

Scalable fabrication of carbon fiber-based cathode with networked heterostructures for structural energy storage composites

Hamed Fallahi¹, Ayush Raj², Farshad Bozorgmehrian³, Homero Castaneda^{2*}, Amir Asadi^{1,2,3*}

¹ Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, USA

² Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77843-3367, United States

³ Department of Engineering Technology and Industrial Distribution, Texas A&M University, College Station, Texas 77843-3367, United States
amir.asadi@tamu.edu
hcastaneda@tamu.edu

Abstract. Carbon fibers, with their exceptional properties, are appealing to explore storage of electrical energy within fiber-reinforced composites. By activating carbon fibers, structural cathodes can be fabricated, which integrate mechanical strength with energy storage capabilities. This study describes a method to graft commercial carbon fibers with assemblies of lithium iron phosphate (LFP) acting as the cathode active material, functionalized carbon nanotubes as conductive network, and polyvinylpyrrolidone (PVP) as the binder agent. Favorable interactions of these particles in the Dimethylformamide (DMF) solvent enable formation of dispersed sub-micron structures in the solution. A uniform, macroscale coating on carbon fibers was achieved with electrophoretic deposition (EPD). Several coating morphologies were investigated to understand trade-offs associated with system properties. It is shown that CNTs can effectively interconnect active materials and carbon fiber both electronically and mechanically. Electrochemical results show promising performance, with reversible capacities of 101 mAh/g after 50 cycles. The excellent rate and cycle performance of cells in multiple C-rates can be attributed to the proposed cathode architecture influenced by small wt% CNT networks. Results indicate positive synergistic effects present in the proposed methodology that enables scalable fabrication of structural cathodes, alongside the flexibility of tuning the morphological characteristics.

Keywords: Structural batteries, Carbon fibers, Composites.

1 Introduction

Structural energy storage has increasingly gained attention over the past years due to demand for lightweight and multifunctional materials in various high-performance applications, which involve bearing mechanical load and storing energy at the same time.

Early attempts in this field simply encapsulated battery pouch cells into the composite layup, however, this approach does not present any gravimetric advantage for the system compared to externally connected batteries, and in fact, results in mechanical disadvantages.

Carbon fibers with their exceptional mechanical, thermal properties and high electrical conductivity present a compelling opportunity to develop this class of multifunctional materials. In fiber-reinforced composites, besides bearing mechanical loads, carbon fibers can serve as active components to store energy. In such a laminated battery architecture, two distinct layers of carbon fibers are used as the cathode and the anode, with an electrolyte in between. Research indicates that carbon fibers can reversibly accommodate lithium ions, achieving capacities up to 350 mAh/g [1], which makes them suitable anodes. However, developing functional cathodes with acceptable capacity is a challenge, as active cathode materials are required to be integrated onto the carbon fibers. Among commercially available lithium sources, including LiCoO_2 and LiMn_2O_4 , lithium iron phosphate (LFP) stands as the prime candidate due to its good theoretical specific capacity and high thermal, chemical, and mechanical stability [2]. Developing next generation cathodes with effective functionality relies on manufacturing capabilities. Several methods have been developed to deposit thin-film cathodes on a variety of substrates including chemical vapor deposition (CVD) [3], electrophoretic deposition (EPD) [4], and atomic layer deposition (ALD) [5]. EPD method could be considered a promising technique to create single-phase thin-film electrodes due to its simplicity, scalability, and efficiency [6]. This method relies on migration of charged particles within a stable colloidal solution towards a conductive substrate under an electric field.

