Crystalline and Amorphous Phosphorus – Carbon Nanotube Composites as Promising Anodes for Lithium-Ion Batteries

Thesis by

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In Partial Fulfillment of the Requirements
For the Degree of

Master of Science

King Abdullah University of Science and Technology
Thuwal, Kingdom of Saudi Arabia

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Committee Member: Prof. Dr. Jurgen Kosel
ABSTRACT

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Jasmin Smajic

Battery research has been going full steam and with that the search for alternative anodes. Among many proposed electrode materials, little attention has been given to phosphorus. Phosphorus boasts the third highest gravimetric charge capacity and the highest volumetric charge capacity of all elements. Because of that, it would be an attractive battery anode material were it not for its poor cyclability with significant capacity loss immediately after the first cycle. This is known to be the consequence of considerable volume changes of phosphorus during charge/discharge cycles.

In this work, we propose circumventing this issue by mixing amorphous red phosphorus with carbon nanotubes. By employing a non-destructive sublimation-deposition method, we have synthesized composites where the synergetic effect between phosphorus and carbon nanotubes allow for an improvement in the electrochemical performance of battery anodes. In fact, it has been shown that carbon nanotubes can act as an effective buffer to phosphorus volumetric expansions and contractions during charging and discharging of the half-cells [1].

By modifying the synthesis parameters, we have also been able to change the degree of crystallinity of the phosphorus matrix in the composites. In fact, the less common phase of red phosphorus, named fibrous phosphorus, was obtained, and that explains some of
the varying electrochemical performances observed in the composites. Overall, it is found that a higher surface area of amorphous phosphorus allows for a better anode material when using single-walled carbon nanotubes as fillers.
ACKNOWLEDGEMENTS

In the name of God, the Most Gracious, the Most Merciful

First and foremost, I thank Allah the Almighty (s.w.t) for granting me the ability to work on and successfully complete this research.

I would like to express my profound gratitude to my research supervisor, Dr. Pedro M. F. J. Costa, for giving me the opportunity to do this work and for his continuous support and advice. He was and continues to be a true role model of what being an excellent researcher really means and he is a source of knowledge that never dries up.

I thank the committee members, Dr. Enzo Di Fabrizio and Dr. Jurgen Kosel, for taking time out of their busy schedules to participate in the thesis defense and be part of this milestone in my research career.

My thanks also go to all of my colleagues in the Laboratory for Carbon Nanostructures, with whom I engaged in endless discussions and from whom I learned a great deal. I would also like to thank the members of the Imaging and Characterization Core Labs for their technical support. Finally, I would like to thank everyone at KAUST for enriching my stay at the university.

Last but not least, my heartfelt gratitude goes to my family for their support, encouragement and patience.
# TABLE OF CONTENTS

EXAMINATION COMMITTEE APPROVALS FORM ........... Error! Bookmark not defined.

ABSTRACT ........................................................................................................................................... 3

ACKNOWLEDGEMENTS .................................................................................................................. 5

TABLE OF CONTENTS ..................................................................................................................... 6

LIST OF ABBREVIATIONS ................................................................................................................. 8

LIST OF ILLUSTRATIONS .................................................................................................................. 10

INTRODUCTION ................................................................................................................................ 13

1.1 General ........................................................................................................................................... 13

1.2 History of Lithium-Ion Batteries ................................................................................................. 15

1.3 Lithium-Ion Battery Working Principle ...................................................................................... 16

1.4 Anode Materials .......................................................................................................................... 19

1.4.1 Intercalation-Type Anodes ...................................................................................................... 19

1.4.2 Alloying-Type Anodes ........................................................................................................... 20

1.4.3 Conversion-Type Anodes ........................................................................................................ 21

1.5 Cathode Materials ....................................................................................................................... 22

1.6 Carbon Nanotubes ...................................................................................................................... 23

1.7 Red Phosphorus .......................................................................................................................... 26

1.8 Scope and Motivation ................................................................................................................... 30

EXPERIMENTAL METHODS AND CHARACTERIZATION ......................................................... 31

2.1 Materials Synthesis .................................................................................................................... 32

2.2 Electrode Fabrication .................................................................................................................. 33

2.3 Electrochemical Measurements .................................................................................................. 34

2.4.1 Powder X-Ray Powder Diffraction .................................................................................... 35

2.4.2 Fourier Transform Infrared Spectroscopy ........................................................................... 36

2.4.3 Raman Spectroscopy ............................................................................................................ 37

2.4.4 Scanning Electron Microscopy ........................................................................................... 38

2.4.5 Transmission Electron Microscopy ...................................................................................... 40

2.4.6 Selected Area Electron Diffraction ....................................................................................... 41
2.4.7 Energy Dispersive X-Ray Spectroscopy ................................................................. 41
2.4.8 X-Ray Photoelectron Spectroscopy ........................................................................ 42
2.4.9 Thermogravimetric Analysis .................................................................................... 43

RESULTS AND DISCUSSION .............................................................................................. 45
3.1 Thermogravimetric analysis of the composites ........................................................... 45
3.2 Raman Spectroscopy and Powder X-Ray Diffraction Analyses .................................... 46
3.3 Electron Microscopy Characterization ......................................................................... 52
3.4 XPS Analysis ................................................................................................................. 60
3.5 FTIR Characterization .................................................................................................. 63
3.6 Electrochemical Characterization .................................................................................. 65

CONCLUSION AND FUTURE WORK .................................................................................. 71

BIBLIOGRAPHY ..................................................................................................................... 73
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>acetylene black</td>
</tr>
<tr>
<td>CB</td>
<td>carbon black</td>
</tr>
<tr>
<td>CCD</td>
<td>charged coupled device</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotube</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>DCM</td>
<td>dimethyl carbonate</td>
</tr>
<tr>
<td>DIW</td>
<td>deionized water</td>
</tr>
<tr>
<td>EC</td>
<td>ethylene carbonate</td>
</tr>
<tr>
<td>EV</td>
<td>electric vehicle</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HEMM</td>
<td>high energy mechanical milling</td>
</tr>
<tr>
<td>HEV</td>
<td>hybrid electric vehicle</td>
</tr>
<tr>
<td>LCO</td>
<td>lithium cobalt oxide</td>
</tr>
<tr>
<td>LIB</td>
<td>lithium-ion battery</td>
</tr>
<tr>
<td>LFP</td>
<td>lithium iron phosphate</td>
</tr>
<tr>
<td>LFSF</td>
<td>lithium iron fluorosulphate</td>
</tr>
<tr>
<td>LMO</td>
<td>lithium manganese oxide</td>
</tr>
<tr>
<td>LNO</td>
<td>lithium nickel oxide</td>
</tr>
<tr>
<td>M</td>
<td>molar mass</td>
</tr>
<tr>
<td>MWCNT</td>
<td>multi-walled carbon nanotube</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>NIB</td>
<td>sodium-ion battery</td>
</tr>
<tr>
<td>NMP</td>
<td>1-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>PVDF</td>
<td>polyvinylidene fluoride</td>
</tr>
<tr>
<td>RBM</td>
<td>radial breathing mode</td>
</tr>
<tr>
<td>RPM</td>
<td>rounds per minute</td>
</tr>
<tr>
<td>SAED</td>
<td>selected area electron diffraction</td>
</tr>
<tr>
<td>SEI</td>
<td>solid electrolyte interface</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>SWCNT</td>
<td>single-walled carbon nanotube</td>
</tr>
<tr>
<td>TLD</td>
<td>through the lens detector</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray powder diffraction</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS

Figure 1.1  Power density and energy density of different energy storage technologies  p. 14

Figure 1.2  Number of publications per year (until 2015) when searching for “lithium”, “ion” and “battery” in the Scopus bibliographic database  p. 15

Figure 1.3  Schematic representation of the inside of a Li-ion electrochemical cell  p. 16

Figure 1.4  Alloying and conversion type anode materials compared according to specific capacity and potential  p. 21

Figure 1.5  Schematic representation of layered, spinel and olivine arrangements  p. 23

Figure 1.6  a) Single-walled carbon nanotubes of different chirality; b) chiral vector  p. 24

Figure 1.7  Structures of a) white P; b) red P; c) one layer of black P (i.e. phosphorene); c) orthorhombic black P  p. 28

Figure 1.8  Atomic structures of (a) Hittorf’s phosphorus and (b) fibrous phosphorus  p. 29

Figure 2.1  Pulverization of P (a) and buffering effect of SWCNTs (b) during electrochemical cycling  p. 31

Figure 2.2  Schematic representation of the red P – SWCNT composite synthesis  p. 33

Figure 2.3  Bragg condition  p. 36

Figure 2.4  Bending modes of vibration  p. 37

Figure 2.5  Stokes and anti-stokes vibrational lines  p. 38

Figure 2.6  Electron beam and sample interaction in SEM  p. 39
Figure 2.7  Electron beam and sample interaction in a TEM  p. 40

Figure 2.8  Generation of x-rays in EDX characterization  p. 42

Figure 2.9  Emission of a photoelectron in XPS  p. 43

Figure 3.1  TGA in N$_2$ flow of a) SWCNT; b) ground red P; c) 7:3 weight ratio composite; d) 8:2 weight ratio composite  p. 45

