



**CHALMERS**  
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# **Green synthesis of LiFePO<sub>4</sub>/graphene coated Carbon Fiber cathodes for high performance structural batteries**

Master's thesis in Materials Engineering

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**DEPARTMENT OF INDUSTRIAL AND MATERIALS SCIENCE**

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CHALMERS UNIVERSITY OF TECHNOLOGY  
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MASTER'S THESIS 2022

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Cover: SEM images of carbon fiber sample coated with active material.

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## Abstract

Carbon fibers (CF), also known as graphite fibers, can be used as multifunctional conductive electrodes in "structural batteries" that simultaneously store electrical energy and carry mechanical loads without additional current collectors. However, there are several challenges in the commercialization of structural batteries. For example, CF-based cathode composites usually suffer from their low energy capacity due to the poor adhesion of active materials on CF surface, and the current fabrication techniques (such as blade coating or spray coating) need to use toxic organic solvents such as N-methyl pyrrolidone (NMP).

In this thesis, we report a green approach that utilizes electrophoretic deposition (EPD) to fabricate novel cathode composites consisting of lithium iron phosphate ( $\text{LiFePO}_4$ ) and graphene nanosheets. Ethanol was used as a green solvent to replace NMP. Meanwhile, Different commercial graphene materials, including 3 kinds of graphene nanoplatelets, 4 kinds of reduced graphene oxide were tested and systematically compared with our homemade graphene. Most of the graphene additives can significantly improve our structural battery performance, with the highest specific capacity of 125 mAhg<sup>-1</sup> and over 80% retention at 2C over 500 cycles. Morphological and structural analyses were conducted by scanning electron microscopy (SEM) and Raman spectroscopy to further understand how the surface and quality of different kinds of graphene can impact the relative battery performance.

Keywords: Green, Structural battery, Graphene, Electrophoretic deposition.



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Zhaoyang Li, Gothenburg, June 2022



# List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

LIB	Lithium Ion Battery
SB	Structural Battery
SBE	Structural Battery Electrolyte
CF	Carbon fiber
EPD	Electrophoretic deposition
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectroscopy
CV	Cyclic voltammetry test
GCD	Galvanic charge and discharge test



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# 1

## Introduction

Introductory chapter to the thesis project of *Green synthesis of LiFePO<sub>4</sub>/graphene coated Carbon Fiber cathodes for high performance structural batteries*. In this chapter, the concise background, main aims and limits of this project are stated.

### 1.1 Background

#### 1.1.1 Lithium ion batteries

With the increasingly serious energy crisis and environmental pollution, the development of new energy storage devices has received extensive attention. Among which, rechargeable batteries, as electrochemical energy storage and conversion devices, could alleviate the environmental pollution caused by traditional energy sources such as coal and fossil fuels and reduce carbon footprint.[1] Lithium-ion battery (LIB) is considered to be one of the most successful rechargeable batteries in the world. After almost 50 years development, LIB has become an indispensable part of our daily life.[2] High-performance LIB can meet the needs of portable electronic devices, such as mobile phones, laptops and electronic wearable devices. Besides that, the huge demand of LIB for electric vehicles, which could provide high energy capacity and long lifetime with zero-emission, is playing an important role in the automotive market.

LIB usually consists of the four key components: positive electrode, negative electrode, electrolyte, and separator. The electrochemical performance of LIB largely depends on the active materials of the electrodes. The active material of the electrode undergoes a redox reaction during the cycle. The electrochemical performance of LIB largely depends on the active materials of the electrodes.[3]

In a LIB device, a potential difference exists between the two electrodes, so that electrons flow and current is generated. The electrons transferring is not completed by the effective collision between the oxidant and the reducing agent, while the reducing agent loses electrons on the negative electrode and undergoes an oxidation reaction.

At present, commercial LIB anode materials are mainly carbon-based, including artificial, natural and composite materials. The principle of graphite as a negative electrode is that Lithium ion (Li<sup>+</sup>) is reversibly inserted and extracted between the graphite hexa-atom carbon layers to form a LiC<sub>6</sub> structure for lithium storage, and its theoretical specific capacity is 372 mAh/g.[4]

However, graphite based LIB anodes suffer from its low mechanical properties, which

cannot function as support structures while maintaining high capacity.

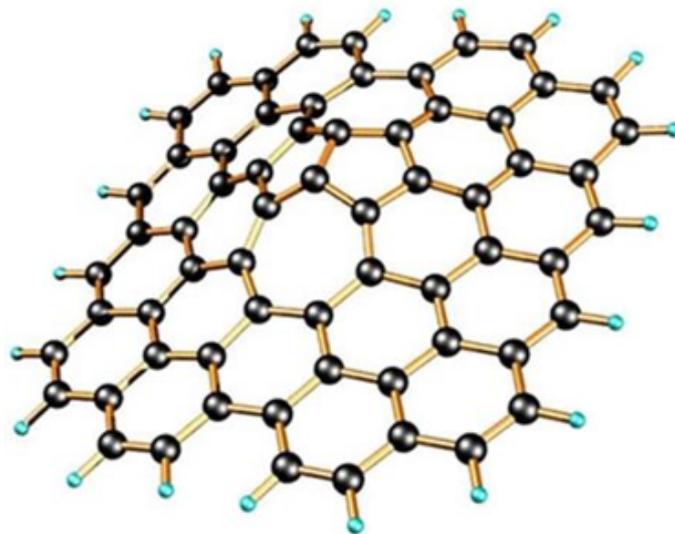
The cathode material largely affects the capacity, thermal stability, and cycle efficiency of LIB. It is the main lithium ion donor in the system and determines the LIB capacity. A cathode material with good performance needs to have the following characteristics: (1) high oxidation potential and large voltage window as possible; (2) as much  $\text{Li}^+$  can be reversibly inserted/extracted, and the structure remains good after multiple charge-discharge cycles; (3) low synthesis cost and easy processing.[5]

Among them,  $\text{LiFePO}_4$  (LFP) has a theoretical capacity of 175 mAh/g. Compared with other cathode materials, LFP, as iron-based compound is the most environmentally friendly, inexpensive and abundant in cathodes applications.[6] However, LFP itself has poor electronic conductivity which need to be solved by the conductive additives.

Commercial LIB battery electrolytes are all composed of organic solvents and lithium salts. The most commonly used electrolytes are organic alkyl carbonates and their mixtures. These liquid electrolyte cannot bear the mechanical load, and therefore cannot be a stressed component.

### 1.1.2 Graphene based 2D materials

Graphene is a two-dimensional (2D) nanomaterial that is made up of carbon atoms with a unique honeycomb structure similar to benzene rings, which has a large number of freely active electron clouds in the vertical direction of the two-dimensional plane, mainly the electron clouds of p electron orbitals. At the same time, its ultra-stable structure makes the transmission of electrons smooth and unimpeded, and it is hardly hindered and collided by atomic nuclei, which also makes its electrical conductivity much higher than that of traditional metals such as copper, iron, and aluminum.[7] It also has other attractive physical and chemical properties such as high surface area, high thermal conductivity, ultra lightweight, and excellent mechanical performance.

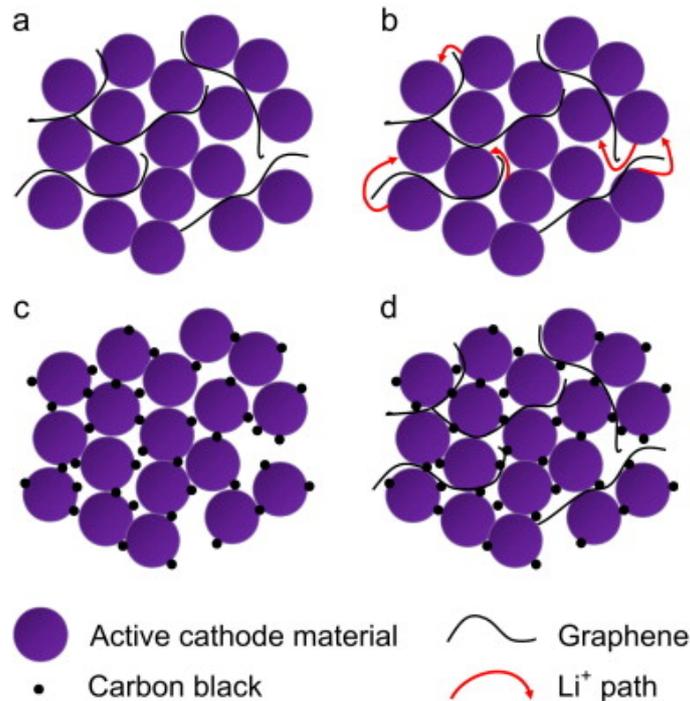


**Figure 1.1:** Schematic graph of graphene

Dependent on the synthesis approaches, graphene based 2D materials, especially the ones exfoliated from bulk graphite, can be named as graphene oxides (GO), reduced graphene oxide (rGO), and graphene nanoplatelets (GNP). In case of GO production, bulk graphite powder or flakes are oxidized into graphite oxide, in which a large number of oxygen-containing functional groups are attached to the graphite surface, and then the oxidized graphite sheets are mechanically exfoliated into atomic-layer-thick GO nanosheets. Subsequently, rGO is the reduction product of GO, which has a similar structure except that the oxygen-containing groups are reduced.