In this study, we developed structural electrodes by depositing heterostructures of lithium iron phosphate (LFP) acting as the cathode active material, functionalized carbon nanotubes as conductive agent, and polyvinylpyrrolidone (PVP) as the binder agent on the carbon fiber. Electrostatic assembly was achieved by probe ultrasonic treatment of components in a solution of Dimethylformamide (DMF), which was used for EPD deposition on the carbon fibers. The quality and morphology of the coatings were studied using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), verifying uniform, conformable, and individual coating of carbon fibers. Coin cells were assembled in a controlled glove box environment with carbon fiber cathodes, lithium hexafluorophosphate as electrolyte, Li chip anodes and microporous polymer separators. Electrochemical results showed a reversible capacity as high as 101 mAh/g after 50 cycles. The remarkable rate and cycle performance at multiple C-rates is ascribed to the proposed cathode structure, which benefits from the small wt% CNT network.

2 Materials and Methods

LiFePO₄ (LFP, Primet Corporation), functionalized carbon nanotubes (fCNT, NanoLab Corporation), and polyvinylpyrrolidone (PVP, Sigma-Aldrich) were dispersed in a dimethylformamide (DMF) solution with a weight ratio of 90:04:06, respectively. Initially, LFP and PVP were ultrasonicated for 2 hours, followed by addition of fCNT and an additional hour of ultrasonication. Carbon fibers were desized by refluxing in acetone for 4 hours to remove surface sizing agents. Subsequently, the fibers were dried in an oven at 80 °C for 12 hours. Materials dispersed in the DMF solution were deposited on the carbon fibers using a two-electrode EPD method, in which carbon fiber acted as the working electrode, with a stainless-steel counter-electrode. The distance between electrodes was fixed at 2 cm, allowing the particles to travel a short distance. The deposition process was carried out at constant voltages between 20 and 80 V for a duration of 2 to 5 minutes at room temperature. The coated fibers were dried in a vacuum oven for 15 hours at 60 °C and were stored in a vacuum chamber.

The electrochemical properties of the LFP-CNT-PVP coating on carbon fiber composite were characterized by using CR2032 coin-type cell with Li chip as a counter electrode. The liquid electrolyte was 1.0M LiPF₆ in the mixture of 1:1 (by volume) Ethylene carbonate and diethyl carbonate (Sigma-Aldrich). Galvanostatic charging/discharging cycles were tested between 2.0 and 4.5 V vs. Li⁺/Li at different rates on a potentiostat (Biologic SP-200). Cyclic Voltammetry (CV) was conducted at a scanning rate of 0.1 mV/s between 2.0 and 4.5 V vs. Li⁺/Li (Interface 1010E, GAMRY Instruments). The electrochemical impedance spectroscopy (EIS) of the batteries was performed in the frequency range from 10000 Hz to 0.01 Hz under an alternating current (AC) with a 10-mV amplitude (Interface 1010E, GAMRY Instruments). The impedance data were fitted using the GAMRY Echem Analyst program.

3 Results and Discussion

Fig. 1 presents morphology and distribution of the LFP-CNT-PVP cathode coatings on the carbon fibers at different magnifications. It is observed that the proposed method can yield a 3D coating on the carbon fibers with a uniform distribution of active materials without agglomeration, which will enable a consistent capacity utilization of the cathode (Fig. 1a-b). Figure 1c shows a close-up view of the deposited heterostructures, in which the intricate network of CNTs is interspersed within the LFP particles. It is shown that the interconnected CNT network bridges LFP particles to each other and to the carbon fiber, making a conductive network that can reduce the internal ohmic resistance of the cathode. The resulting porous nano/microstructure facilitates fast and easy ion transport, which is essential for high-rate performance [7]. Moreover, the increased surface area of the electrode and the electrolyte will enhance kinetics of electrochemical reactions and double-layer capacitance.

Carbon fiber cathodes were investigated after 50 electrochemical cycles to examine their durability (Fig. 1d-e). No significant morphological changes or cathode detachment were observed, indicating that PVP binder established strong adhesion between

the components. Additionally, the carboxyl groups on the CNTs are expected to contribute by providing additional anchoring sites for the LFP, PVP, and carbon fibers. High mechanical integrity of the cathode is essential in the face of challenges such as volume change of active materials, unstable and irreversible phase transformations, and side reactions during the electrochemical processes.