Figure 3.2  Raman spectroscopy of starting materials and final composites  p. 47

Figure 3.3  Lorentzian line shapes of the G$^+$ and G$^-$ peaks of the SWCNTs  p. 49

Figure 3.4  (a) XRD patterns of starting materials and final composites and (b) comparison between XRD patterns of fibrous P, red P and 8:2 composite  p. 51

Figure 3.5  SEM images of (a) red P and (b) SWCNTs  p. 52

Figure 3.6  Figure 3.6 SEM images of (a) 7:3 composite and (b) 8:2 composite (red arrows point towards coated bundles of nanotubes)  p. 53

Figure 3.7  Figure 3.7 SEM images of (a,b) 7:3 composite and (c,d) 8:2 composite (red arrows point towards coated bundles of nanotubes)  p. 54

Figure 3.8  (a) TEM image of red P, (b) HRTEM image of red P, (c) SAED image of red P, (d) TEM image of SWCNTs  p. 55

Figure 3.9  (a) TEM image of 7:3 composite, (b) HRTEM image of 7:3 composite, (c) TEM image of 8:2 composite and (d) HRTEM image of 8:2 composite  p. 56

Figure 3.10  HRTEM image of the 8:2 composite  p. 58

Figure 3.11  (a) TEM image of the 8:2 composite and (b) its SAED pattern  p. 60
Figure 3.12  The EDX spectrum of (a) the 7:3 composite and (b) the 8:2 composite confirming the presence of P and C p. 59

Figure 3.13  XPS spectra of 7:3 composite: (a) survey spectrum, (b) O 1s level spectrum, (c) C 1s level spectrum and (d) P 2p level spectrum p. 60

Figure 3.14  XPS spectra of 8:2 composite: (a) survey spectrum, (b) O 1s level spectrum, (c) C 1s level spectrum and (d) P 2p level spectrum p. 62

Figure 3.15  Image of the bubble formation on the electrode of the 7:3 composite p. 64

Figure 3.16  FTIR graph of the 7:3 composite p. 65

Figure 3.17  Electrochemical performance of (a) red P at 50 mAh g⁻¹ and (b) SWCNTs at 150 mAh g⁻¹ p. 66

Figure 3.18  Electrochemical performance at 150 mAh g⁻¹ of (a,b) 7:3 composite and (c,d) 8:2 composite p. 67

Figure 3.19  Cyclic voltammetry response for (a) 7:3 composite and (b) 8:2 composite p. 69
Chapter 1
INTRODUCTION

1.1 General

Lithium-ion batteries (LIBs) have proved to be one of the most important energy storage systems by permeating through every aspect of our everyday life [2]. They have enabled the wireless revolution of mobile phones, laptops and tablets through small scale rechargeable energy storage and are now poised to become a crucial element in large scale energy storage [3]. LIBs are the most promising candidate for electric vehicles (EV) and hybrid electric vehicles (HEV) and could thus catalyze the transition towards the renewable energy future [4]. That being said, LIBs presently found on the market are not good enough for the challenges ahead and they must be improved if the current trend of gadget rich society and ambition of lowering the dependency on fossil fuels is to be continued [2, 5-7].

A number of different battery chemistries have been studied, yet none meets the advantages of having high energy density (Figure 1.1), long life cycle, low self-discharge (typically <5% per month) and being lightweight that LIBs provide [2, 8-10]. On the other hand, LIBs need integrated protection mechanisms that will keep the battery within safe electrochemical and thermal operating parameters [11]. They also have an issue with aging and Li is currently highly priced, although this is poised to change with the improvement of Li processing techniques [12, 13].
The motivation behind using a battery based on Li\textsuperscript{+} ion chemistry stems from the fact that Li is the most electropositive (-3.04 V vs SHE) [15], the lightest (M=6.94 g mol\textsuperscript{-1}) and the least dense (0.53 g cm\textsuperscript{-3} at 20°C) metal [6], enabling the engineering of lightweight batteries with high energy densities. In addition, thanks to nanostructured materials, today’s research in LIBs can further boost power densities, bringing us closer to the energy and power densities commonly offered by internal combustion engines (Figure 1.1) [16, 17].
1.2 History of Lithium-Ion Batteries

The history of the battery goes back to the end of the 18\textsuperscript{th} century and the invention of the first battery is attributed to the Italian researcher A. Volta [18]. He invented the electrochemical source of energy termed voltaic pile [19]. The idea of the rechargeable battery was developed at the beginning of the 19\textsuperscript{th} century by J. W. Ritter and N. Gautherot, but the first effective rechargeable battery was not invented until the 1860s when G. Planté developed the lead and sulphuric acid based rechargeable battery [20].

![Figure 1.2 Number of publications per year (up to 2015) when searching for “lithium”, “ion” and “battery” in the Scopus bibliographic database](image)

The first LIB was made by M.S. Whittingham in 1976 [17]. The same year J.O. Besenhard proposed a reversible intercalation of Li\textsuperscript{+} ions into graphitic anodes and oxide cathodes [21, 22]. In 1980 K. Mizushima and J. Goodenough presented LiCoO\textsubscript{2} as high energy and high voltage cathode material [23]. In 1983 R. Yazami and Ph. Touzain demonstrated a
16

reversible intercalation of Li\textsuperscript{+} ions into graphite [24]. The first commercialization of rechargeable LIBs was done by Sony Corporation in 1991 [25]. Since then, the number of commercially available LIBs, as well as the number of scientific publications on the topic of Li-ion batteries has been rapidly increasing (Figure 1.2).

1.3 Lithium-Ion Battery Working Principle

The term “battery” refers to two or more electrochemical cells put together that convert chemical energy into electrical energy. That being said the term is often used interchangeably with a single electrochemical cell.

![Figure 1.3 Schematic representation of the inside of a Li-ion electrochemical cell [26]](image)

The LIB electrochemical cell consists of two electrodes: an anode, which is usually some mixture with graphite, and a cathode, which is usually a lithium metal oxide (e.g. LiCoO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4}, LiFePO\textsubscript{4}). Between them, there is a microporous polymer sheet (\textit{i.e.} separator)
which is soaked in an electrolyte consisting of a lithium salt (e.g. LiPF₆), dissolved in one or more component organic solvent, *e.g.* ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 volume ratio. The electrolyte conducts ionic charges which travel between the electrodes but does not allow the transport of electric charges which have to travel through an external circuit where they do work (Figure 1.3). The role of the separator is to prevent contact between the two electrodes (*i.e.* short-circuiting the battery) and to allow the transport of ions in the electrolyte [27]. Since the ionic conductivity of the electrolyte is much smaller than the electronic conductivity in the metal, the LIB cell is made of large area electrodes separated by a narrow electrolyte film [26]. The electrical energy is generated at the surface of the electrodes where redox chemical reactions convert chemical into electrical energy. These reactions are reversible in a rechargeable battery. The LIB setup can be represented by the following shorthand notation:

\[ \text{C} | \text{LiPF}_6, \text{EC}, \text{DCM} | \text{LiCoO}_2 \]

By convention, the electrode on which oxidation happens during discharge of the battery is termed anode, while the one where reduction happens during discharge is termed cathode [28].

The commercial anodes typically consist of graphite, mixed with carbon black (CB) as a conducting agent to improve the electrical conductivity and polyvinylidene fluoride (PVDF) as a binder to hold together the particles of the active material and the conductive agent and to properly attach them to the current collector (*e.g.* Cu) which then connects the redox region of the battery to the external circuit [29, 30]. Similarly, the cathode
consists of LiCoO$_2$ powder mixed with CB and PVDF and it also rests on a current collector (e.g. Al) [31].

The working principle of the battery can be explained as a migration of Li$^+$ ions from one electrode to the other (Figure 1.3). During the charging process, there is a transfer of Li$^+$ ions from the LiCoO$_2$ electrode towards the graphitic electrode, where they get intercalated in between the graphite layers. In that case, on the cathode, there is the oxidation reaction, while on the anode there is the reduction reaction. During the discharging process, the opposite happens. That is, Li$^+$ ions get transferred from the anode towards the cathode, with the oxidation now happening on the graphitic electrode, while the reduction takes place on the LiCoO$_2$ electrode. In both cases, during the oxidation, there is a release of electrons that travel through the current collector towards the outside circuit where they provide electrical energy for an electrical load. This process of charging and discharging an LIB can be repeated a number of times and the overall redox reactions for the typical LIB cell can be described by:

- **Half-reaction 1:** $C_y + xLi + xe^- \leftrightarrow C_yLi_x$
- **Half-reaction 2:** $LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$
- **Overall redox reaction:** $LiCoO_2 + C_y \leftrightarrow Li_{1-x}CoO_2 + C_yLi_x$

The first step in an LIB cell is always the delithiation/oxidation of LiCoO$_2$ together with the lithiation/reduction of graphite. At that time, there is also the formation of passivating layers on both cathode and anode, with the one on the anode being called solid electrolyte interphase (SEI), due to decomposition of the electrolyte that prevents further
irreversible processes and provides metastable conditions for the reversible charging and discharging of the battery. In fact, the formation of the SEI layer presents a number of advantages some of which is that the SEI is electrically insulating and is almost impenetrable to the electrolyte molecules which, in turn, suppresses the further growth of the SEI layer. Otherwise, all Li$^+$ ions would be used for SEI formation and the cycling of the batteries would be impossible. Lithium ions, instead, can pass through the SEI layer and can proceed to lithiate or delithiate the active material of the anode [32].