A large number of oxygen-containing functional groups, such as  $-\text{COOH}-$ ,  $-\text{OH}-$ ,  $-\text{O}-$ , etc., are grafted on the edge of the GO honeycomb structure. As a result, although rGO reduces some of the groups, it usually contains residual oxygen and other heteroatoms, as well as structural defects, and the quality is lower than that of pristine graphene produced directly from graphite. On the other side, GNP produced by direct physical exfoliation such as bath sonication and mechanical shearing is a much simple process than that of GO/rGO from chemical exfoliation. It is worth noting that each manufacturer produces their graphene based materials with different processes and parameters, so the morphology and quality of their products in the final application could be quite different.[7]

Previously, graphene has been demonstrated as a conductive network in the cathode material of lithium-ion batteries.[8] At the same time, graphene can carry more active materials owing its large specific surface area. All of these increase the mobility of electrons while enhancing the capacity and excellent rate capability of the material. Due to its high electronic conductivity and large specific surface area, graphene seems to be one of the best candidates to be used as conductive additives for electrode materials of lithium-ion batteries.



**Figure 1.2:** The role of Graphene in Cathode materials of lithium-ion batteries

### 1.1.3 Structural battery

The growing demand for high-capacity, high-stiffness batteries in aviation, automotive and other fields has profoundly affected the development of batteries. Researchers want to look for batteries that can carry mechanical loads and store electrical energy at the same time. One approach is to abandon heavy battery packs and use batteries as part of the structure to reduce weight. A battery that can meet both the mechanical performance requirements and the electrochemical performance requirements has been designed, that is, the "structural battery".[9] Structural batteries (SB) are consisted with a composite architecture including cathode, anode, structural battery electrolyte and separator. The structural battery electrolyte (SBE) is a bicontinuous polymer electrolyte system, which holds promising electrochemical and mechanical properties in previous studies.[10] The negative electrode material is composed of carbon fiber, which has high electrical conductivity and high stiffness. The positive electrode usually uses carbon fiber as the scaffold, and it needs to be functionalized with active material. In this way, the carbon fiber acts as a reinforcing agent and a current collector, which should greatly improve the mechanical performance of the battery while maintaining the electrical capacity.

Active materials using in SB cathode are limited by their poor electrical conductivity. Besides, poor adhesion between these electroactive materials and the carbon fiber substrate results in battery degradation. Carbon Black, a commercial conductive material in Li-ion batteries, is usually performed as an additive for improving the interface conductivity between electrode materials and the substrates. Recently, graphene has been introduced in battery industry as both binder and conductor, due to its unique properties such as large surface area, high electrical conductivity, and high affinity for carbon-based materials.[11]

Among different kind of electrode material coating processes, electrophoretic deposition (EPD) is one of the promising low-cost and scalable techniques in industry for precise deposition. During the EPD process, charged particles will move to the target electrode surface driven by a electric field.[12] Either positive or negative composite can be assembled directly on the surface of carbon fiber.

Previously [13], researchers at Chalmers have successfully fabricated structural batteries based on graphene-LiFePO<sub>4</sub> electrodes. However, dimethylformamide (DMF) was used as a solvent in the EPD coating, this toxic substrate would bring environmental considerations despite its superior dispersion behavior. Therefore, it is crucial to replace DMF with environmental preferable solvents. Also, the universality of this method should be extended to the introduction of other graphene based 2D materials.

## 1.2 Aim

The aim of this master thesis is to find a scalable and green solution to synthesize LiFePO<sub>4</sub> (LFP)/Graphene on carbon fiber as cathodes for high performance structural batteries.

### 1.3 Approach

The objectives of the project can be roughly divided into several points.

- Electrophoretic coating of Carbon Fiber (CF) with different types of graphene
- Structural and elemental characterization of graphene materials and CF cathodes.
- Half cells assembly (in pouch cells vs Li metal in the liquid electrolyte) and electrochemical characterization.
- Evaluation of graphene quality and morphology; try to find the relationship between graphene quality and half cells electrochemical performance.

### 1.4 Limits

It is necessary to consider the electrochemical performance of using SBE as the electrolyte of the full cell, for this master thesis project. However, due to the time duration, the electrochemical performance in SBE is not involved in this project. Turning to consider the half cells electrochemical performance in liquid electrolytes. In addition, because there are many parameters that affect the results of this project, and the impact is very large, parameters (such as sample size, EPD time, solution concentration, etc.) are all set to fixed values. Therefore, the scope of this project will not focus on parameters except for the types of graphene. Meanwhile, based on the green synthesis strategy, only the absolute ethanol coating solution is considered. On this basis, the only parameter change will be determined as the reduction grade of graphene, the oxygen content. Yet, according to the actual situation, the change of surfactant type will be considered.

# 2

## Literature review and theory

### 2.1 Structural battery

Commercial lithium batteries cannot be the realistic "mass-less" energy storage device to simultaneously carry mechanical loads and store electrical energy. A lightweight multifunctional composite material is expected to realize this vision. Batteries made of this material could enable mass-less operation in vehicles. It can significantly reduce energy consumption by acting as a structural part of the vehicle while ensuring energy delivery to the vehicle. Carbon fiber (CF) plays an important role in the lightweight multifunctional composite battery of this structure. Carbon fiber has a high elastic modulus, from the point of view of mechanical properties. In terms of electrochemical performance, carbon fiber was found to have a similar crystal structure to commercial graphite electrodes[14]. Its ability to store and release lithium ions, ie, lithiation/delithiation, is similar to that of commercial graphite electrodes. Researchers [15] have explored that the electrochemical properties of several carbon fiber and found that polyacrylonitrile-(PAN-)-based carbon fibers could serve as an alternative to commercial graphite electrodes. Among them, the T800 carbon fiber reaches a capacity of 290 mAh/g at low charging rates. Kjell et al. [16] and in other tests later [9], some carbon fiber even outperformed state-of-the-art graphite battery electrodes.

The above studies proves that CF itself is a good electrode material in LIB devices. At the same time, it can also be used as a reinforcement to play the role of a load-bearing mechanical structure. Such a battery is called a Structural battery (SB). The SB should consist of a cathode, an anode, a separator, and a structural battery electrolyte. The constructed structural battery achieves excellent performance with an elastic modulus of 25 GPa in the carbon fiber direction and an energy density of 24 Wh/kg.[17]

#### 2.1.1 Electrolyte

Structural battery electrolyte (SBE) [10] is another important key for structural batteries. Its composite function requires electrolytes to balance ionic mobility and mechanical properties. This electrolyte solidifies into a bi-continuous polymer electrolyte system with a porous structure. The skeleton formed after curing can effectively improve the mechanical properties. The pores are filled with a flowing liquid electrolyte, which allows the flow of lithium ions to achieve the electrochemical performance of its ion migration.

### 2.1.2 Anodes

In the current research on structural batteries, there are many studies on carbon fiber acting as anodes. Since carbon fiber can be naturally used as anodes without any functionalization, the study of the electrochemical properties of unfunctionalized (without any potential addition from the outside) carbon fiber is the study of carbon fiber anodes. Researchers have studied carbon fiber anodes from multiple perspectives, including mechanical properties, electrochemical properties, and even piezo-electrochemical effects.[18]

### 2.1.3 Cathodes

Compared to anodes, less research has been done on cathodes due to their inherent problems. Unlike being an anode, CF needs to generate an electrical potential in the case of a cathode, which it cannot do by itself. So the CF cathode needs to be functionalized with active materials. The main way to functionalize carbon fiber is to attach a potential active cathode material, such as LFP, to the carbon fiber in some way. Hagberg et al. [11] investigated a method for fabricating structured cathodes by electrophoretic deposition (EPD) of  $\text{LiFePO}_4$  (LFP), carbon black, and polyvinylidene fluoride (PVDF) onto carbon fiber. Electrochemical characterization shows that the specific capacity up to 110 mAh/g has good rate capability and high Coulombic efficiency. The battery maintained high stability during cycling, with a capacity retention rate of about 50% after 1000 cycles. Mechanical tests were also performed to show that the coating adhered strongly to the fiber. Bouton et al. [19] presented a method for coating carbon fiber with hot dip coating LFP particles. After coating, the method can produce coatings several hundred nanometers thick. The impregnated carbon fiber are heated to 450°C to carbonize the organic binder used in the solution. The electrode shows a specific capacity close to 100 mAh/g. This is close to the capacity of commercial cathode LFP-coated aluminum foils in conventional battery cells. The structured batteries developed by Asp et al.[17]. and Xu et al.[20] both use commercial  $\text{LiFePO}_4$  cathode foils, carbon fiber anodes, glass fiber separators, and structured battery electrolytes, showing good multifunctional performance. But carbon fiber was not used as the cathode. The performance of carbon fiber as a cathode in battery deserves further investigation.