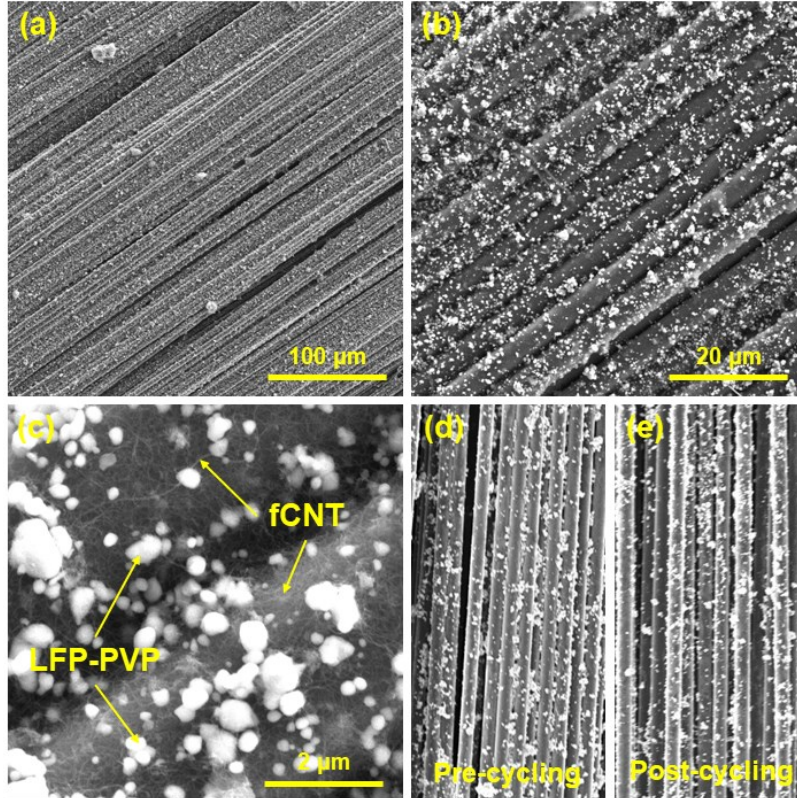


Fig. 1. (a-b) Low magnification SEM images of coated carbon fibers, illustrating the overall coating uniformity. (c) Close-up SEM image highlighting the networked LFP-PVP-CNT heterostructure. (d-e) SEM images of carbon fibers before and after 50 electrochemical cycling.

The EDS maps in Fig. 2 show the distribution of iron, phosphorus, and oxygen within the cathodes before and after cycling. The phosphorus (P) and iron (Fe) EDS maps of carbon fibers indicate consistent distribution of LFP particles before and after cycling, and efficiency of binding agents in the material system. The observed increase in oxygen level (Table 1) after cycling is related to the formation of solid electrolyte interphase (SEI) layer, which contains oxygen-rich compounds [8]. Additionally, it was shown that decomposition of LiPF_6 electrolyte during cycling can generate oxygen-containing species that further contributes to the observed increase [9]. However, given

that there is no noticeable loss in cathode capacity after cycling, the rise in oxygen content is less likely to be a result of adverse reactions with LFP or its oxidation.

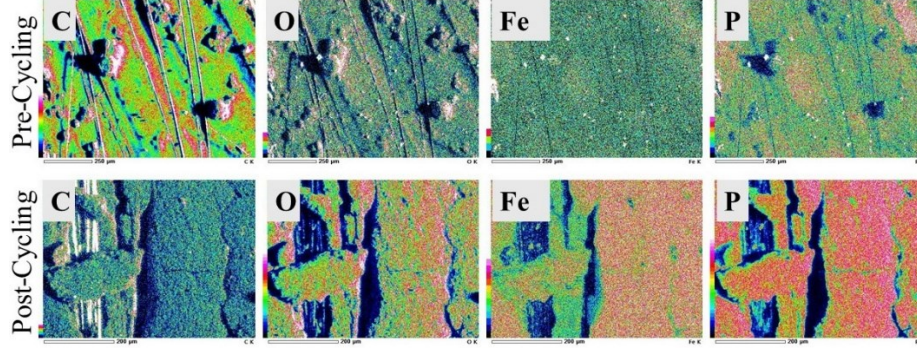


Fig. 2. EDS Maps of pre-cycled and post-cycled LFP-CNT-PVP coated carbon fibers.

