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Hybrid Carbon Nanostructures for Li-based Energy Devices

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Abstract

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In this work, we explored the use of carbon nanostructures as host materials, interlayers, and electrodes for high-performance lithium-sulfur (Li-S) batteries, as well as lithium-ion (Li-ion) capacitors. The adverse effects of CO$_2$ on the environment have driven the transition to a more carbon-neutral society, where batteries and capacitors play a crucial role by making possible self-sustained renewable sources and electric transportation. However, these applications demand the development of devices with higher energy densities or that they can withstand harsh conditions. Herein, the use of nanostructures based on carbon nanotubes, graphene, and graphene nanoribbons to stabilize the sulfur cathode and the lithium metal anode is presented. Also, this thesis describes the use of the same structures to fabricate an all-carbon Li-ion capacitor capable of performing at high pressures. Our results indicate that 3D conductive carbon networks are essential to obtain high capacities and good rate capabilities; however, the cycle stability can only be obtained when the lithium polysulfide diffusion is mitigated. In the case of lithium metal anodes, a lithiated carbon nanotube interface can control the Li$^+$ flux and suppress the growth of lithium dendrites. Lastly, pressure can improve the energy and power densities of Li-ion capacitors, but there is a balance where it can also affect the performance. Future research could undertake to explore more carbon materials for the stabilization of sulfur cathodes and lithium metal anodes and to identify the changes that the electrodes experience while performing in harsh conditions.
In memory of my beloved grandmother Virginia,

and my grandfather Atanacio.
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Preface

This thesis is based on research projects conducted with Professor James M. Tour at Rice University from January 2015 to November 2018.

Chapter 3 was done in close collaboration with Caitian Gao, Ph.D., and Rodrigo Villegas Salvatierra, Ph.D. Most of the results were filed for a patent and licensed to Tubz LLC. Technology title: Sulfurized carbon as stable high capacity cathodes in high concentrated electrolytes. Rice Tech ID: 2017-018.

Chapter 4 was done in close collaboration with Rodrigo Villegas Salvatierra, Ph.D. The results were filed for a patent and licensed to Tubz LLC. Technology title: Lithiated carbon films as dendrite suppressors and protective coatings for Li metal anode. Rice Tech ID: 2017-048. The results were also accepted for publication in Advanced Materials: Suppressing Li metal dendrites through a solid Li-ion backup layer (Communication, No. adma.201803869).

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* = Authors have contributed equally.

Chapter 5 was done in close collaboration with Rodrigo V. Salvatierra, Ph.D., and Carter Kittrell. The manuscript is under preparation for submission.
Chapter 1

Introduction

"Fire made us human, fossil fuels made us modern, but now we need a new fire that makes us safe, secure, healthy and durable."

- Amory Lovins
This thesis investigates the use of hybrid carbon structures as components of the electrodes of energy storage devices, such as batteries and electrochemical capacitors, to achieve higher energy densities and stability.

My thesis is organized as follows: Chapter 1 contains a brief introduction to energy storage devices (specifically batteries and capacitors). Chapter 2 includes the methodology and all experimental details used for the three different projects described in this thesis. Two of the projects focused on lithium-sulfur (Li-S) batteries, and the other one is about Li-ion capacitors for subsea or high-pressure applications. In Chapter 3, a brief introduction of Li-S batteries is included; this chapter is focused on the main challenges with sulfur cathodes and the approaches that I followed. The first approach consists of the use of hybrid carbon nanotube-graphene nanostructures as host materials for sulfur to provide cathodes with high capacity and high sulfur loadings. The second approach includes the use of carbon interlayers to suppress the diffusion of intermediate species during the discharge cycle of the battery and to improve the cycling stability. Lastly, the third approach consists in the fabrication of sulfurized polyacrylonitrile cathodes for better cycle life. This chapter describes the main findings.

Chapter 4 focuses on the lithium metal anode for Li-S batteries. This chapter contains a brief introduction on the main challenges for Li metal anodes and a solution, which uses a carbon nanotube layer as a controlled Li\(^+\) diffusion interface that suppresses the growth of Li dendrites by regulating the Li\(^+\) ion flux during the charge and discharge cycles. Chapter 5 discuss the advantages of Li-ion capacitors and my approach to fabricate all-carbon Li-ion capacitors composed of hybrid carbon fibers-carbon nanotubes structures and free-standing graphene nanoribbons films. This chapter also contains the results and discussion of the performance of the Li-ion capacitors under high pressure for subsea applications. Finally, Chapter 6 summarizes the main findings of the three different projects and explores future work. For the rest of this chapter, I will discuss the importance of energy storage devices that motivated the projects in this thesis.
The production of energy in the world and its consumption generates approximately two-thirds of anthropogenic global greenhouse gas emissions, which are atmospheric gasses that are thought to cause global warming and climate change. These include carbon dioxide (CO$_2$), methane (CH$_4$) and nitrous oxide (N$_2$O). The adverse effects of these gases on humanity and the Earth originated in a green movement towards a transition to a carbon neutral society. This movement has been reflected in different policies, such as the Paris Agreement, which moves the global climate agenda towards net-zero CO$_2$ emissions from the energy and industrial sector by 2075. As part of the climate change mitigation, the generation of electricity from renewable sources (water, solar energy, and wind power) and the electrification of transportation have become critical human interventions.$^{1-3}$