1.4 Anode Materials

The best anode material, capacity-wise, would be pure Li. It has the highest theoretical specific gravimetric capacity (3860 mAh g$^{-1}$), but its big disadvantage is that Li metal suffers from poor cyclability. Besides, Li metal exhibits dendritic growth during lithiation/delithiation which can short-circuit the battery creating safety issues [33]. All of that propelled the search for other candidates to replace Li and today the selection of possible anodes is quite wide.

Various anode materials have different Li$^+$ ion storage mechanisms and as such they can be divided into intercalation, alloying and conversion-type anodes.

1.4.1 Intercalation-Type Anodes

The most famous representative of this group is graphite. The rest of the members comprise other C materials, as well as some Ti-based compounds (e.g. TiO$_2$, Li$_4$Ti_5O$_{12}$). The storing mechanism is based on the intercalation of Li$^+$ ions in between the layered
structure of the host material, without destroying its original crystal, and subsequent de-intercalation of the same Li$^+$ out from the host material. For that to happen the host material must be crystalline and it must have empty spaces to store guest ions [34]. Although graphite has been used commercially, its biggest disadvantage is the fact that it has low energy densities.

1.4.2 Allowing-Type Anodes

This type of anodes store Li$^+$ ions according to an alloying/de-alloying mechanism (at potentials less than 1 V vs. Li/Li$^+$) and has been the focus of much of the recent research effort on LIBs. These materials alloy with Li$^+$ ions and form various compounds according to the following equation: $X + yLi \leftrightarrow Li_yX$

The examples of materials comprising this group are Si, P, Sn, Ge, SiO and SnO. The most sought after parameter of these anodes is their specific charge capacity (Figure 1.4) which ranges from around 990 mAh g$^{-1}$ for Sn, up until 3579 mAh g$^{-1}$ for Si [35]. When that is compared to the theoretical specific capacity of graphite (372 mAh g$^{-1}$), it is easy to see why these materials are attractive. Their main drawback, however, is the fact that they have poor life cycle due to the enormous volume expansion and contraction during the lithiation and delithiation. That causes the pulverization of the anode and the subsequent loss of contact with the current collector. The most promising ways of overcoming these problems usually revolve around using nano-sized alloying materials and/or making composites of these materials together with some other that may act as a buffer aimed
at mitigating the huge volumetric changes in these anodes. That way the contact with the current collector is preserved.

Figure 1.4 Alloying and conversion-type anode materials compared according to specific capacity and potential (LTO = lithium titanate) [33]

1.4.3 Conversion-Type Anodes

This group consists of transition metal compounds such as phosphides, sulfides, oxides, nitrides. The mechanism is based on the oxidation (or reduction) of transition metals together with formation (or decomposition) of lithium compounds that can be expressed as (X=transition metals and Z = S, P, O, N):

\[ X_mZ_n + yLi + +ye^- \leftrightarrow Li_yZ_n + mX \]

These anodes have higher reversible capacities than the graphite ones (Figure 1.3), but the problem lies with the fact that large overpotentials are needed to drive the reactions
which results in big initial irreversible capacities. These anodes are also tested in large voltage ranges versus Li, reducing the voltage difference between the anode and the cathode and reducing the energy density and efficiency of the battery [35].

1.5 Cathode Materials

The most commercially successful cathodes are the intercalation-type ones, with LiCoO$_2$ (also LCO) being the most prominent example. These types of cathodes can reversibly store guest ions (e.g. Li$^+$) into a host network that is usually made of metal chalcogenides, transition metal oxides and polyanion compounds. Although LiCoO$_2$ is commercially successful, research has been focusing on improving the stability and reducing the cost of batteries. Therefore, Mn, Ni and Fe-based compounds have also been proposed as cathode materials. LiNiO$_2$ (LNO), which forms a layered structure, where Li$^+$ ion transport is achieved in two dimensions between the layers, is cheaper and has better charge capacity than LiCoO$_2$, but it is also less stable with the tendency of nickel ions to occupy Li$^+$ sites. LiMn$_2$O$_4$ (LMO) forms a spinel structure where Li$^+$ pathways are a three-dimensional network of channels instead of planes that are present in a layered structure. It is cheaper and safer than LiCoO$_2$, but it has lower charge capacity than the cathode materials with a layered structure [36]. LiFePO$_4$ (LFP) is the most commonly used phosphate for cathodes and is part of polyanion compounds. It has an olivine structure, where Li$^+$ ion transport is possible only in one dimension and has a good thermal stability and high power capability. Its major drawback is its low potential and low electrical and ionic conductivity.
There are also conversion-type cathodes, where a redox reaction, during lithiation/delithiation, causes the recombination of the chemical bonds and changes the crystalline structure by subsequent breaking and reforming of chemical bonds. These usually include various metal halides with two or more valence metal ions [33]. Conversion-type cathodes usually offer a higher energy storage than the intercalation-type cathodes where only one Li$^+$ ion per structural unit is allowed to be inserted [38].

1.6 Carbon Nanotubes

Carbon is a group IV element that can be present in several allotropic forms. One of these are carbon nanotubes (CNTs) which exhibit high thermal and electrical conductivities and which are characterized by extremely high strength and stiffness (high tensile strength.
and elastic modulus). These are the result of the bonding between carbon atoms in individual tubes. A carbon nanotube is a one-dimensional material made up of hexagonally arranged C atoms connected to each other by $sp^2$ hybridized bonds. It can be envisioned as a single graphene layer rolled up to form a tube, if we are talking about single-walled carbon nanotubes (SWCNTs, with usual diameters of around 1 nm). Alternatively, as more graphene layers are considered and rolled up to form concentric tubes, then we refer to multi-walled carbon nanotubes (MWCNTs, with usual diameters from few to tens of nanometers). This rolling up can be done in a way to obtain chiral or non-chiral geometries. The former (also known as helical structures) comprise of geometries in which all of the C-C bonds are at a certain angle to the tube axis, whereas the former comprise of those geometries more commonly known as armchair and zigzag. In the armchair geometry, a pair of C-C bonds on opposite sides of each hexagon are perpendicular to the tube axis while in the zigzag geometry, these same bonds are parallel to the tube axis (Figure 1.5 a).

![Figure 1.6 a) Single-walled carbon nanotubes of different chirality; b) chiral vector][39]
The chirality can be represented by the chiral vector $\mathbf{C}_y = n \mathbf{a}_1 + m \mathbf{a}_2$ ($n$ and $m$ being vector coefficients while $\mathbf{a}_1$ and $\mathbf{a}_2$ being unit vectors) which determines in what direction the graphene sheet is rolled up (Figure 1.5 b) as well as the diameter of the nanotubes and whether the nanotube will be metallic or semiconducting. The head and tail of this chiral vector, defined by an origin lattice point $(0,0)$ and another lattice point $(n,m)$, are then overlapped obtaining a carbon nanotube. If $m = 0$, the nanotube will be in a zigzag configuration and if $n = m$ or $n = 2k$ and $m = -k$, resulting in a $(2k,-k)$ vector, the nanotube will be in an armchair configuration. Every other combination will result in a chiral configuration. Carbon nanotubes will be metallic if they are in armchair configuration or more generally if the following equation is satisfied:

$$\frac{2n + m}{3} = \text{integer}$$

If the above equation is not satisfied, the nanotubes will be semiconducting [39].

Three different techniques are usually used to produce carbon nanotubes and these are electric-arc discharge, pulsed laser deposition and chemical vapor deposition (CVD). Electric-arc discharge method consists in creating a direct current (DC) arc discharge between two graphite rods in an inert atmosphere at low temperature, where carbon is vaporized from one rod and deposited as nanotubes, together with many C impurities, on the other. To obtain SWCNTs, one composite rod, made of graphite and various transition metal catalysts (Ni, Fe, Co) is usually needed.[40] Pulsed laser deposition enables the production of nanotubes of high quality and purity. The operational principle is based on
laser evaporation of a graphite target with C atoms then depositing on a substrate in the form of nanotubes. Using a graphite with incorporated transition metal catalysts enables the formation of SWCNTs, where catalysts act as nanotube growing sites. Otherwise, MWCNTs are formed. CVD is the most common method for the production of nanotubes for lab-scale usage and it is based on the decomposition of precursor gasses (e.g. acetylene) which act as a source of carbon atoms that impregnate the transition metal catalyst particles from which the nanotubes grow [41].

Carbon nanotubes have been extensively used for various electrochemical purposes. Due to their high theoretical electrical conductivity and low mass, they have been used as conductive additives for anodes and cathodes in batteries, enabling to reach good conductivities with a low additive weight which results in better charge capacities. In addition, CNTs have good thermal conductivity, allowing for better heat dissipation and thus making composite electrodes much safer. They also have excellent strength and flexibility, which is useful to prevent cracking of composite electrodes, especially those that use alloying-type materials [42].

1.7 Red Phosphorus

Phosphorus is a group V element and may thus benefit from increased Li$^+$ conductivity when compared to group IV alloying-type materials (e.g. Si, Ge, Sn). It is also in period III which means that it may have more valencies than the ones in group II and has enough mass to remain in the solid state at room temperature [35]. Elemental P has a high theoretical gravimetric capacity of 2596 mAh g$^{-1}$, by forming a Li$_3$P phase, and the highest
volumetric one at 2266 mAh cm\(^{-3}\) [33]. It is the 11\(^{th}\) most prevalent element in the Earth’s crust [43] and is obtained from phosphate rock deposits for commercial purposes [44].