Table 1. EDS elemental quantitative analysis of Pre- and Post-cycled carbon fibers.

| Elements | Pre-cycled CFs Mass (%) | Post-cycled CFs Mass (%) |
|----------|----------------------------|-----------------------------|
| C | 65.31 | 56.56 |
| O | 21.41 | 32.65 |
| Fe | 32.43 | 29.45 |
| P | 4.35 | 7.29 |

The battery's charging and discharging performance, as determined by galvanostatic charging and discharging, shows stability over 50 cycles. To evaluate the rate capability of the structural batteries, we tested 50 cycles at C/20 rate and 10 cycles at C/10 rate as shown in Fig. 3. Overall, the maximum capacity obtained was 101 mAh/g with an average capacity retention of 98%. The initial irreversible capacity arises from multiple factors, such as SEI layer formation, electrolyte decomposition, loss of electrical contact, lithium trapping, and phase changes. The newly formed resistive SEI layer adds an impedance to the battery. Irreversible capacity and the nature of the SEI layer have been shown to be strongly dependent on the cycling conditions [10].

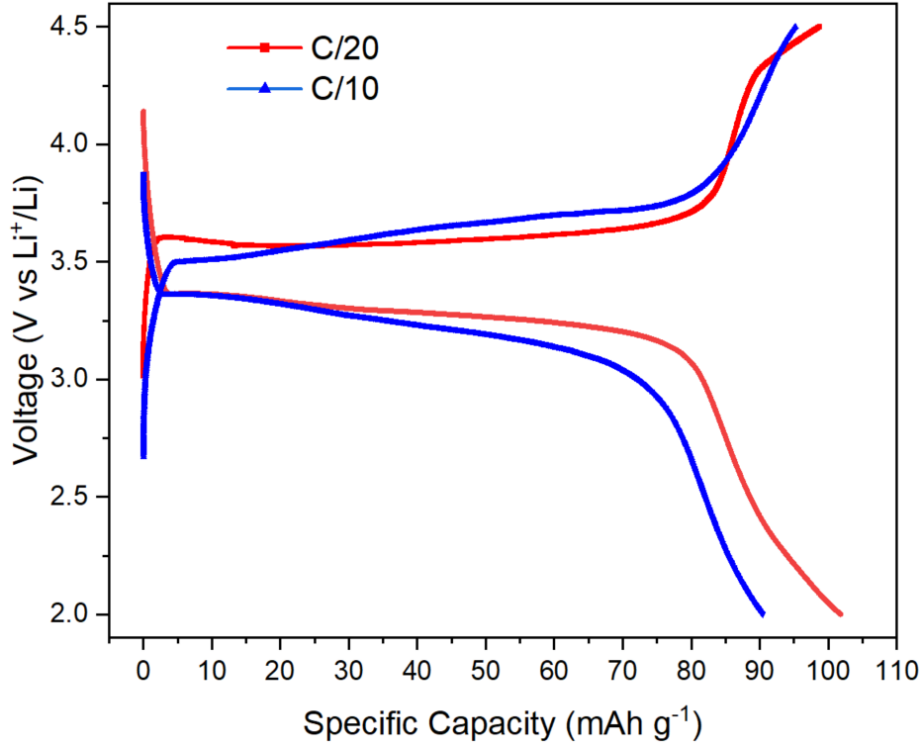


Fig. 3. First Charging and discharging profiles at C/20 and C/10 rate.

