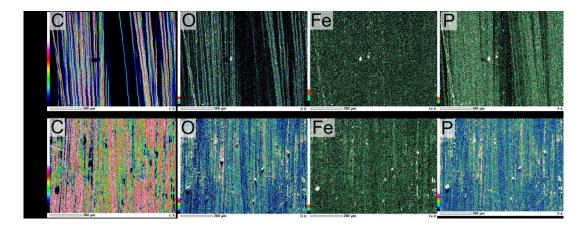


Figure 2. EDS Maps of pre-cycled and post-cycled LFP-CNC-GNP coated carbon fibers

TABLE I. EDS ELEMENTAL QUANTITATIVE ANALYSIS of PRE- and POST-CYCLED CARBON FIBERS

Elements	Pre-cycled CFs	Post-cycled CFs
	Mass (%)	Mass (%)
C	90.12	75.19
0	6.75	21.01
Fe	0.59	1.72
P	2.34	2.07

The battery's recharging performance, as determined by cyclic voltammetry analysis, shows stability over 200 cycles. From 5th cycle onwards, the battery exhibits a stable behavior with an energy density of 62.67 Wh/kg, power density of 122.38 W/kg, and specific capacitance of 72.7 mAh/g, as summarized in Table II. However, as the battery reaches the 200th cycle, it starts to face challenges in maintaining its energy and power density. This decline in performance can be attributed to the generation of Li-metal

oxide compounds during the electrochemical cycling process, as indicated by the EDS quantitative analysis. The formation of Li-metal oxide compounds is likely a result of side reactions or degradation processes occurring within the battery during cycling. These compounds have an impact on the battery's overall performance, leading to a gradual decrease in energy and power density over time. Possible strategies to mitigate the formation of Li-metal oxide compounds and improve the battery's long-term stability and performance could include modifying the electrolyte composition, enhancing electrode materials, or adjusting cycling protocols.

TABLE II. ELECTROCHEMICAL PERFORMANCE OF LFP-CNC-GNP COATED CARBON FIBERS UP TO 200 CYCLES BY CYCLIC VOLTAMMETRY

Energy Density	Power Density	Capacitance
Wh/kg	W/kg	mAh/g
62.67	122.38	72.7

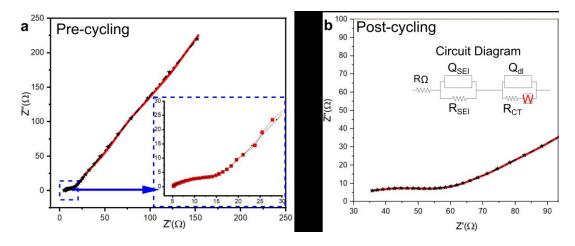


Figure 3. EIS characteristics (Nyquist plots with real (Z') and imaginary (Z")) (a) pre-cycling and (b) post-cycling LFP-CNC-GNP coated carbon fibers with the fitted circuit diagram.

Electrochemical Impedance Spectroscopy (EIS) is a useful tool to characterize the electrolyte and the electrode/electrolyte interface. Herein, applying a small oscillating signal, e.g., a sine wave, to a system while keeping the potential or current controlled, allows measuring the impedance. EIS can be interpreted in terms of electrical components such as resistors, capacitors, and inductors, and most of the time, a combination of these elements represents the complex processes occurring in the system. Figures 3 a and 3 b show the Nyquist plot along with the fitting curve according to the equivalent circuit (shown in Figure 3b). The intercept at the real axis (Z') in high frequency corresponds to the resistance of the electrolyte. The semicircle in the high-middle frequency corresponds to the charge transfer resistance (R_{CT}). The inclined line at the low frequency represents the Warburg impedance (W), which is attributed to the diffusion of Li+. In addition, the Warburg diffusion element (e.g., W) is used to quantify any diffusion processes that might be occurring in the system using elements representing semi-infinite linear and finite-length diffusion processes.