It is speculated that P has multiple allotropic forms, out of which white, red and black are the most common ones and confirmed experimentally. White P has a tetrahedral crystal structure with a very high angular strain, as the angle is at 60 °. Because of that, it is the least stable and the most reactive (self-ignition temperature being 34 °C in air) allotrope [45]. In addition, it is very toxic excluding it from LIB applications. Black P is the least reactive and the most stable form that can be present in an orthorhombic, rhombohedral, cubic and amorphous forms. The most common structure is orthorhombic which is composed of puckered layers of P atoms, making it structurally similar to graphite. Black P is, however, notoriously hard to produce, needing inert atmosphere, high temperature, high pressure and it is hard to come by on the market [46]. That leaves us with red P (Figure 1.5) which is widely available, safe and inert. Red P is famous for its amorphous structure, however, there is some uncertainty on the exact atomic structure which is still a matter of debate in the scientific community [37, 47]. The classical view, depicted in Figure 1.7b, represents red P as made of pyramidal subunits with one P-P bond broken, which causes the lowering of the angular strain and thus making red P less reactive[45, 48]. The latest conclusion, however, which agrees with neutron diffraction data, presents red P as made of triangular and tetrahedral subunits linked by chains of P atoms [47].
Figure 1.7 Atomic structures of a) white P; b) classical representation of red P; c) one layer of black P (i.e. phosphorene); c) orthorhombic black P

On the other hand, it is also known that red P can exhibit a number of crystalline modifications [49]. Out of these, two crystalline structures are recognized as Hittorf’s violet phosphorus [46] and fibrous red phosphorus [50]. Both variations consist of pentagonal tubes of covalently bonded P atoms, while the tubes themselves are held together by weak van der Waals forces. The difference between the two lies in the fact that, for the Hittorf’s violet phosphorus (Figure 1.8a), the layers of these pentagonal tubes are stacked one over the others in a way that the tubes are always parallel to each other. For fibrous red phosphorus (Figure 1.8b) these layers of pentagonal tubes are placed orthogonally on top of each other [50].
The biggest problem with red P is that it stores Li\textsuperscript{+} ions through the alloying mechanism and thus it suffers from enormous volumetric changes during lithiation and delithiation, causing rapid capacity fading, due to loss of electrical contact with the current collector. The current consensus is that batteries based on P should be prepared as nanocomposites where P nanoparticles should be finely dispersed in between some form of C materials that will act as conductive pathways and as a buffer to P expansion during lithiation/delithiation. The logic behind nanosizing P is to have a more intimate contact between P and C and to have a non-localized expansion induced strain from P.

There have been several attempts of using red P for LIBs and Na-ion batteries (NIBs). The employed strategies were always revolving around using P and some allotrope of C as a composite material. The synthesis of the composites was either through high energy mechanical milling (HEMM) [52, 53] or various sublimation-adsorption techniques [1, 54-58]. Yuan et al. [53] obtained a red P - carbon nanotube composite by ball milling red P and carbon nanotubes in the 8:2 weight ratio for 48 h. Li et al. [57] used the vaporization and subsequent deposition of red P on porous carbon nanofibers inside an Ar-filled
stainless steel vessel. Marino et al. [56] used the mixing of red P and activated carbon for 15 min before using an evacuated silica ampoule to vaporize red P and deposit it on the activated carbon.

1.8 Scope and Motivation

In the search for better battery anodes for lithium-ion batteries, there has been relatively little work done on phosphorus-based anodes. Phosphorus is known to have extremely high gravimetric and volumetric specific charge capacities and as such it is an attractive material for battery anodes. Its big disadvantage, however, is that upon lithiation and delithiation the volume of P changes a lot, causing the pulverization of the anode. From the literature search, it was seen that nano-sizing P and using various C materials to limit its expansion during lithiation and delithiation proved to be an effective strategy for improving the electrochemical performance of the half-cells. Herein, we will attempt to improve the lithium-based electrochemical behavior of red P by making composites with different weight ratios of P and single-walled carbon nanotubes, where the nanotubes will act a buffer to the big changes in volume and thus mechanically stabilize the anode. Furthermore, the composites will be characterized by TGA, Raman spectroscopy, XRD, electron microscopy, XPS and FTIR to determine the amount, morphology and structure of the individual constituents of the composites. In the end, electrochemical characterization of the composites will be done.
Chapter 2

EXPERIMENTAL METHODS AND CHARACTERIZATION

The main idea behind this work is to obtain a composite of phosphorus and SWCNTs, where the latter act as a buffer to phosphorus volumetric expansion. It is a known fact that, because of the alloying mechanism of storing Li\(^+\) ions, phosphorus changes its volume drastically during lithiation and delithiation or sodiation and desodiation [59-62].

Figure 2.1 Pulverization of P (a) and buffering effect of SWCNTs (b) during electrochemical cycling
That causes loss of contact with the current collector and subsequent rapid capacity fade, rendering P useless as a material for battery anodes (Figure 2.1a). If phosphorus is mixed with SWCNTs in a uniform manner, it is possible to mitigate this expansion and improve the anode electrochemical behavior (Figure 2.1b).

2.1 Materials Synthesis

The SWCNT and red P composite has been synthesized through the sublimation-deposition method (Figure 2.2). The process started with the washing of red P in deionized water (DIW) with magnetic stirring at 300 RPM for 20 min. That was followed by vacuum filtering to separate solid red P particles from water and further drying in vacuum at 100 °C overnight. This step is crucial since phosphorus particles, when exposed to oxygen and humidity, get covered with hygroscopic and acidic oxides, giving them a wet and sticky appearance (Figure 1.5) and raising the possibility of suppressing the sublimation and/or introducing impurities in the final material [58].

The next step consisted in hand grinding red P and SWCNT in a weight ratio of 7:3 for 60 min and sealing the as-obtained mixture in a quartz ampoule under vacuum (<10⁻³ mbar). The glass ampoule was then heated to 600 °C to sublimate P, which has a sublimation point of 416 °C, and held at this temperature for 2 h. The temperature was deliberately chosen way over the sublimation point to better promote the diffusion of P gas in between the SWCNTs so that red P becomes well dispersed and the strain caused by its change of volume during lithiation/delithiation is not concentrated in a few points but is spread throughout the SWCNT network. Afterward, the temperature was lowered to 300
°C and held at this temperature for 48 h to help convert white P to red P [48, 63]. After the ampoule naturally cooled down to room temperature, it was opened inside a fume hood and the composite was collected. This composite was referred to as “7:3 composite”.

For comparison, the same procedure was applied to obtain a red P and SWCNT composite in 8:2 weight ratio. This composite was referred to as “8:2 composite”.

![Figure 2.2 Schematic representation of the red P – SWCNT composite synthesis](image)

### 2.2 Electrode Fabrication

The as-prepared composite was mixed with polyvinylidene fluoride (PVDF, Sigma-Aldrich) and acetylene black (AB, Alfa Aesar) in a weight ratio of 85:10:5, to form a slurry which was then cast on a Cu foil with a simple laboratory spatula. After that the electrodes were dried in vacuum at 100 °C overnight and pressed, which was followed by an after-drying
step in vacuum at 100 °C for 1hr and one more pressing step. This double drying is done to ensure that electrodes are absolutely dry, so that no NMP is introduced into the electrochemical cell. All electrodes were 5 x 10 mm in dimensions and had an active material loading around 2 mg cm⁻².

2.3 Electrochemical Measurements

All electrochemical measurements were done on a Bio-Logic potentiostat (VMP3, Bio-Logic Science Instruments SAS, France) using LIR2032-type coin cells in a half-cell format. The cells were assembled inside an Ar-filled glovebox (LABstar, MBraun) with the composite material acting as working electrode and Li metal as counter and reference electrodes. Celgard 2325 (25 µm pore diameter, PP/PE/PP trilayer membrane) microporous polymer film was used as separator and 1.0 M LiPF6 in EC:DEC (1:1 by volume) was used as electrolyte.

The galvanostatic charge-discharge profiles were tested at current densities from 150 mA g⁻¹ to 1000 mA g⁻¹, between 0.001 and 2 V (vs. Li/Li⁺). After the cells had reached the cutoff voltage they were relaxed for 1 s before continuing with the measurements. The cyclic voltammetry (CV) was cycled between 0.001 and 2.5 V (vs. Li/Li⁺) at a scan rate of 0.5 mV s⁻¹.

All specific charge capacities mentioned where calculated on the basis of the weight of the whole red P and SWCNT composite. We believe it is important to mention this detail
since many scientific publications on the topic report the specific charge capacity on the basis of the weight of red P only and thereby inflate the capacity values of their anodes.

2.4 Materials Characterization

The techniques used for the characterization of the composites were powder x-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDX), x-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA).