Figure 4. shows the cyclic voltammetry results of the LFP-CNT-PVP coated carbon fibers at a scan rate of 0.1 mV/s. The two-electrode system shows typical distinct oxidation/reduction peaks during the anodic/cathodic scan, corresponding to the reversible redox reaction between the $\text{Fe}^{2+}/\text{Fe}^{3+}$ in LFP particles. Nevertheless, their shape, the potential intervals between the two redox peaks, and current density of peak are different. The presence of high asymmetric peaks within a small potential window shows the low polarization and high reversibility of the samples.

The reduction in current peaks is associated with a decrease in the number of electrons associated with redox process over the subsequent cycles, which is often attributed to a decrease in the electroactive surface area. The surface area decreases, and fewer electrons are needed to accommodate the redox activity of active electrode materials. This behavior is consistent with the charge/discharge profiles, wherein also there is a loss of capacity after the first charge and discharge cycle since the electroactive surface area decreases.

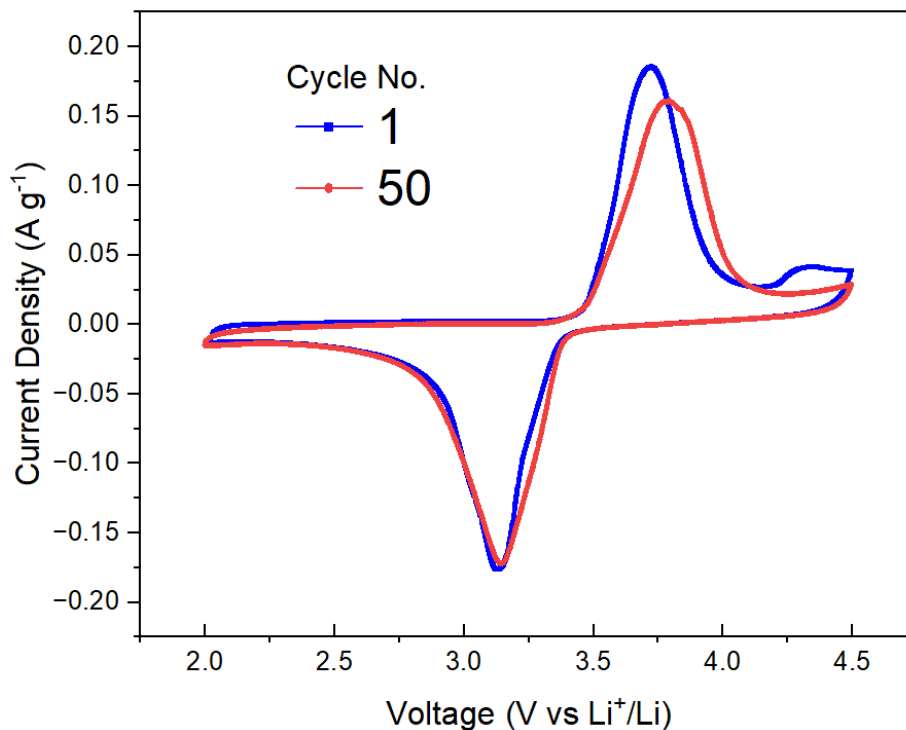


Fig. 4. Cyclic voltammetry at scan rate of 0.1 mV/s

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. Fig. 5. Shows the Nyquist plot for pre and post cycling after 50 cycles of CV at 0.1 mV/s scan rate). 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 (RCT). 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 2 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-CNT-PVP coated carbon fiber and neat carbon fiber battery. The EIS spectra (Nyquist plot) with equivalent circuit diagrams as shown in Figures 5 for pre- and post-cycling, respectively. The circuit diagram (in the set of Figure 5) represents the series resistance, which includes the resistance of coated and neat

carbon fiber counter electrodes. R_{Ω} is the electron-transfer resistance at the interface, and R_{CT} is the charge-transfer resistance at the interface. It is shown that although the resistance of the SEI layer, R_{SEI} , increases after cycling, R_{Ω} and R_{SEI} decrease over cycles. This is evident in Fig. 5, where the radius of the parabola gets smaller after cycling. 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 increases with electrochemical cycling. Overall, the electrochemical results indicate that although the battery performance is slightly affected by cycling, the LFP-CNT-PVP coated carbon fiber and neat carbon fiber battery are efficient for over 50 cycles.