## 2.2 Electrophoretic deposition

Electrophoretic deposition (EPD) is essentially a method based on the movement of charged particles under an electric field and deposition onto conductive electrodes to form layers of uniform and tunable thickness. EPD does not require electrodes to have a special shape, and any shape can be used in it. Its method is simple and easy to operate, so it is widely used in industrial and experimental scenarios. The EPD coating of negatively charged particles aggregates and adsorbs to the anode due to the attraction of the anode electric field. The opposite is true for anode charged particles.[? ] Researchers widely use EPD for the preparation of lithium-ion battery electrodes. Both Keshmarzi et al.[21] and Yang et al.[22] used an electrophoretic

deposition process to prepare binder-free anodes for lithium-ion batteries. Yang et al.[23] prepared a (EPD  $\text{Co}_3\text{O}_4/\text{G}$ ) hybrid electrode using  $\text{Co}_3\text{O}_4$  and graphene. During the EPD process,  $\text{Co}_3\text{O}_4$  intercalates into the numerous pores of graphene, while also maintaining its unobstructed graphene conductive network. The prepared lithium-ion battery has excellent rate performance and durability. Xu et al.[24] used nanoscale needle-like  $\text{MnO}_2$  to bind reduced graphene oxide and annealed after electrophoretic deposition. The as-prepared binder-free anode for lithium-ion half cells has a capacity of up to 616.8 mAh/g. Yang et al.[25] also extended the EPD method to Si electrodes and  $\text{Fe}_3\text{O}_4$  electrodes. His research group used anodized Si and acetylene black (AB) particles, carbon-coated Si/reduced graphene oxide (Si@C/rGO),  $\text{Fe}_3\text{O}_4/\text{CNTs}$  (carbon nanotubes)/rGO (reduced graphene oxide) to fabricate electrodes, respectively, its half cells all exhibit high capacity and excellent rate performance. EPD has been widely used to fabricate a variety of lithium-ion battery electrodes with desirable electrochemical performances. This is enough to illustrate the universality of EPD. Unlike conventional electrode, electrode prepared by EPD process does not require addition of polymer binders such as polyvinylidene fluoride (PVDF). Thus, it is also beneficial to save materials and realize a green synthesis process.

In our previous study, Sanchez et al. [13] reported a structural battery cathode manufacturing method. The cathode was composed of electrochemically exfoliated graphene oxide (EGO), Polydiallyldimethylammonium chloride (PDDA), LFP and Carbon black (CB). By using electrophoretic deposition process, they made high performance structural battery cathodes with specific energy density of 222.14 Wh/kg. They had also deeply discussed the role of EGO and CB in making Carbon fiber cathodes of structural battery. Carbon fiber cathodes without either EGO or CB were synthesized for comparison. The sample without CB gave a nearly flat redox reaction peak in Cyclic voltametry test (CV), due to the poor conductivity of the  $\text{LiFePO}_4$ . The sample without EGO showed broader and smaller peaks in CV peak, in other words, weaker redox reaction. It proved that EGO strongly enhanced the ion mobility during lithiation and delithiation process. Nevertheless, DMF (N,N-Dimethylformamide) based suspension was used here as the EPD dispersion. However, DMF can cause chronic health effects due to its toxicity. Though the method is innovative and impressive, it is not environmentally friendly.

# 3

## Methods and Materials

### 3.1 Manufacturing

#### 3.1.1 Carbon fiber sample preparation

Here, We used PAN-based carbon fiber (T800SC-12K-50C) manufactured by Toray Composite Materials America, Inc. The filament tow composed of ca. 12000 CF was spread by Oxeon AB Sweden to an approximate width of 15 mm in order to obtain thin layers and maintain the shape.

As-received T-800 CF were made into a 60 mm long and 15 mm wide shape. Using Polytetra fluoroethylene (PTFE) tape and plate clamp here to assemble the CF bundle made CF tidy and stable.

The carbon fiber used here are sized by polymer layer when manufacturing and previous research [13] showed that the sizing polymer will strongly cover the CF surface as the result stop the particles deposition. So that the desizing process were performed here to wash off the polymer sizing layer. CF samples were treated with refluxed Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) for 8 h to remove the sizing agent completely.

#### 3.1.2 Electrophoretic deposition (EPD) of $\text{LiFePO}_4$ /graphene

##### 3.1.2.1 Electrophoretic deposition (EPD) dispersion preparation

To prepare the dispersion. First, 500 mg of  $\text{LiFePO}_4$  powder was dispersed in 50 mL of Absolute Ethanol using a Sonics VCX-750 Vibra-Cell Ultrasonic Liquid Processor for 10 minutes. At same time, we added 25 mg graphene in 50 mL Absolute Ethanol with carbon black (CB, Super P). CB performed as carbon-based conductivity increasement to the dispersion. 500 L of surfactant was added here to tune the surface charge of particles in dispersion together with graphene and CB. After sonicating for 10 minutes, two suspensions mixed and continued to sonicate for 10 minutes to make sure they dispersed well in 100 mL Absolute Ethanol. About the surfactants using here, we will discuss in the dispersion stability study. Table 3.1 shows the the content of the dispersion.

**Table 3.1:** Content of the EPD dispersion

Materials	Graphene	Carbon Black	Surfactant	LFP	Absolute Ethanol
Content	25 mg	25 mg	500 $\mu\text{l}$	500 mg	100 ml

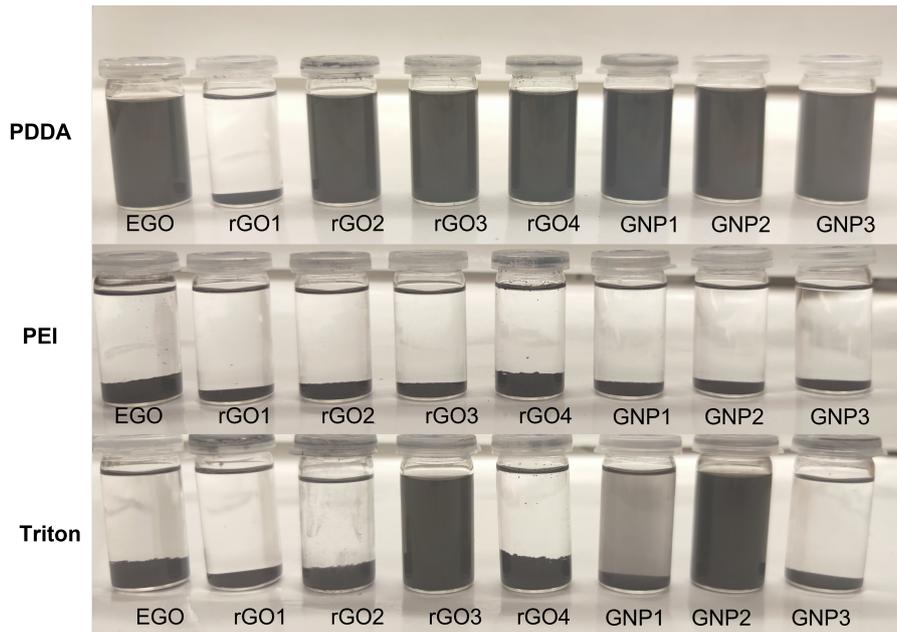
### 3.1.2.2 Dispersion stability study

To find out the performance when using different graphene and surfactants in the SB cathode synthesis process, we chose 8 different kinds of graphene here to prepare the dispersion, including a kind of exfoliated Graphene Oxide (EGO), 3 kinds of Graphene Nanoplatelet (GNP), and 4 kinds of reduced Graphene Oxide (rGO). Below are the information of the 8 kinds of graphene in Table 3.2.