Table III shows the values of parameters obtained from circuit fitting before and after cycling the battery using EIS measurements that were carried out to understand the transport properties of LFP-CNC-GNP coated carbon fiber and neat carbon fiber battery. The EIS spectra (Nyquist plot) with equivalent circuit diagrams as shown in Figures 3 a and 3 b for pre- and post-cycling, respectively. The circuit diagram (in the set of Figure 3b) represents the series resistance, which includes the resistance of coated and neat carbon fiber counter electrodes. R is the charge-transfer resistance at the LFP/carbon interface and R_{CT} is the charge-transfer resistance at the interface. Both electrolyte and interface (e.g., $R\Omega$ and R_{SEI}) increase with cycling as reported in Table III. It can be interpreted from Figure 3a that the large parabola in the high-frequency region indicates higher transportation and exchange resistance from the LFP to the carbon counter electrode. On the other hand, the smaller parabola reflects lower transportation resistance (e.g., R_{CT}) due to the improved kinetics of charge transfer during cycling. Warburg diffusion element (e.g., W) shows that Li-ion transfer slightly reduces with electrochemical cycling. Overall, the electrochemical results indicate that although the battery performance is slightly affected by cycling, the LFP-CNC-GNP coated carbon fiber and neat carbon fiber battery are efficient for over 200 cycles.

TABLE III. EIS MEASUREMENT OF PRE-CYCLING AND POST-CYCLING LFP-CNC-GNP COATED CARBON FIBERS WITH THE FITTED CIRCUIT DIAGRAM

	Pre-cycled CFs	Post-cycled CFs
$\mathbf{R}\Omega\left(\mathbf{\Omega}\right)$	5.00	23.18
$R_{SEI}(\Omega)$	10.8	34.25
$R_{CT}(\Omega)$	21.18	3.28
$W(S.s^{1/2})$	$4.05\ 10^{-3}$	7.85 10 ⁻²

CONCLUSION

This study explores the scalable and safe fabrication of structural battery composites composed of water-based LFP-CNC-GNP-coated carbon fibers as the cathode and neat desized carbon fiber fabric as the anode. The SEM morphology characterization reveals two important findings: (i) LFP-CNC-GNP adheres well to the carbon fiber, and (ii) the morphology of the coated carbon fiber fabric remains unchanged during electrochemical cycling. Additionally, EDS analysis confirms the homogeneous dispersion of LFP-CNC-GNP on the carbon fiber fabric. The batteries developed in this research exhibit a specific energy density of 62.67 Wh/kg and a specific capacity of 72.7 mAh/g. Furthermore, cyclic voltammetry experiments demonstrate that the LFP-CNC-GNP-coated carbon fiber batteries maintain stability over 200 cycles without degradation. According to EIS characterization, electrochemical cycling leads to an increase in electrolyte and interface resistivity; nevertheless, the battery performs efficiently throughout the 200 cycles. This research paves the way for engineering hybrid nanostructured battery laminates using innovative water-based coated carbon fibers, thereby opening up new possibilities for the development of advanced lithium-ion structural batteries.

REFERENCES

- Hagberg, J., Maples, H. A., Alvim, K. S., Xu, J., Johannisson, W., Bismarck, A., ... & Lindbergh, G. (2018). Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries. Composites Science and Technology, 162, 235-243.
- 2. Xu, J., Geng, Z., Johansen, M., Carlstedt, D., Duan, S., Thiringer, T., ... & Asp, L. E. (2022). A multicell structural battery composite laminate. EcoMat, 4(3), e12180.
- Sanchez, J. S., Xu, J., Xia, Z., Sun, J., Asp, L. E., & Palermo, V. (2021). Electrophoretic coating of LiFePO4/Graphene oxide on carbon fibers as cathode electrodes for structural lithium ion batteries. Composites Science and Technology, 208, 108768.
- 4. Berhaut, C. L., Lemordant, D., Porion, P., Timperman, L., Schmidt, G., & Anouti, M. (2019). Ionic association analysis of LiTDI, LiFSI and LiPF 6 in EC/DMC for better Li-ion battery performances. RSC advances, 9(8), 4599-4608.
- Kaynan, O., Hosseini, E., Zakertabrizi, M., De Castro, E. M., Pérez, L. M., Jarrahbashi, D., & Asadi, A. (2023). Multifunctionality Through Embedding Patterned Nanostructures in High-Performance Composites. Advanced Materials, 2300948.