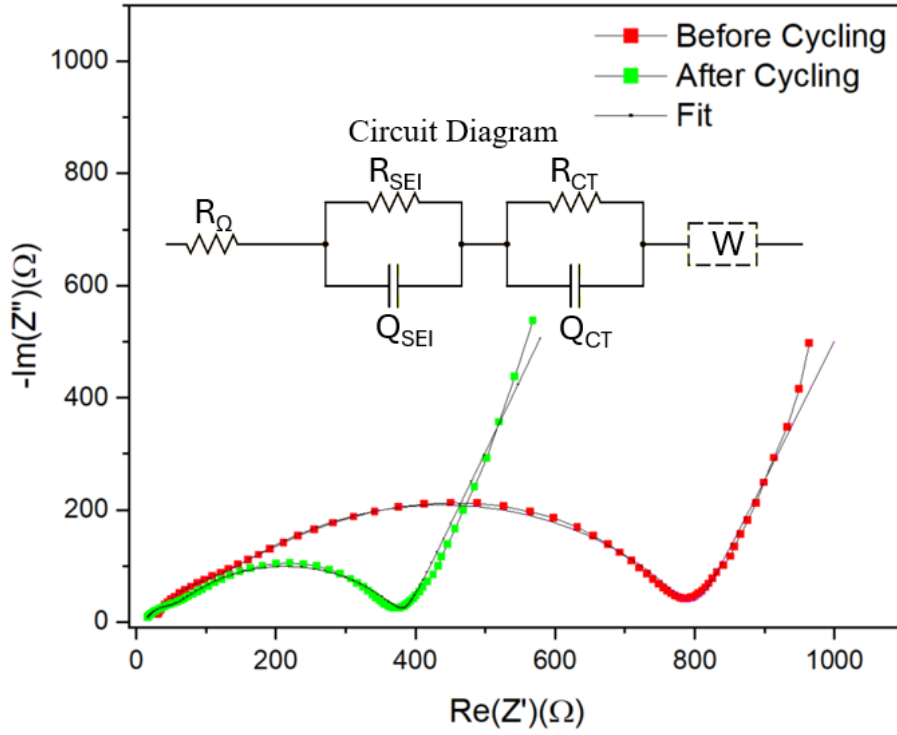


Figure 5. EIS characteristics (Nyquist plots with real (Z') and imaginary (Z''))

Table 2. EIS measurement of pre-cycling and post-cycling LFP-CNT-PVP coated carbon fibers with the fitted circuit diagram.

| | Pre-cycled CFs | Post-cycled CFs |
|---------------------------|----------------|-----------------|
| R_{Ω} (Ω) | 16.24 | 7.528 |
| R_{SEI} (Ω) | 15.6 | 41.27 |
| R_{CT} (Ω) | 31.24 | 6.98 |
| W ($S.s^{1/2}$) | 1.074E-03 | 2.825E-03 |

4 Conclusion

In this study, we demonstrate a scalable method for fabricating networked LFP/CNT/PVP heterostructures on carbon fibers, aimed at developing structural cathodes for energy storage in fiber-reinforced composites. The proposed material system and electrophoretic process enable an efficient way of electrochemically activating carbon fibers. Results indicate that 3wt% addition of functionalized carbon nanotubes enhances cathode's electrical, mechanical, and electrochemical characteristics. The coated nano/microstructures retained their structural cohesion through 50 charge-discharge cycles. In the proposed material ratio, Binding sites on the CNT do not show to impede Li ion kinetics during charge-discharge. PVP exhibits positive interactions with CNTs, potentially improving CNT dispersion in the cathode, and promoting CNT-LFP binding. Batteries developed in this work have yielded a stable capacity of 101 mAh/g measured over 50 cycles. The carbon fiber cathode response was shown to be influenced by SEI formation. The ability to achieve a uniform and conformal coating with desirable mechanical and electrochemical properties highlights the potential for large-scale production of cathodes and their integration into multifunctional composite materials for structural energy storage.