**Table 3.2:** Information of the graphenes from the company

Serial number	Commercial name	Specific surface area (SSA) ( $m^2 g^{-1}$ )	oxygen content percent	Producer
rGO1	RGO	486±35	14.2±0.5	Graphenea
rGO2	Partly Reduced Graphene Oxide Powder	415 ±15	13 ±0.9	Abalonyx
rGO3	SE1231	234±5	2.8±0.3	Sixth element
rGO4	AVA-FLG 23	190±4	4.2±0.5	Avanzare
GNP1	Waste-tire driven Graphene nanoplatelets	130	9	Nanografen
GNP2	GC1	83±5	3.6±0.4	Graphene supermarket
GNP3	XGNP C750	745±50	6.3±0.5	Xg Science
EGO	Electrochemically exfoliated graphene oxide	-	12.1±0.5	reference[26]

Dispersion stability is an essential pre-work to the electrophoretic deposition. The dispersion with good stability may lead to a good EPD layer quality. We tried to know the stability of different couples (a kind of graphene and a kind of surfactant) in Absolute Ethanol. 3 commonly used surfactants were added. Polydiallyldimethylammonium chloride (PDDA; Sigma Aldrich) is a cationic polymer used industrially to adjust the surface charge of particles. Triton X-100 used as surfactant and detergent in laboratories, while it is the non-ionic surfactant performing as a control group here. Polyethylenimine (PEI) is commonly used to change the particle surface to the positive charge. Dispersion were made in a transparent glass bottle, mixing graphene and surfactant with 10 mL Absolute Ethanol. The bottles were sonicated with Sonics VCX-750 Vibra-Cell Ultrasonic Liquid Processor by 20 minutes. After 0 h, 1 h, 2 h, 24 h, 48 h, 72 h, 108 h, the photos were taken respectively to show the trend with the time going. After 1 h, the graphene with PEI dispersion were getting to agglomerate and precipitate. After 2 h, the all 8 kinds of graphenes with PEI dispersion almost precipitated. On the contrary, the graphene with PDDA dispersion performed so well and they have not precipitated for 108 h or longer, as the Figure 3.1 shows. Based on their dispersion stability, we chose PDDA here as the consistent surfactant in the electrophoretic deposition process.



**Figure 3.1:** Dispersion of 8 kinds of graphene materials mixed with 3 kinds of surfactants in Absolute Ethanol, 108 h after sonicated

It is worth mentioned that rGO3, GNP1 and GNP2 with 3 surfactants dispersion performed the best among 24 kinds of dispersions. The best-performance graphene in half cells with Lithium metal as anode will be explored in the electrochemical performance tests.

### 3.1.2.3 Electrophoretic deposition (EPD) process

After preparing the graphenes dispersion, the CF samples as the negative electrode connected to the negative charge were immersed into the dispersion and the platinum electrode performed as positive electrode connected to the positive charge. Then we applied a negative bias to the CF samples. A black composite layer was observed to be growing on its surface in quite a few moments. The electrophoretic deposition in Absolute Ethanol dispersion was attracted and carried by cathodic electric field. Using Absolute Ethanol here rather than DMF (Dimethylformamide) greatly reduced the toxic pollution. At the same time, the Absolute Ethanol dispersion does not cause electrolysis, which is common in water based dispersion. This prevent the oxidative damage of CF samples.

The CF samples (negative electrode) was set to be paralleled to the platinum electrode (positive electrode). The distance in between was 40 mm. The deposition was observed only on the CF samples surface, while no deposition was on the surface of platinum electrode, confirming that the negative electric field attracts the positively charged particles. We chose to use 70 V as the ideal voltage to precisely control the amount of deposited material based on previous study. The EPD time was all controlled to 20 minutes, which is also due to the previous study.[13]

### 3.1.3 Half cell assembling

The liquid electrolyte was made in glovebox in the Argon atmosphere to prevent the exposure to air and moisture. Propylene carbonate (PC) and ethylene carbonate (EC) were mixed by 1:1 w/w. Then 1.0 M LiTFS and 1.0M LiBoB were adding to the solution and sonicated until dissolving completely.

To make a half cell, the pouch bag is cut into the shape in the figure and folded in half, as symmetrical as possible. Two pieces of white insulating tape were cut and attached to the top of the outside of the bag, and a small piece of tape was folded over the top of the bag. Hot melt glue was applied in place under the insulating tape, and then the current collectors were added. Separators used here were glass fiber weaves called Whatman. Aluminum current collector was connected to the CF cathode and Nickel current collector was connected to the Lithium metal anode. Afterwards, the pouch bags were sealed on the top once before drying in the oven at 50°C under vacuum for around 12 h. The Lithium metal was cut in the glovebox into 15 mm x 30 mm, the same size as the CF cathodes. Then both cathodes and anodes were placed in the pouch bag, all connected to the current collector. After adding enough liquid electrolyte until the separator was completely wet, the finished half cells were vacuum sealed in the glovebox. The finished pouch cell had the dimensions 80 mm x 60 mm.

## 3.2 Characterization

The characterization of the samples was divided thoroughly into two parts, structure/elemental test and electrochemical test. Structure and elemental test focuses on the elemental and essential information on graphene coated CF cathodes such as element content, surface morphology, and molecular structure. While the electrochemical test leads to the evaluation of the half cells performance.

### 3.2.1 Structure and Elemental test

#### 3.2.1.1 Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) were used to investigate the quality and composition of the EPD coated CF. SEM images of the samples were collected using a JEOL JSM-7800F Prime at an acceleration voltage of 10 kV.

#### 3.2.1.2 Raman Spectroscopy

Raman spectroscopy is an analysis method that analyzes the scattering spectrum different from the incident light frequency to obtain the molecular vibration and rotation information of graphene and is applied to the study of graphene structure. Here, a WITec alpha300 R was used. The  $I_D/I_G$  ratio between the D band and G band intensities is often used to estimate defect levels in graphene.

### **3.2.2 Electrochemical test**

#### **3.2.2.1 Cyclic voltammetry test (CV)**

Cyclic Voltammetry (CV) was conducted at a scanning rate of 0.1 mV/s between 2.6 and 4.2 V vs. Li/Li<sup>+</sup> using Bio-Logic SP-300 station.

#### **3.2.2.2 Galvanic charge and discharge test (GCD)**

Galvanic charge and discharge test were conducted between 2.6 and 4.2 V vs. Li/Li<sup>+</sup> at different rates using Bio-Logic SP-300 station. And a long time galvanic charge and discharge cycles were recorded for up to 500 cycles at 2 C.

#### **3.2.2.3 Electrochemical Impedance Spectroscopy (EIS)**

Electrochemical Impedance Spectroscopy (EIS) measurements were performed in the frequency range from 200 kHz to 1 Hz under an alternating current (AC) in Bio-Logic SP-300 station.

# 4

## Results

### 4.1 Morphology and quality of different types of graphene

It can be seen from Figure 4.1 and 4.2 that compared with rGOs, GNPs show more lamellar structure with thicker coating layer. While the morphology of EGO is in between GNP and rGO, but better adhesion to the silicon wafer substrate. It is worth mentioning that the morphology of GNP1 is similar to rGOs to some extent, and its lamellar structure is slightly different from that of GNP2 and GNP3.