2.4.1 Powder X-Ray Powder Diffraction

X-ray diffraction (XRD) is a technique used for analyzing the atomic and molecular arrangement of materials. With it we can identify the material, we can determine its crystal structure and degree of crystallinity, we can obtain the size of crystallites, the size of the unit cells, etc. The operating principle relies on the fundamental property of waves, which is diffraction. Diffraction is defined as a phenomenon where an incoming wave is scattered by a periodic array of obstacles, producing constructive interference at certain angles [64]. Since atoms in a crystal are periodically arranged, x-rays will be scattered by them and unique diffraction peaks on the XRD spectrum will be visible. In an amorphous material, there is no long range order and therefore no peak can be obtained. For a peak to appear, Bragg's law must be satisfied (Figure 2.3): \[ 2d \sin \theta = n\lambda \]
In the above equation \( d \) is the distance between two planes of atoms, \( \theta \) is the angle of incidence of the wave, \( n \) is a positive integer and \( \lambda \) is the wavelength of the incident wave. The obtained XRD spectrum will then be a plot of peak intensity as a function of angle \( \theta \).

![Figure 2.3 Bragg condition [65]](image)

XRD has been used to confirm the presence of red P and SWCNT in the composites. We used a Bruker D8 ADVANCE (Bruker, USA) from \( \theta = 10^\circ \) to \( \theta = 90^\circ \) with a scan rate of 5 deg min\(^{-1}\) and increment of 0.02 deg.

2.4.2 Fourier Transform Infrared Spectroscopy

FTIR is a characterization technique where a plot of the absorption of different infrared wavelengths is obtained. A big advantage of this technique is that materials in any state may be studied (liquids, solutions, powders, pastes, films, fibers, ...) [66]. It is based on passing an infrared radiation through a sample and then determining what fraction of the incident radiation is absorbed at what energies. Each energy value with a peak in the spectrum corresponds to the frequency of vibration of part of the sample. For the
molecule to be "infrared-active", the electric dipole moment of the molecule must change during the vibration, therefore molecules that are homonuclear and diatomic are not "infrared-active". The term "vibrations" in this case connotes either the change in bond length (i.e. stretching) or the change in bond angle (i.e. bending). The former can be in phase (i.e. symmetrical stretching) or out of phase (i.e. asymmetric stretching), while the latter can result in deformation, rocking, wagging, twisting (Figure 2.4) and for more complex molecules, in-plane bending and out-of-plane bending.

![Figure 2.4 Bending modes of vibration][66]

The FTIR used in this work was the Thermo Scientific Nicolet iS 10 FT-IR Spectrometer (Thermo Fisher Scientific, Massachusetts, USA). It has been used to determine the nature of bubble formation on the electrodes, which have been analyzed before and after the hydraulic pressing. The characterization was done in the transmittance mode with the resolution of 32 cm\(^{-1}\) and the number of scans being 16. The source used was IR from 400 to 4000 cm\(^{-1}\).

2.4.3 Raman Spectroscopy

This is a technique that can give plenty of information regarding the quality, structure and type of material. The operating principle is such that when a material is irradiated by laser
source in the ultraviolet (UV) – visible region, a *Rayleigh* scattering happens which will have the same frequency as the incident beam or a *Raman* scattering happens which will end up having a $v_0 \pm v_v$ frequency, where $v_0$ is the frequency of the incident beam and $v_v$ is the vibrational frequency of the molecule. For $v_0 - v_v$ and $v_0 + v_v$ we end up having *Stokes* and *anti-Stokes* lines, respectively. What is measured is, thus, the vibrational frequency as a shift with respect to the incident beam frequency (Figure 2.5) [67].

![Figure 2.5 Stokes and anti-Stokes vibrational lines](image)

In this work *Witec alpha 300 RA* (Witec, Ulm, Germany) has been used with the laser source of 633 nm. It has been used to confirm the presence of red P and SWCNTs in the composite, to see the quality of the nanotubes and to verify P-C bonding. All of the spectra were taken with the 10x objective lens, integration time of 0.5 s and 10 accumulations. The sample was prepared by manually pressing the synthesized material on microscope glass slide.

### 2.4.4 Scanning Electron Microscopy

SEM is part of electron microscopy techniques where the image is obtained by a focused beam of electrons. The beam is generated by an electron gun and then passed through a
series of electromagnetic lens (condenser and objective) that help decrease the probe size of the electron beam to few nanometers. The beam of electrons is constantly under vacuum and after hitting the sample various signals are generated (Figure 2.6). With the help of the scanning coils, the beam is moved in a raster pattern.

Figure 2.6 Electron beam and sample interaction in SEM [69]

The SEM that was used was the FEI Nova NanoSEM (FEI Company, Oregon, USA). The sample was prepared as a 0.2 mg ml$^{-1}$ suspension of the material in ethanol. The suspension was then sonicated for 30 min in a bath sonicator and drop cast on an aluminum SEM stub. SEM was operated at 5 kV and the sample was positioned 5 mm from the polepiece. The images were obtained by capturing secondary electrons with the "through-the-lens" detector (TLD). SEM characterization was done to analyze the morphology of the composite material.
2.4.5 Transmission Electron Microscopy

TEM is an electron microscopy technique where the beam of electrons is passed through the sample and the shadow image is collected on the charge coupled device (CCD) underneath it. The electrons that are generated by the electron gun pass through a series of electromagnetic lens in the vacuum that allow directing, focusing and controlling the size of the electron beam which then passes through the sample generating signals (Figure 2.7). The apertures that are present in between the lens allow the control of diameter and intensity of the electron beam.

![Figure 2.7 Electron beam and sample interaction in a TEM [70]](image)

The TEM used for this work was the FEI Titan (FEI Company, Oregon, USA) operated at 300 kV. The first condenser aperture was 2000 µm, the second condenser aperture was 150 µm while the objective aperture was not used. TEM was done to analyse the
morphology of the composite. The sample was prepared for TEM analysis by making a suspension of 0.2 mg ml\(^{-1}\) of the material in ethanol. The suspension was then sonicated for 30 min in a bath sonicator and drop casted on a lacey carbon TEM Cu grid. The grid was then left to dry in air.

2.4.6 Selected Area Electron Diffraction

Selected area electron diffraction (SAED) is closely related to TEM and is in fact done inside the TEM. It is a crystallographic technique where the electrons, taking into consideration their wavelike nature, interact with atoms and because the wavelength of the electrons is around hundred times smaller than the spacing between the atoms, the atomic crystal structure acts as a diffraction grating so the electrons are diffracted. The electrons then, according to the Bragg reflection (Figure 2.3) [71], form a diffraction pattern out of which the orientation, state of the matter, lattice spacing and other information can be deduced. SAED has been used to verify the structure of the materials.

2.4.7 Energy Dispersive X-Ray Spectroscopy

EDX is an analytical technique used for the chemical characterization of the sample. It uses an excitation source, either electron beam or x-rays, to eject electrons from the inner shells of the atoms, creating a hole which is then filled by another electron from a shell with higher energy value (Figure 2.8). To get to the lower energy shell, the electron has to lose energy and this is achieved by emitting x-rays. The energy of the emitted x-rays are specific to each and every element and as such various elements present in the sample
can be detected. The number and energy of these x-rays are then plotted to obtain an EDX spectrum.

![Diagram of x-ray generation in EDX characterization](image)

**Figure 2.8 Generation of x-rays in EDX characterization[72]**

The EDX used in this work was the *EDAX Octane Silicon Drift Detector* (EDAX, Inc., New Jersey, USA) connected to the FEI Titan TEM. The elemental analysis was done during the TEM characterization of the sample. The second condenser aperture of the TEM during the EDX measurements was at 30 µm and there was no tilting of the stage.

### 2.4.8 X-Ray Photoelectron Spectroscopy

XPS is used to analyze the surface chemistry of the sample. Its operating principle is based on the photoelectric effect, that is irradiation of the material by X-rays and the measurement of the kinetic energy of the emitted photoelectrons (*i.e.* electrons ejected from the material by electromagnetic radiation) from the material's surface (Figure 2.9). If the energy of the incident photon is known, the measured energy of the ejected
photoelectron can then be used to measure the binding energy of the electronic orbit from which it has been ejected [73].

In this work *Amicus* XPS (Kratos, Manchester, UK) has been used. The synthesized material has been subjected to XPS characterization to verify the existence of bonding between red P and C.

![Figure 2.9 Emission of a photoelectron in XPS [73]](image)

2.4.9 **Thermogravimetric Analysis**

TGA is a technique whose principle of operation is based on changes in the mass of the sample as a function of temperature. The sample is usually heated at a constant rate and the atmosphere used may be reactive, oxidizing or inert. The results are typically plotted as a curve in a mass versus temperature/time graph. Taking the first derivative of the obtained curve with respect to temperature/time will yield a differential thermogravimetric plot (DTG). It is used for the study of those phenomena which are accompanied by the change of mass with the change of temperature. Some examples
include sublimation, adsorption, desorption, uptake or loss of water and decomposition [74].

For this work *NETZSCH TG 209 F1 Libra* TGA (NETZSCH Group, Selb) has been used with the temperature range from room temperature to 1000 °C, with a flow of N₂ gas at the purge rate of 20 ml min⁻¹. The heating rate was 10 °C min⁻¹. All samples were loaded on alumina crucibles with the loading mass of about 5 mg. Before the start of TGA of the composite, TGA measurements were done firstly by performing a blank measurement (*i.e.* empty crucible) to correct the buoyancy effect because of variations in the density of the gas as the temperature changes and secondly by performing the TGA of calcium oxalate monohydrate to assess the accuracy of the instrument.
Chapter 3
RESULTS AND DISCUSSION

3.1 Thermogravimetric analysis of the composites

The synthesized composites, with weight ratios of 7:3 and 8:2, were first subjected to a TGA to confirm the amount of individual constituents in the composites.