5 Acknowledgments

This material is based upon work supported by the National Science Foundation under Grants #1930277 and #2143286. Use of the Texas A&M University Soft Matter Facility (RRID:SCR_022482) is acknowledged.

Reference

1. Sanchez JS, Xu J, Xia Z, Sun J, Asp LE, Palermo V. Electrophoretic coating of LiFePO₄/Graphene oxide on carbon fibers as cathode electrodes for structural lithium ion batteries. *Compos Sci Technol* 2021;208:108768. <https://doi.org/https://doi.org/10.1016/j.compscitech.2021.108768>.
2. Berhaut CL, Lemordant D, Porion P, Timperman L, Schmidt G, Anouti M. Ionic association analysis of LiTfD, LiFSI and LiPF₆ in EC/DMC for better Li-ion battery performances. *RSC Adv* 2019;9:4599–608. <https://doi.org/10.1039/C8RA08430K>.
3. Hou Q, Cao G, Wang P, Zhao D, Cui X, Li S, et al. Carbon coating nanostructured-LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode material synthesized by chemical vapor deposition method for high performance lithium-ion batteries. *J Alloys Compd* 2018;747:796–802. <https://doi.org/https://doi.org/10.1016/j.jallcom.2018.03.115>.
4. Moyer K, Carter R, Hanken T, Douglas A, Oakes L, Pint CL. Electrophoretic deposition of LiFePO₄ onto 3-D current collectors for high areal loading battery cathodes. *Mater Sci Eng B* 2019;241:42–7. <https://doi.org/https://doi.org/10.1016/j.mseb.2019.02.003>.
5. Xie J, Sendek AD, Cubuk ED, Zhang X, Lu Z, Gong Y, et al. Atomic Layer Deposition of Stable LiAlF₄ Lithium Ion Conductive Interfacial Layer for Stable Cathode Cycling. *ACS Nano* 2017;11:7019–27. <https://doi.org/10.1021/acsnano.7b02561>.
6. Chakrabarti BK, Gençten M, Bree G, Dao AH, Mandler D, Low CTJ. Modern practices in electrophoretic deposition to manufacture energy storage electrodes. *Int J Energy Res* 2022;46:13205–50. <https://doi.org/https://doi.org/10.1002/er.8103>.
7. Zhu P, Slater PR, Kendrick E. Insights into architecture, design and manufacture of electrodes for lithium-ion batteries. *Mater Des* 2022;223:111208. <https://doi.org/https://doi.org/10.1016/j.matdes.2022.111208>.
8. Cherkashinin G, Nikolowski K, Ehrenberg H, Jacke S, Dimesso L, Jaegermann W. The stability of the SEI layer, surface composition and the oxidation state of transition metals at the electrolyte–cathode interface impacted by the electrochemical cycling: X-ray photoelectron spectroscopy investigation. *Phys Chem Chem Phys* 2012;14:12321–31. <https://doi.org/10.1039/C2CP41134B>.
9. Xiang HF, Wang H, Chen CH, Ge XW, Guo S, Sun JH, et al. Thermal stability of LiPF₆-based electrolyte and effect of contact with various delithiated cathodes of Li-ion batteries. *J Power Sources* 2009;191:575–81. <https://doi.org/https://doi.org/10.1016/j.jpowsour.2009.02.045>.
10. Snyder JF, Wong EL, Hubbard CW. Evaluation of Commercially Available Carbon Fibers, Fabrics, and Papers for Potential Use in Multifunctional Energy Storage Applications. *J Electrochem Soc* 2009;156:A215. <https://doi.org/10.1149/1.3065070>.