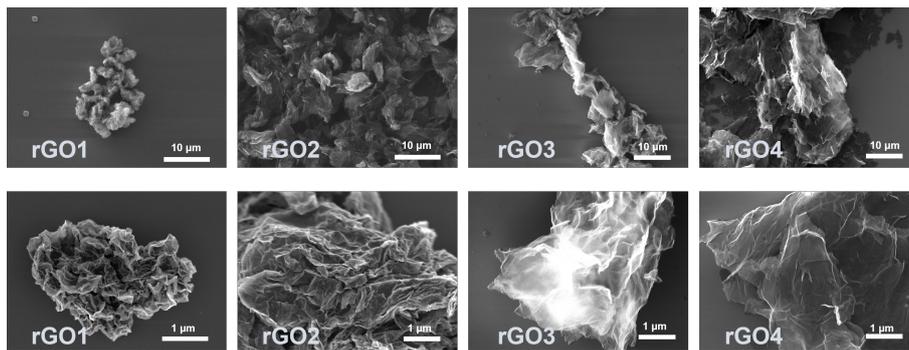


Figure 4.1: Low and high resolution SEM images of rGO1, rGO2, rGO3, rGO4

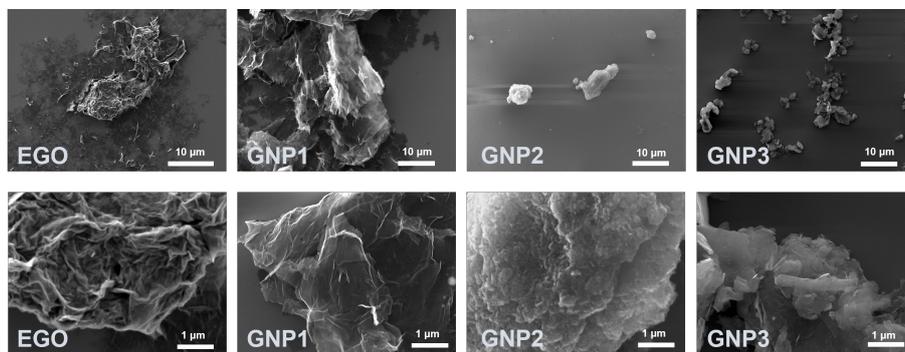
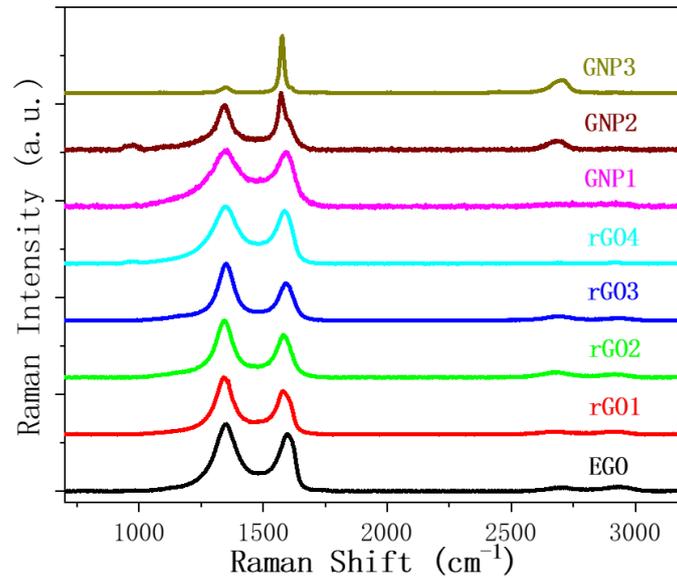


Figure 4.2: Low and high resolution SEM images of EGO, GNP1, GNP2, GNP3



**Figure 4.3:** Raman spectroscopy of 8 kinds of graphene materials

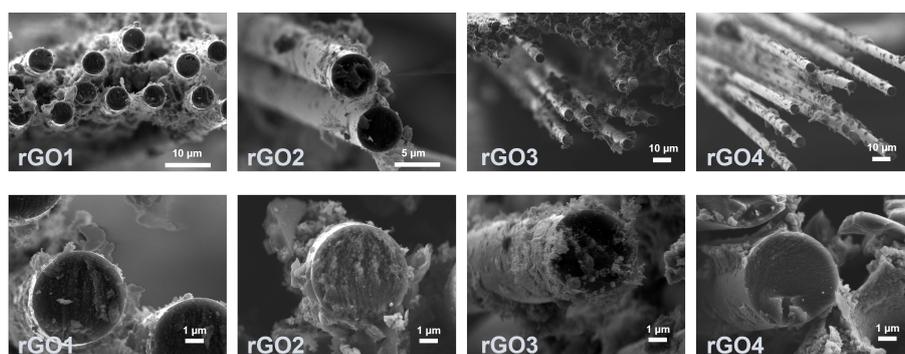
As seen in Figure 4.3, among all graphene materials here, two characteristic peaks can be easily found. They are all positioned at around  $1340\text{ cm}^{-1}$  of the D band and  $1580\text{ cm}^{-1}$  of the G band. The D band is produced by out-of-plane vibrations due to structural defects while the G band originated from the in-plane vibrations of  $sp^2$  carbons. The defect level can be evaluated by the intensity ratio of D band and G band. The  $(I_D/I_G)$  ratio of 4 kinds of rGO are all above 1.0, which are the same with the ratio of EGO (1.18). The  $(I_D/I_G)$  ratio of rGO3 even reaches 1.54, which is the highest among all 8 kinds of graphene materials. The high ratio usually indicates the high level of defect level. While GNPs have the  $(I_D/I_G)$  ratio far lower than the ratio of EGO (1.18), except for the GNP1. The ratio of GNP1 (1.04) is approaching the ratio of EGO. The intensity of D peak of GNP2 and GNP3 are much lower than the others, showing that they are more like graphite rather than graphene.

2D band is the secondary D band at around  $2700\text{ cm}^{-1}$ . It is usually used for judging the thickness of the graphene layer. However, in our case, all rGO, EGO and GNP1 samples show a broad and low intensity 2D band. It is possibly due to the oxidation during the fabrication process that broke the stacking order of adjacent graphene layers and introduced amorphization of carbon atoms. So we cannot estimate the layer thickness information from the 2D band. The features in the Raman spectrum all corroborate the phenomena observed in the SEM.

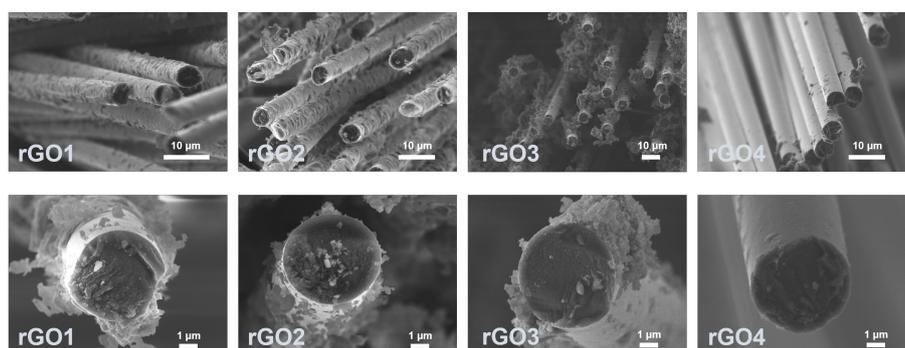
## 4.2 Morphology of Carbon fiber using different types of graphene

In Figure 4.4 and 4.5, it can be found that all types of graphene are uniformly attached to the carbon fibers and they maintain the original sheet structure to

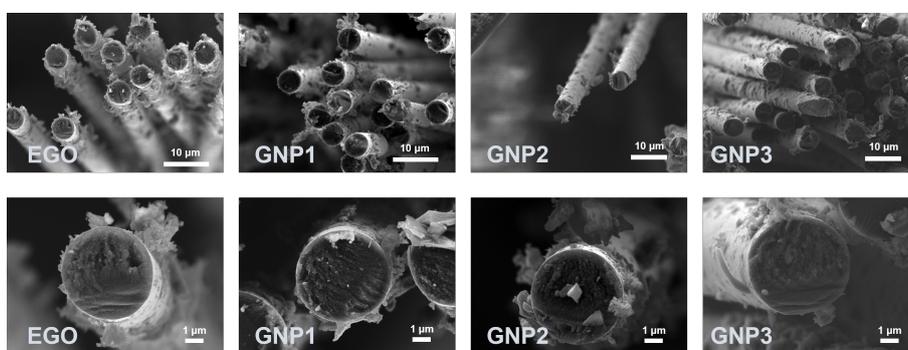
some extent. By observing the electron microscope images under low and high resolution, it can be found on the CF surface that the dark region is from CB and graphene which process good conductivity, while the bright region is from lithium iron phosphate with poor conductivity due to the electrons retarding. Amount of the active material on CF surface of GNPs are observed relatively less than that of adding rGOs. The phenomenon fits well with the active materials coating mass being weighed after the EPD process.