Figure 3.1 TGA in N₂ flow of a) SWCNT; b) ground red P; c) 7:3 weight ratio composite; d) 8:2 weight ratio composite
For SWCNTs (Figure 3.1a) there is a constant and moderate loss of weight due to the vaporization of various functional groups. Figure 3.1b shows that red P starts sublimating at around 400 °C with the degradation of the material characterized by a sudden gain of weight before rapidly losing it, and ends the sublimation process at around 500 °C [74]. Figure 3.1c and Figure 3.1d show a similar behavior with the sublimation of phosphorus between 400 °C and 500 °. The weight loss after 500 °C is attributed to the vaporization of functional groups from CNTs. From Figure 3.1c it can be seen that the 7:3 composite ends up having around 59.5 % of red P and 40.5 % of SWCNTs, despite the fact that during the synthesis of the material 70 % of the total mass was allocated to red P and 30 % to SWCNTs. Figure 3.1d similarly shows that the 8:2 composite ends up having 68 % of red P and 32 % of SWCNTs despite starting the synthesis of the material with 80 % of the total mass being red P and 20 % SWCNTs. These differences in weight ratios are due to the fact that some of the material is lost during the synthesis of the composites (i.e. red P depositing on the walls of the glass ampoule during the heat treatment).

### 3.2 Raman Spectroscopy and Powder X-Ray Diffraction Analyses

Raman spectroscopy and powder XRD analyses have been performed to verify the presence and the structure of the different phases in the final composites.
In the Raman data (Figure 3.2), the radial breathing mode (RBM) and D and G bands of the SWCNTs are clearly visible. The RBM is unique to the carbon nanotubes and it is present due to the “breathing” motion of the nanotubes (i.e. C atoms moving in phase in a radial direction of the tube). It has a dominant peak at 251 cm$^{-1}$ which would correspond to an average diameter of the nanotubes being approximately 1 nm [75-77]. The value was obtained using the equation that relates the frequency of the radial vibration to the tube diameter:

$$\omega_{\text{RBM}} = \frac{c_1}{d} + c_2$$

Nanotube diameter is represented by $d$ and the frequency of the radial vibration is represented by $\omega_{\text{RBM}}$, while $c_1$ and $c_2$ are empirically obtained coefficients that depend on the in-plane graphite lattice constant [78]. It is important to note that this equation
gives only an approximate value of the nanotube diameter since the nanotubes are approximated by a homogeneous cylinder [76].

The D band at around 1300 cm\(^{-1}\) can be assigned to the breathing motion of \(sp^2\) bonded atoms in a ring configuration at the edges of graphene layers and the breaking of symmetry due to defects, discontinuity in the crystallites and stacking disorder in the crystal structure of graphite [56, 79, 80]. Since the relative intensity of the D band is very low, it can be concluded that SWCNTs used in this work have very little of the above-mentioned defects. Moreover, there is no noticeable shift in the D band of the composites compared to the D band of starting SWCNTs, which indicates that there is no chemical bonding between C and P [81]. This will be further confirmed by the XPS analysis.

In Figure 3.2, it can be seen that the G band consists of two, clearly separated components. The higher frequency component is labeled as \(G^+\), while the lower frequency component is labeled as \(G^-\). Their existence confirm the single walled-nature of the nanotubes. On the other hand, the splitting of the G band in MWCNTs is usually not noticeable and it ends up having an asymmetric line shape [82]. The \(G^+\) peak, at around 1580 cm\(^{-1}\), originates from the C-C bond stretching in the axial direction of the nanotubes. The additional \(G^-\) peak, at around 1547 cm\(^{-1}\), is separated from the \(G^+\) one and it usually gets separated even more as the diameter of the tubes decreases. It originates from the C-C bond stretching in the circumferential direction of the nanotubes [82]. Finally, the shapes of the G band peaks (Figure 3.3) confirm that the SWCNTs are mostly semiconducting [83, 84]. The difference between semiconducting and metallic nanotubes
can be inferred by the line shape of the G peaks. In semiconducting SWCNTs both $G^+$ and $G^-$ peak have a Lorentzian line shape and the intensity of the $G^+$ peak is much stronger than the one for the $G^-$ peak. In metallic SWCNTs both components have similar intensity and the $G^-$ peak exhibits the asymmetric Breit-Wigner-Fano line shape [85].

![Lorentzian line shapes of the $G^+$ and $G^-$ peaks of the SWCNTs](image)

Figure 3.3 Lorentzian line shapes of the $G^+$ and $G^-$ peaks of the SWCNTs

In Figure 3.2 we can also see the Raman data of red P and the composites. Red P is characterized by a number of peaks between 300 cm$^{-1}$ and 500 cm$^{-1}$, which is consistent with the literature [86-88]. The peak at around 349 cm$^{-1}$ can be assigned to the B1 mode, the peak at around 392 cm$^{-1}$ can be assigned to the A1 mode and the peak around 458 cm$^{-1}$ can be assigned to the E1 mode [81]. Both composites show a similar Raman
fingerprint, with the peaks corresponding to red P being very low in intensity. We can conclude that Raman spectroscopy confirms the existence of both SWCNTs and P in the final composites and that since there is no detectable peak shift, these composites are a purely physical mixture of phosphorus and SWCNTs, which agrees with the previous research done on carbon-phosphorus composites [1, 53, 81].

Figure 3.4a shows the XRD diffraction peaks of the starting materials and the final composites. Phosphorus shows an amorphous structure that can be attributed to the red allotrope, with broad peaks at 15.5 ° and 34 ° [54, 57]. There is no presence of white P [89] or black P peaks [90, 91]. SWCNTs show peaks at 22 ° and 43 °. The former can be attributed to the (002) plane of the turbostratic structure, which, due to the translation and/or rotation of graphene layers, has a larger interlayer distance than that of graphitic structure. In fact, because of the extremely weak peak at 26 ° it can be concluded that there is a relative shortage of graphitic particles [92]. The SWCNTs peak at 43 ° corresponds to the (100) plane with SWCNTs having only one rolled graphene sheet [93].

The broadness of the SWCNTs peaks points toward the lack of the long range order in the sample owing to the random directions the nanotubes are pointing at.

For the 7:3 composite it can be seen that the broad peaks corresponding to red phosphorus at 15.5 ° and 34 ° are still present, while the peaks for SWCNTs are buried under the noise. Overall, there doesn’t seem to be much difference between the starting red P and the 7:3 composite, from which we can conclude that amorphous phosphorus is mostly covering the nanotubes and there is no noticeable phase change. The 8:2
composite, on the other hand, shows an increase in the sharpness and the number of diffraction peaks, indicating a transition towards new, more crystalline phases. It can be noticed, in fact, that the broad red P peaks at around 15.5 ° and 34 ° are decidedly sharper and surrounded by other smaller peaks. Comparing this XRD data to the XRD data of the fibrous phosphorus it can be seen that the peak positions and intensities are closely matching (Figure 3.4b). Fibrous phosphorus crystallizes in a triclinic system with a P-1 space group (JCPDS no. 04-012-1669). Other known crystalline forms of phosphorus, like Hittorf’s violet phosphorus and black phosphorus have been excluded on the basis that their XRD data does not match the diffraction peak positions for the 8:2 composite as well as the fibrous phosphorus XRD data does. The peak at around 15.5 ° can be assigned to the (200) plane, while the peak at around 34 ° can be assigned to the (232) plane. In the end, it is possible to conclude that what is obtained is an SWCNTs, amorphous red P and fibrous P heterogeneous mixture.

Figure 3.4 (a) XRD patterns of starting materials and final composites and (b) comparison between XRD patterns of fibrous P, red P and 8:2 composite
The same procedure has been employed to make both the 7:3 and 8:2 composite, with the only difference being the different weight ratios of the red P and the SWCNTs. So how come the 8:2 composite shows a much more crystalline structure than the 7:3 composite? The answer may be found in the fact that during the synthesis a similar amount of starting materials have been used and the volume of the ampoules was also similar. It must follow then, that in the case of the 8:2 composite, greater pressure is produced inside the ampoule since all of the phosphorus gets sublimated, as has been confirmed by optical microscopy where it was seen that no phosphorus grains were present after the heat treatment, whereas they were present before the heat treatment. This greater pressure, in addition to the confined spaces between the SWCNTs, forces the P atoms to favor a crystalline structure in the form of fibrous phosphorus.

3.3 Electron Microscopy Characterization

The SEM characterization of the samples of shown in Figure 3.5.

![SEM images of (a) red P and (b) SWCNTs](image.png)

Figure 3.5 SEM images of (a) red P and (b) SWCNTs
The red P is firstly ground and then characterized and in Figure 3.5a it can be seen that the size of the majority of the particles ends up in the single digit micron size (it was not possible to obtain the size distribution of the particles because of the inherent irregularity of their morphology). This confirms that manual grinding for 60 min using pestle and mortar is an effective way to reduce the particle size, in addition to breaking the branch-like structure of the starting red P. In Figure 3.5b it can be seen that the SWCNTs are closely interconnected, with empty spaces in between the bundles, and considering the innate high tensile strength of the SWCNTs [94, 95], it can be concluded that this structure has a potential to mechanically withstand the P volumetric expansions. Taking into consideration the latter and the fact that smaller particle sizes of the red P are obtained, it is believed that a more homogeneous mixture of SWCNTs and red P is obtained, which allows for a more intimate contact between them and thus for a more mechanically stable composite during lithiation and delithiation of P.