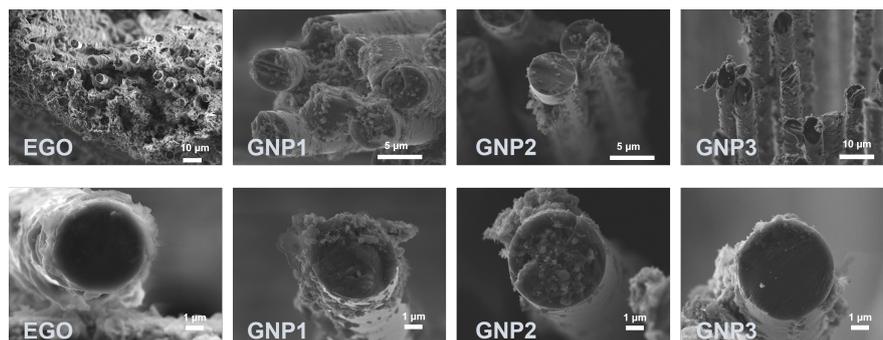
**Figure 4.4:** Low and high resolution SEM images of the coated carbon fibers with rGO1, rGO2, rGO3, rGO4 before electrochemical test



**Figure 4.5:** Low and high resolution SEM images of the coated carbon fibers with rGO1, rGO2, rGO3, rGO4 after electrochemical test



**Figure 4.6:** Low and high resolution SEM images of the coated carbon fibers with EGO, GNP1, GNP2, GNP3 before electrochemical test



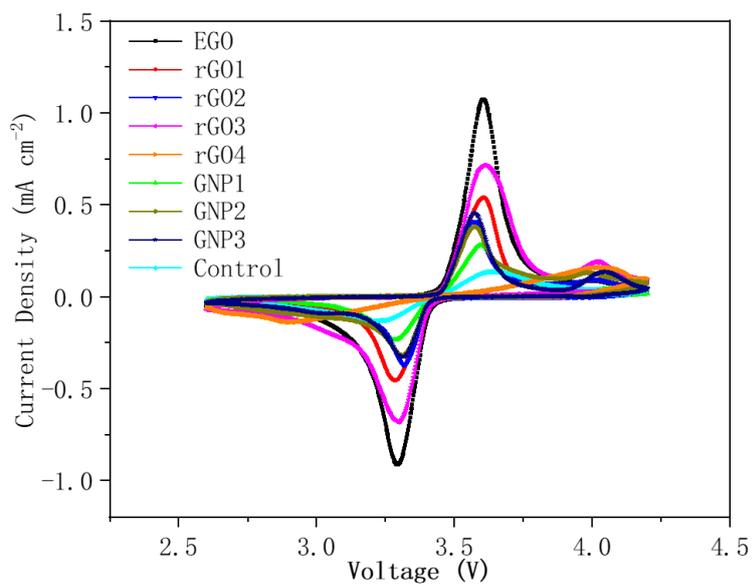
**Figure 4.7:** Low and high resolution SEM images of the coated carbon fibers with EGO, GNP1, GNP2, GNP3 after electrochemical test

After the cycling test at 2 C over 500 times, the active material was still uniformly attached to the carbon fibers and only slight peeling was observed in Figure 4.6 and 4.7, except for rGO4 CF cathode. In this rGO4 CF cathode sample, most of the active materials were detached after cycling. This might attribute to the contamination from the manufacturing process which was supported by our previous study with the existence of Manganese(i.e.  $\text{MnO}_2$ ,  $\text{KMnO}_4$ ).

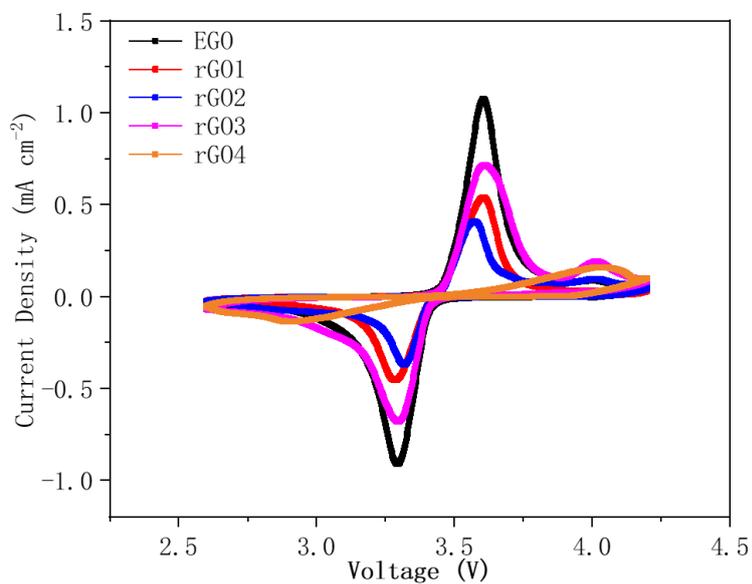
### 4.3 Half cell device performance

Figure 4.8 shows the CV curves of the samples coated with different kinds of graphene materials at a scan rate of 0.1 mV/s in a voltage range of 2.6V - 4.2V vs  $\text{Li}^+/\text{Li}$ . Typical oxidation/reduction peaks were observed in all samples during anodic/cathode scanning, which were caused by the reversible redox reaction  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in  $\text{LiFePO}_4$ .

However, the peak shape, current density, and potential separation between the two redox peaks were significantly different. The EGO cathode composite sample exhibits sharp and highly symmetrical peaks with the smallest potential difference between the anodic and cathodic peaks, indicating that the composite has low polarization and high redox reversibility. The EGO cathode composite shows the highest specific current density. rGOs cathode composite samples, on the other hand, shows lower current density than that of EGO while reaching the oxidation reaction peak at around 3.6 V, which was similar to the EGO cathode composite samples. The similarity of the redox reaction peak indicates that EGO cathode composite samples has the resemblance in electrochemical performance with the rGOs. GNPs cathode composite samples show apparently different specific current density value, which is almost half of that of EGO. The result indicates the electrochemical performance of the GNPs were worse than EGO and rGOs. A secondary irreversible oxidation reaction peak was observed at 4.0 V - 4.1 V in all kinds of graphene materials except for EGO cathode composite samples. The oxidation reaction here might come from defects on graphene surface (i.e., oxygen functional groups such as  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{O}-$ , etc). Dismissing oxygen-containing functional groups made seldom impact on the electrochemical performance of devices, which can be proved by the following



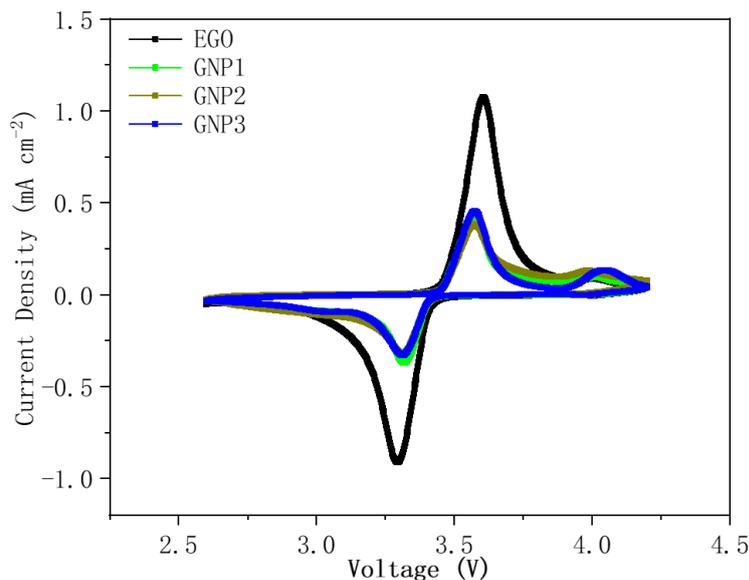
**Figure 4.8:** Cyclic voltammetry test results of 8 kinds of graphene materials composite cathode half cell and control group



**Figure 4.9:** Cyclic voltammetry test results of 4 kinds of rGO composite cathode half cell and EGO composite cathode half cell

tests.

Among all kinds of rGOs cathode composite samples, rGO1 and rGO3 have better electrochemical performance here, while GNP1 has a good redox reaction peak



**Figure 4.10:** Cyclic voltammetry test results of 3 kinds of GNP composite cathode half cell and EGO composite cathode half cell

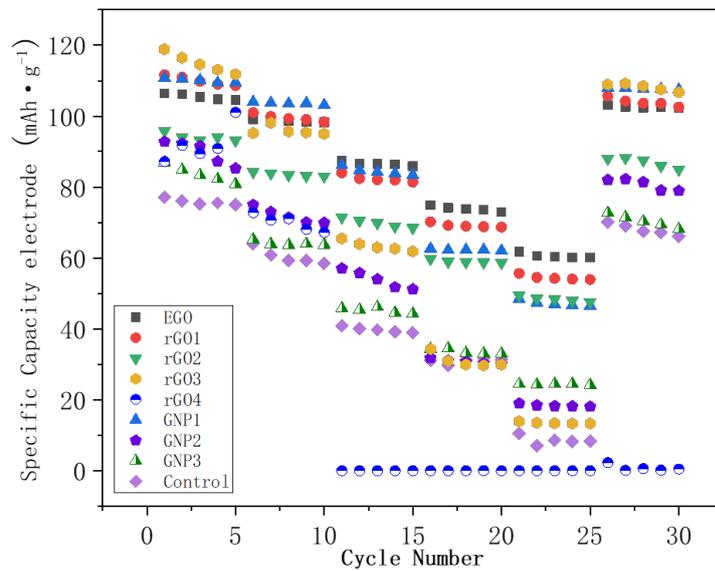
among all kinds of GNPs. rGO4 cathode composite sample shows abnormal behaviour during the test. The two redox peaks are flat and limited by the voltage of 2.6 V - 4.2 V, which do not stand for the good battery electrochemical performance in this voltage window.

The stability of half cells with 8 kinds of graphene composite cathode at different C rates of 0.1 C, 0.2 C, 0.5 C, 1 C, and 2 C were summarized in Figure 4.11. A control group was conducted by without the addition of graphene.

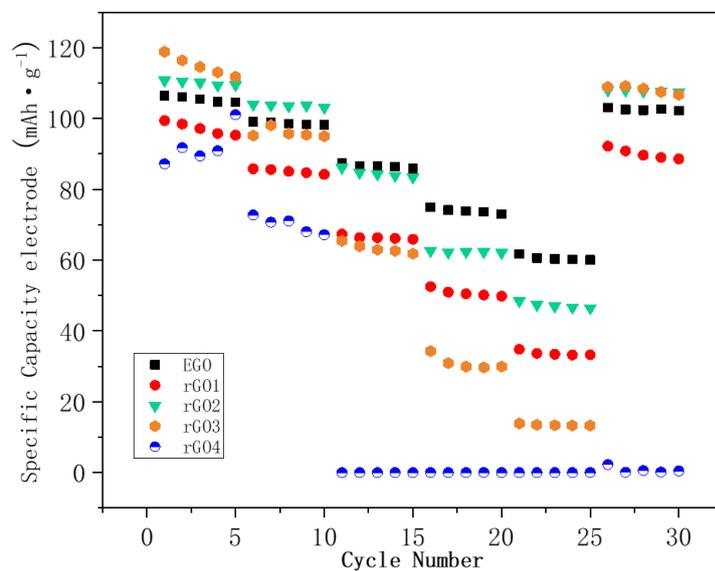
EGO cathode composite half cells shows a stable electrochemical performance, with a specific capacity of 61.7 mAh/g at 2 C. Most of the positive half cells using rGO possess higher specific capacity compared to GNPs. rGO3 cathode composite half cell exhibits the best rate performance among all the samples at 0.1 C, with a discharge capacity of 125 mAh/g. While the high rate performance of rGO3 half cell is worst among them. Compared to rGO3, rGO1 and rGO2 show a more stable charge/discharge performance at all rates. rGO4 is observed no specific capacity after several cycling at 0.2 C. This is presumed inherent to the active materials detachment, as proved by the SEM images after cycling (see Figure 4.5).

Among all GNPs half cells, GNP1 is the most stable one, with the specific capacity of 111.6 mAh/g at 0.1 C and 55.6 mAh/g at 2 C respectively. The electrochemical performance of GNP1 is similar to that of rGOs. While GNP2 and GNP3 composite cathode half cells have the electrochemical performance approaching to the control group. As analyzed in Raman spectra, the intensity of D peak shows that they are more like graphite rather than graphene. The observed result might explain the bad electrochemical performance here.

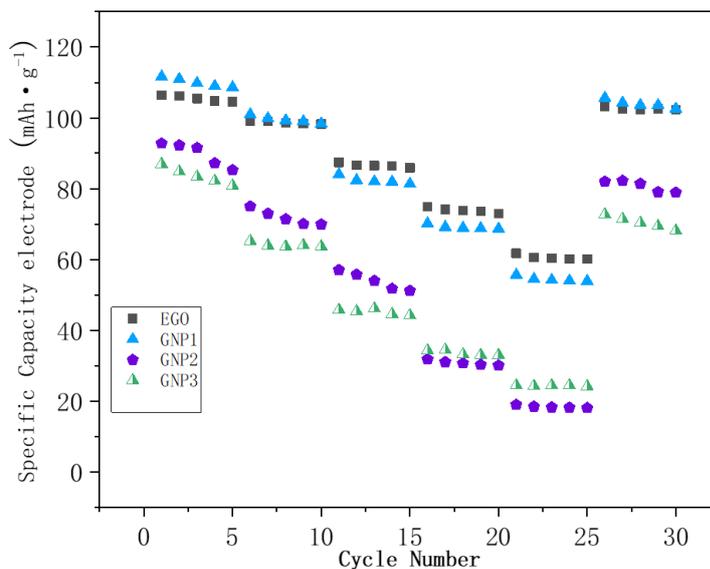
The specific capacity of all samples decreases with increasing C-rate. This process



**Figure 4.11:** Galvanic charge and discharge profiles of 8 kinds of graphene materials composite cathode half cell and control group at 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 0.1 C; from left to right



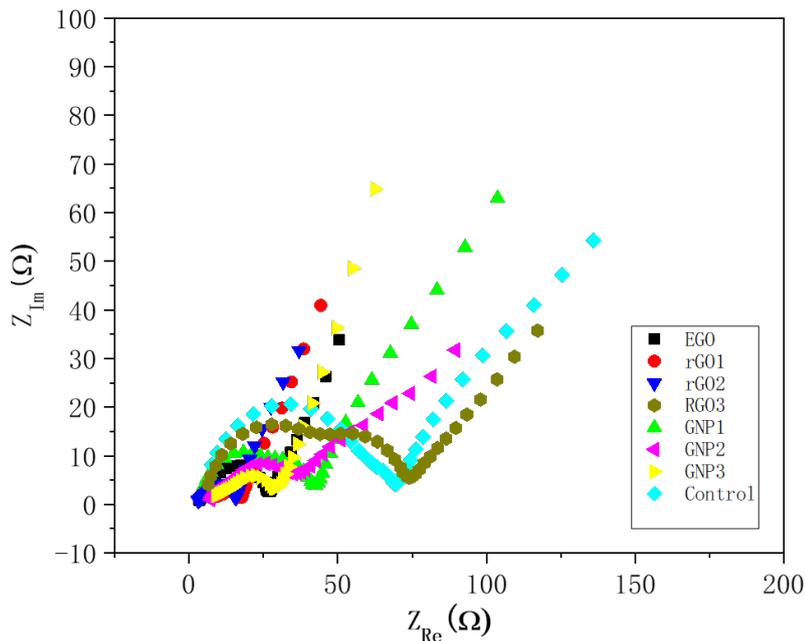
**Figure 4.12:** Galvanic charge and discharge profiles of 4 kinds of rGO composite cathode half cell and EGO composite cathode half cell at 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 0.1 C; from left to right



**Figure 4.13:** Galvanic charge and discharge profiles of 3 kinds of GNP composite cathode half cell and EGO composite cathode half cell at 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 0.1 C; from left to right

was confirmed to be reversible, and most of the graphene composite cathode half cells recovered their initial capacity after returning to 0.1 C. This is in line with what was confirmed by the SEM images after cycling, as no detachment of active materials was observed. Running half cells at high voltages (more than 3.9 V) causes them to undergo irreversible oxidation reactions which is founded in the CV test. However, this irreversible peak disappeared after certain charge/discharge cycles and the long time cycling test was not affected by these initial side reactions.

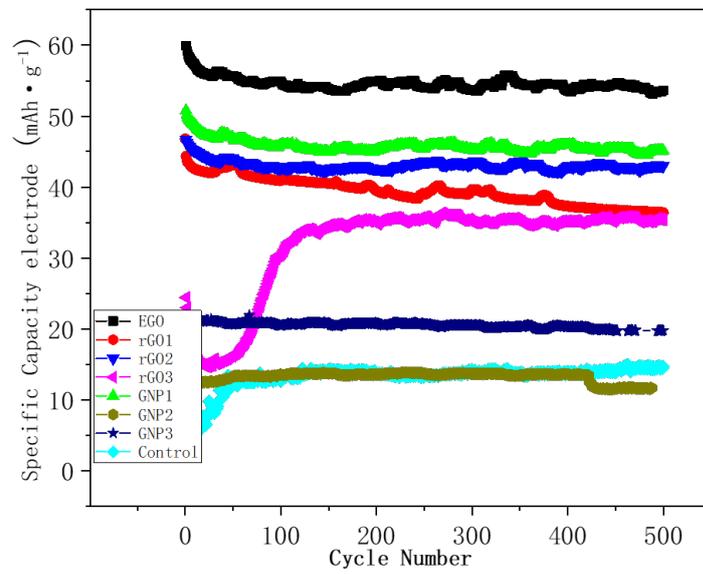
In electrochemical impedance spectroscopy (EIS), the mid- and high-frequency semi-circles represent the charge transfer resistance ( $R_{ct}$ ) of the reaction. The smaller the semi-circle, the more favorable the interfacial redox reaction occurs on the electrode surface. In figure 4.14, most rGO cathode half cells delivered small  $R_{ct}$  values. On the other hand, the semi-circles of GNP cathode half cells are larger, which implies their more difficult interfacial redox reaction. The result could explain by the SEM and Raman analysis, that GNP samples have thick layer which is similar to the structure of graphite.