![SEM images of (a) 7:3 composite and (b) 8:2 composite (red arrows point towards coated bundles of nanotubes)](image-url)
Figure 3.6a and Figure 3.6b show the SEM characterization of the 7:3 and 8:2 composites, respectively. In both cases, it can be seen that the composites are made of a disordered network of SWCNTs that are coated with thick layers of P. In Figure 3.6b the nanotube bundles are harder to discern because of the higher amount of P that is covering them (the position of the bundles is shown by red arrows). Figure 3.7b and Figure 3.7c show a higher magnification image of the composites where the nanotube bundles are easier to locate.

Figure 3.7 SEM images of (a,b) 7:3 composite and (c,d) 8:2 composite (red arrows point towards coated bundles of nanotubes)
Comparing the 7:3 composite in Figure 3.6a and Figure 3.7b it can be seen that the morphology is highly heterogeneous and that it varies depending on the location on the composites. That is due to the uneven coating of SWCNTs and due to the fact that keeping P for a long period of time at 300 °C causes the aggregation of white P tetrahedrons into red allotrope P chains and thus P accumulates in certain locations on the composites.

Figure 3.8 (a) TEM image of red P, (b) HRTEM image of red P, (c) SAED image of red P, (d) TEM image of SWCNTs
The TEM characterization was done to complement the findings of the SEM characterization. Figure 3.8a and Figure 3.8b show the TEM and HRTEM micrographs of the ground red P. It can be seen that the structure is completely amorphous, confirming the XRD findings. Final proof was given by the selected area electron diffraction (SAED) image (Figure 3.8c) characterized by a single diffuse ring that is typical of amorphous materials. Figure 3.8d shows the TEM image of bundles of CNTs that confirm the previous conclusion that the nanotubes are tightly woven together with empty spaces in between, that may be occupied by phosphorus after the sublimation-adsorption process.

Figure 3.9 (a) TEM image of 7:3 composite, (b) HRTEM image of 7:3 composite, (c) TEM image of 8:2 composite and (d) HRTEM image of 8:2 composite
The TEM characterization of the composites expands on the SEM findings by showing that in both composites P is present all over and in between the carbon nanotube bundles.

In Figure 3.9a, it can be seen that in the 7:3 composite phosphorus remains in the amorphous state randomly agglomerating at various points, in addition to completely coating the carbon nanotube bundles (Figure 3.9b). These findings confirm the XRD conclusions, where it was seen that the 7:3 composite remained mostly amorphous, having very wide XRD peaks.

The 8:2 composite (Figure 3.9c and Figure 3.9d), instead, shows mixed crystalline and amorphous features that excessively cover the carbon nanotube bundles. From the XRD spectra, it was concluded that the crystallinity arises from the crystallization of red P into the fibrous phosphorus. In Figure 3.9d the red arrows points towards crystalline regions of the composite.

Figure 3.10 shows an HRTEM image of the 8:2 composite where region “1” shows the crystalline part and region “2” shows the amorphous part. It can be seen that the crystalline part is characterized by lattice fringes spaced around 0.55 nm one from the other and that corresponds to the (200) plane of the fibrous phosphorus. The fringes spaced around 0.28 nm one from the other would correspond to the (400) plane of the fibrous phosphorus [96]. Finally, it can be concluded that the TEM analyses confirm the XRD findings that the 8:2 composite is a heterogeneous mixture of SWCNTs, amorphous red P and crystalline fibrous P. This conclusion is reinforced by Figure 3.11 where the SAED pattern confirms the presence of both the amorphous and the fibrous red
phosphorus (i.e. interlayer distances obtained from SAED match with those obtained from XRD)

Figure 3.10 HRTEM image of the 8:2 composite

Figure 3.11 (a) TEM image of the 8:2 composite and (b) its SAED pattern
The EDX characterization has been done to confirm the chemical nature of the composites and, as it can be seen in Figure 3.12a and Figure 3.12b, the presence of both P and C has been confirmed for both composites.

Figure 3.12 EDX spectrum of (a) the 7:3 composite and (b) the 8:2 composite confirming the presence of P and C.
3.4 XPS Analysis

The XPS analysis has been done to analyze the interaction between C and P after the synthesis process and to verify the presence of phosphorus oxides. The analysis has been done on both 7:3 and 8:2 composites and because of the nature of the technique, the results are valid only for the surface of the electrodes.

Figure 3.13 XPS spectra of 7:3 composite: (a) survey spectrum, (b) O 1s level spectrum, (c) C 1s level spectrum and (d) P 2p level spectrum
In the survey spectrum of the 7:3 composite (Figure 3.13a) and that of the 8:2 composite (Figure 3.14a), it can be seen that the obtained peaks match very well with the positions of the ones reported in literature [97, 98] and these peaks confirm the presence of P, C and O, as expected. The peaks around 130 eV and 187 eV can be attributed to P 2p and P 2s levels respectively while the peaks around 284 eV are assigned to C 1s level and the peaks around 533 eV are assigned to O 1s level. For the 7:3 composite, the oxygen peak in the O 1s level spectra (Figure 3.13b) can be deconvoluted into three different peaks, one at around 531.5 eV that can be attributed to the double bonded oxygen with carbon and phosphorus (C=O and P=O), one at around 532.8 eV is attributed to the single bonded oxygen in C-O and C-O-P and one at around 533.1 eV can be attributed to the symmetric oxygen bridging in P-O-P [99, 100]. In Figure 3.13c three different peaks can be identified for C 1s level, out of which one is at approximately 284.1 eV and is attributed to C-C bond, one is at 285.3 eV for the C-O bond and the one at 289.3 eV is attributed to the O-C=O bond [99, 101]. The P 2p level spectrum (Figure 3.13d) consists of two peaks. One of them is attributed to the phosphorus bonding in P-P and is located at around 129.9 eV, while the other one is attributed to phosphorus oxides (P=O / P-O-P) at 134.1 eV [99].

In Figure 3.14a, the survey spectrum of the 8:2 composite is shown. When compared to the spectrum of the 7:3 composite (Figure 3.13a) it can be seen that the peak for C 1s is much less intense, while the peaks for P 2p and 2s are stronger in intensity. That is a consequence of the different weight ratios used, since we obviously have more phosphorus and less carbon in the 8:2 composite than in the 7:3 composite.
Figure 3.14 XPS spectra of 8:2 composite: (a) survey spectrum, (b) O 1s level spectrum, (c) C 1s level spectrum and (d) P 2p level spectrum

Figure 3.14b shows the O 1s spectrum and it can be seen that we have only peaks corresponding to oxygen single bonding with P or C. We are missing the double bonded oxygen that is present in the O 1s spectrum of the 7:3 composite (Figure 3.14b) and that can be a consequence of the fact that the 8:2 composite has been exposed to oxygen for a much shorter period of time than the 7:3 composite. The peak at around 532.6 eV is attributed to oxygen single bonding with P and C and the one at 533.8 eV is attributed to the symmetric oxygen bonding with P [99, 100]. For the C 1s spectrum (Figure 3.14c) three
peaks are present: one at 284.9 eV for C-C bonding, one at 285.3 eV for C-O bonding and one at 289 eV for O-C=O bonding [99, 101, 102]. The P 2p spectrum consists of two peaks, one at 129.9 eV attributed to the P-P bonding and one at 134.7 eV attributed to the presence of phosphorus oxides (P-O-P / P=O) [99].

3.5 FTIR Characterization

FTIR characterization has been done to verify the nature of the unknown liquid bubbles that were gradually forming on the surface of the fabricated electrodes. In Figure 3.15 it can be seen that the bubbles appear and then grow over time until a saturation point is reached after approximately 15 min, after which there is no noticeable increase in the wetting of the electrode surface. If the electrodes are then dried and left again in the air, the bubble formation is repeated.

Thus, FTIR characterization has been done prior and after removal of the droplets from the surface to confirm the identity of the said liquid bubbles. The result is evident in Figure 3.16 where it can clearly be seen, for the 7:3 composite, that the water O-H stretch peak intensity decreases significantly after the bubble removal. From that we can safely conclude that the identity of the bubbles is water.
But where did this water come from? Considering the XPS results, which confirmed the presence of phosphorus oxides and considering that the aforementioned oxides are extremely hygroscopic [103-106], it can be concluded that the water is the moisture coming from the air surrounding the electrodes. That makes perfect sense considering that one form of phosphorus oxide, phosphorus pentoxide $P_2O_5$, is used as a powerful desiccant [107, 108].

Extreme care should be employed in this case, since water contact with the LiPF$_6$ based electrolytes will induce the formation of hydrofluoric acid HF and will as a consequence decompose the electrolyte [109, 110], hampering the electrochemical performance of the battery.

It is, thus, of extreme importance to minimize the contact of the electrodes with air and/or moisture during the preparation of the electrodes and that was done by storing them either in vacuum or in the inert Ar-filled glovebox. Once the half-cells are
assembled, however, the electrodes are safe, since inside the half-cells, oxygen and/or moisture levels are minimal.

![FTIR graph of the 7:3 composite](image)

**Figure 3.16 FTIR graph of the 7:3 composite**

### 3.6 Electrochemical Characterization

The electrochemical performance of only red P is depicted in Figure 3.17a. As it can be seen there is a dramatic capacity fade from the first discharge, that is at 1204 mAh g⁻¹, to subsequent ones that fall under 50 mAh g⁻¹. This measurement was done at 50 mA g⁻¹, between 0.001 and 2 V. At higher current densities red P seems to be completely inactive and does not show any lithiation/delithiation plateaus, which are expected during charge/discharge, indicating that the alloying reaction is a slow reaction and forcing a
higher current density does not allow P to alloy with Li$^+$ ions. Figure 3.17b shows the electrochemical performance of only SWCNTs, also between 0.001 and 2 V. Furthermore, they exhibit huge capacity fading with the initial discharge being at 1806 mAh g$^{-1}$, while the later ones fall under 200 mAh g$^{-1}$. Hence, both materials show promising electrochemical behavior with high initial capacities but they cannot be practically viable unless the challenge of the big capacity loss after the first discharge is addressed.

![Figure 3.17](image1.png)

**Figure 3.17** Electrochemical performance of (a) red P at 50 mAh g$^{-1}$ and (b) SWCNTs at 150 mAh g$^{-1}$

Figure 3.18a and Figure 3.18b shows the electrochemical behavior of the 7:3 composite at 150 mAh g$^{-1}$. In the first 14 cycles there is a rise in specific capacity of both charge and discharge. The maximum specific capacity for charge is 539 mAh g$^{-1}$, while the maximum specific capacity for discharge is 541 mAh g$^{-1}$. After 50 cycles these values fall down to 399 mAh g$^{-1}$ and 400 mAh g$^{-1}$, respectively. The Coulombic efficiency has an initial very low
value of 28 %, but then rises over 90 % after the fifth cycle and peaks at 99.5 % where it remains until the end.

Figure 3.18 Electrochemical performance at 150 mAh g\textsuperscript{-1} of (a,b) 7:3 composite and (c,d) 8:2 composite

Figure 3.18c and Figure 3.18d shows the electrochemical behavior of the 8:2 composite at 150 mAh g\textsuperscript{-1}, which seems to show more instability since there is a faster capacity loss. The charge specific capacity starts at 550 mAh g\textsuperscript{-1}, increases during the first three cycles only and then reaches its maximum at 599 mAh g\textsuperscript{-1}. It falls down to 220 mAh g\textsuperscript{-1} after the 50 cycles. The discharge starts at 1029 mAh g\textsuperscript{-1} and continually decreases with every cycle,
until it reaches 225 mAh g\(^{-1}\) at the end. The initial Coulombic efficiency is at 54 % and after three cycles becomes over 90 % and then oscillates around 98 % until the end.

Having capacity loss and low Coulombic efficiency in the first cycles is expected because of the SEI formation, but when compared to only the red P, which has the lowest Coulombic efficiency of 9 %, or only to the SWCNTs electrode, which has the lowest Coulombic efficiency of 15 %, the Coulombic efficiency has been improved. In both composites we can see the typical lithiation plateau at around 0.7 V, while the delithiation plateau is situated a bit higher, at around 1.1 V [35].

It can be seen that the 8:2 composite, which employs a partially crystalline form of phosphorus, shows less stability and although it starts at slightly higher capacity values, they quickly diminish with cycling. The 7:3 composite employs a completely amorphous phosphorus and shows a much more stable performance. This is consistent with literature where it was seen that employing ball milling to completely destroy C and P crystalline structures and thus obtain a completely amorphous composite, yielded very good electrochemical performances [53, 91, 111]. That may be explained by the fact that amorphous materials have a bigger surface area [112, 113] and as such amorphous phosphorus would have more area to alloy itself with Li\(^+\) ions.

The capacity fade that accompanies the electrochemical cycling is attributed to the inability of the lithium insertion into the active material [114]
At higher current densities, no consistent results have been obtained and as such they have been omitted in this work. It is known that at higher charge/discharge rates, the internal resistance of the battery is larger than when cycled at lower charge/discharge rates and it is this rise in internal resistance, characterized by slower Li⁺ ion movement, that causes the specific charge capacity fading [114]. The SEI formation also contributes to the specific charge capacity fading with the decomposition of the electrolyte and the loss of Li⁺ ions that go on to form various compounds (i.e. lithium oxides and lithium carbonates) that become part of the SEI layer. This usage of Li⁺ ions competes with the desirable Faradaic reaction at the electrode surface and mostly happens in the first cycle [115].

Figure 3.19 Cyclic voltammetry response for (a) 7:3 composite and (b) 8:2 composite

Figure 3.19a shows the cyclic voltammetry result of the 7:3 composite for the initial five cycles between 0.001 V (vs. Li/Li⁺) and 2.5 V (vs. Li/Li⁺). During the first cathodic scan, two very broad peaks are visible, one at around 0.4 V (vs. Li/Li⁺) which is thought to be the activation process of Li⁺ ion insertion into phosphorus [116], and one at around 1.0 V (vs. Li/Li⁺).
Li/Li\(^+\)) that can be attributed to the decomposition of the electrolyte to form the SEI layer [1]. The next cathodic scans exhibit a dominant peak at around 0.5 V (vs. Li/Li\(^+\)), whose height gradually increases indicating an improvement in the lithiation kinetics. There is also the presence of weak peaks at around 0.7 V (vs. Li/Li\(^+\)) and 0.8 V (vs. Li/Li\(^+\)) and all of these three peaks may be attributed to the continuous lithiation of phosphorus to form Li\(_x\)P \((x=1, 2, 3)\) phase [35]. During the anodic scan one dominant peak is present at around 1.4 V (vs. Li/Li\(^+\)) which corresponds to the delithiation of Li\(_x\)P compounds [1].

In Figure 3.19b, the first cathodic scan is characterized by two broad peaks at around 0.45 V (vs. Li/Li\(^+\)) and at around 1 V (vs. Li/Li\(^+\)), that can attributed like in the 7:3 composite to the activation of Li\(^+\) ion insertion into phosphorus and to the decomposition of the electrolyte to form SEI layer, respectively. The subsequent cathodic scans show an increase in the intensity of the 0.5 V (vs. Li/Li\(^+\)) peak, in addition to the presence of the weak peaks at 0.7 V (vs. Li/Li\(^+\)) and 0.8 V (vs. Li/Li\(^+\)). All these peaks are attributed to the lithiation of P to form various Li\(_x\)P phases \((x=1, 2, 3)\). For anodic scans there is only one peak at around 1.4 V (vs. Li/Li\(^+\)) which is attributed to the delithiation of Li\(_x\)P phases.

Overall, the two voltammograms are very similar with a notable difference being in the peak current intensities which for the 8:2 composites are much higher, reaching the values of 1.5 mA, while for the 7:3 composite they reach only the 0.7 mA value. This is in agreement with the findings of the galvanostatic charge/discharge curves (Figure 3.13) where it was seen that the initial specific capacities for the 8:2 composite where higher than the ones for the 7:3 composite.
CONCLUSION AND FUTURE WORK

In a bid to make use of the notorious gravimetric and volumetric specific charge capacities of phosphorus, a composite of phosphorus matrix and carbon nanotube filler has been successfully synthesized. Since the electrochemical performance of phosphorus is hindered by its large volumetric changes upon lithiation and delithiation, a network of single walled carbon nanotubes has been used as a buffer to mitigate these and provide conductive pathways for electrons. For all of that to happen, however, the intrinsic properties of carbon nanotubes (e.g. electrical conduction) should be preserved during the synthesis process, so a non-destructive sublimation-deposition method has been used.

The weight ratios of phosphorus and carbon nanotubes were 7:3 and 8:2. It was seen that in the first case, the composite matrix is mostly amorphous matching the initial state of red P. For the latter case a polycrystalline material was obtained and identified as the structural phase of red phosphorus called fibrous phosphorus. This was unexpected and we believe that the influence of the higher synthesis pressure and confined interstitial spaces between carbon nanotube bundles were the main cause of inducing the crystallization.

It was also seen that the electrodes with these composites are very hygroscopic, due to the formation of phosphorus oxides. Therefore, extreme care should be used to minimize contact with air and moisture as that can ultimately hinder the electrochemical
performance. In practical applications it means the material should be stored in an inert atmosphere.

As for the electrochemical response, we saw that these composites show notable improvement, with the 7:3 composite being more stable. The 8:2 composite appears to have too much phosphorus and thus its volumetric expansion cannot be effectively limited. In addition, at higher current densities, the composites seem to be either electrochemically inactive or show inconsistent results. We believe that further nano-sizing of the phosphorus could solve this issue (e.g. by ball milling).

Further work should take two different directions. One direction should be the investigation of the formation of fibrous phosphorus as a consequence of different pressures in the ampoule/vessel. Pure fibrous phosphorus should be obtained and a more detailed study carried out on its electrochemical response. The other direction should be optimizing the specific charge capacities of SWCNTs and fibrous phosphorus composite, as the latter is a less-common structural phase of P.
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