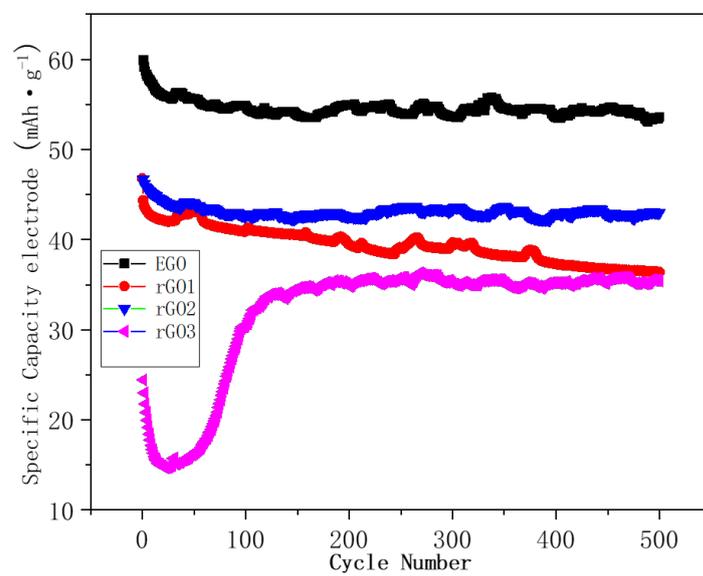
**Figure 4.14:** Nyquist Plots of 8 kinds of graphene materials composite cathode half cell and control group

Long time cycling stability is another core requirement of electrode materials for lithium-ion battery, also for the structural battery. As shown in figure 4.15, high capacity retention (around 90%) are achieved for most graphene composite cathode material at 2 C over 500 cycles. Although the retention rate of the rGO1 composite cathode half cell is as low as 80.5%, it remains stable for up to 500 cycles. This strongly confirms the validity and universality of the green synthesis adopted in this Master thesis.

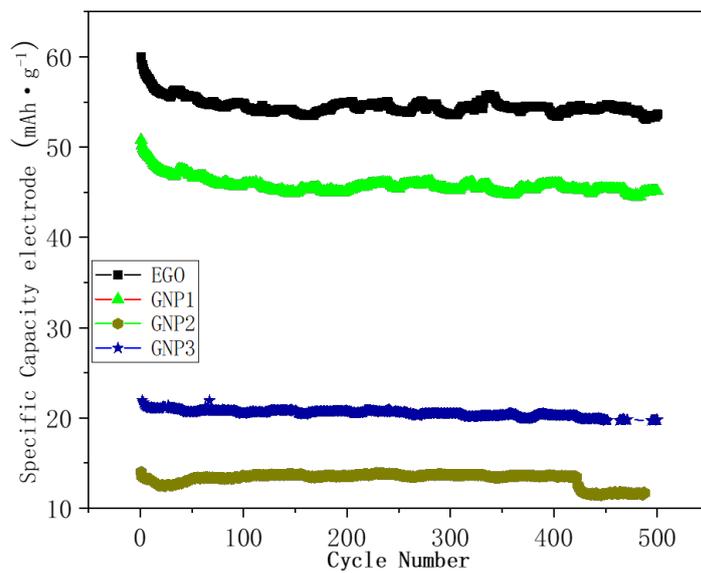
It is worth mentioning that rGO3 composite cathode half cell behaved abnormally at the beginning of the long cycle, but quickly reverted to similar characteristics to other rGOs. However, its specific capacity reaches 34.0 mAh/g at 2 C, which is inconsistent with the performance in galvanic charge and discharge experiments. It is inferred here that it may be due to problems arising in battery assembly, which will be further explored in future work. Also, the GNP2 composite cathode half cell is observed a sudden dash after 425 cycles. It might be due to the leakage of liquid electrolyte that reduce the electrochemical performance of the GNP2 composite cathode half cell. This also should be further studied in the future work.



**Figure 4.15:** 500 times cycling performance of 8 kinds of graphene materials composite cathode half cell and control group at 2 C



**Figure 4.16:** 500 times cycling performance of 4 kinds of rGO composite cathode half cell and EGO composite cathode half cell at 2 C



**Figure 4.17:** 500 times cycling performance of 3 kinds of GNP and EGO at 2 C

# 5

## Conclusion

In conclusion, this thesis reports a green approach to fabricate novel cathode composites composed of lithium iron phosphate ( $\text{LiFePO}_4$ ) and graphene nanosheets using electrophoretic deposition (EPD). In this work, ethanol was introduced as a green solvent to replace NMP or DMF and we successfully fabricated structural battery cathode composite based on different types of graphene.

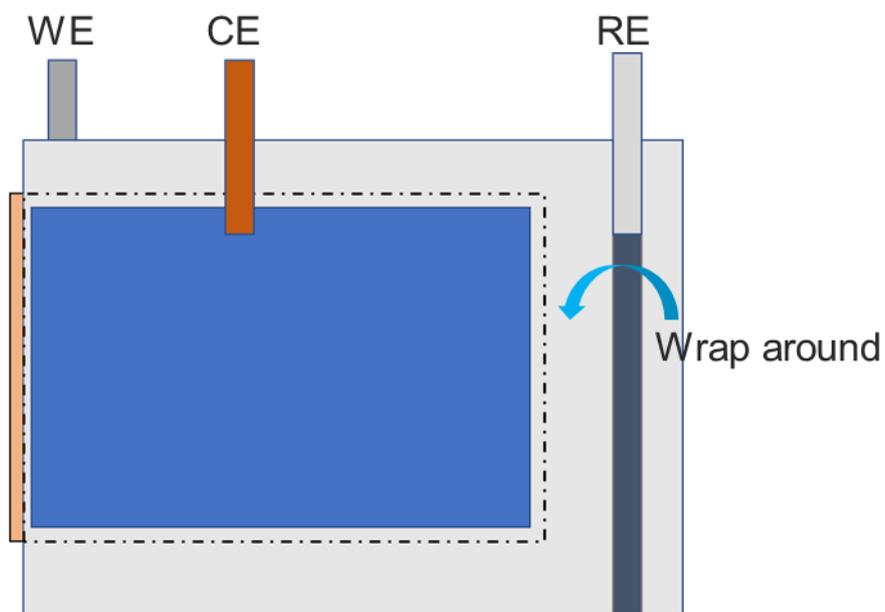
Generally, different commercial graphene materials, including 3 kinds of graphene nanoplatelet (GNP) and 4 kinds of reduced graphene oxide (rGO), were characterized by SEM and Raman spectroscopy within the comparison of homemade EGO. For most rGO and GNP coated CF cathodes, the active materials well attached on CF surface even after long-time cycling, guaranteeing good cycling performance of the half cell devices.

Most of the graphene additives in structural battery cathodes can significantly improve the relative electrochemical performance, as compared to the control group without graphene. The highest specific capacity of 125 mAh/g was achieved on rGO3 based cathode. Meanwhile, for most of the graphene based cathodes, the retention rates are over 90% after 500 cycles at 2 C. Among them, the electrochemical performance of the rGOs and GNP1 composite cathodes are better than that of GNP2 and GNP3. EGO still show the most stable electrochemical performance compared to the others, with a high specific capacity of 61.7 mAh/g at 2 C.

# 6

## Future work

Although the master's dissertation has been completed, some potential developments worthy of future research appear in this paper. The first is the optimization of the manufacturing method. During the entire experiment, the success rate of battery fabrication was only 50%, and most of the failures were due to improper and unstable human operation. This is almost unavoidable in the use of manual operations. If possible, robust, stable and efficient cell fabrication methods should be developed. The second is an in-depth exploration of the rGO3 and GNP2 composite cathode half cells, due to some differences in performance from other graphene materials in the GCD test.



**Figure 6.1:** A model of 3-electrode system

The third is the performance test of the full cell. In a full cell with carbon fiber as the anode and the composite reported in this paper as the cathode, using SBE as the electrolyte, the electrochemical performance was tested and its performance was observed. In addition to conventional electrochemical performance tests (CV, GCD, EIS) in order to independently monitor the Cathode (WE) and Anode (CE) by using Reference electrode (RE), a three-electrode system was designed. Its pattern is shown in Figure 6.1. Among them, WE is a graphene composite cathode, CE is a carbon fiber, and RE is a lithium metal electrode. Due to time constraints, although

this three-electrode system has been devised, it has not been adequately tested. This will be carried out in future work. Finally, it has been found in this paper that the addition of graphene could effectively promote the performance of structural batteries. Different kinds of electrode active materials and exploring the possibility of more kinds of additives will be the focus of future research.

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