The support from the government of different countries around the world has made possible the rapid growth of solar and wind energy technologies, as well as the electrification of transportation. However, their success in mitigating climate change will depend on their self-sustainability. Here is where low-cost and efficient energy storage devices play a crucial role by converting the intermittent energy from renewable sources to electricity on demand and making electric vehicles competitive with oil/diesel based vehicles.$^{4-6}$ There are two main groups of energy storage devices that are thought will facilitate this transition: lithium-based batteries and the electrochemical capacitors. Figure 1 shows the Ragone plot for these systems, which describes these devices regarding power against energy density. The energy storage mechanisms of these systems give them different properties. As seen in the Ragone Plot, lithium-ion (Li-ion) batteries are capable of storing large amounts of energy, but they do not deliver this energy at faster rates; whereas electrochemical capacitors can provide large amounts of energy in short times, but they do not store large quantities.$^{7-12}$ Hence, during my research, I focused on new carbon-based technologies to improve the device performances.
Figure 1 | Ragone plot for different energy storage devices. The specific power energy density shows how fast the energy can be delivered, and the specific energy density shows how much energy can be stored by the devices. The time describes the time constants of the different devices and were obtained by dividing the energy density by the power density. Image reproduced from reference 12, © 2008 Nature.

1.1 Li-ion batteries

A simple definition of battery is a device that enables the conversion of chemical energy into electricity, relying on electrochemical reactions. Originally, the batteries that predominated were non-rechargeable; devices that could only be used once since the active materials were entirely consumed when the cell was discharged. The possibility of rechargeable batteries started years later when, in the late 1970s, Armand introduced the concept of intercalation electrodes,¹³ chemical compounds with a host lattice structure capable of intercalating ions when a potential is imposed.¹⁴ This novel idea pro-
moted researched on numerous works to find the ideal negative\textsuperscript{4,15-16} and positive\textsuperscript{17-20} electrodes that worked mainly with Li\textsuperscript{+} ions. Eventually, this work resulted in the development of the first rechargeable Li-ion battery, a name that comes from the intercalation of Li\textsuperscript{+} ions between the positive and negative electrodes. Samsung commercialized the first Li-ion battery in 1991.\textsuperscript{14} Since then; extensive research has been done to improve the energy storage, safety, and life of Li-ion batteries.

A Li-ion battery, like other types of batteries, is composed of four main components: a cathode or positive electrode, an anode or negative electrode, an electrolyte or lithium salt solution, and a separator or porous polymer membrane (Figure 2). The anode and the cathode are typically attached to a metal foil such as copper or aluminum, which act as current collectors for the electrodes. The storage of energy in a Li-ion battery is through the movement of Li\textsuperscript{+} ions back and forth between the cathode and anode. Thus, this type of battery received the name of "lithium rocking chair battery."\textsuperscript{21-23} Commercial Li-ion batteries used lithium metal oxide compounds as the cathode and graphite as the anode. Since during the fabrication of the battery, the Li\textsuperscript{+} ions are in the cathode, the battery is in the discharged state. Therefore, during the charge cycle, the Li\textsuperscript{+} ions flow from the layered structure of the cathode to the anode through the electrolyte, whereas electrons flow from the cathode to the anode through the current collector and an external circuit. The battery is completely charged when no more Li\textsuperscript{+} ions can be moved. During the discharge cycle, the Li\textsuperscript{+} ions de-intercalate from the graphite layers and flow back to the cathode; the electrons flow from the anode to the cathode through the external circuit for their utilization to power devices.\textsuperscript{9,22}
1.1.1 Beyond Li-ion batteries

Li-ion batteries have already revolutionized the world by making portable electronics devices possible. Over the years, this technology has been improved with higher energy densities and lower costs. However, the energy densities are reaching their theoretical values since there is a limited amount of Li$^+$ ions that can be intercalated in the electrodes. Achieving higher energy densities has promoted the transition to the next generation of batteries or the so-called batteries beyond Li-ion. The next generation of batteries differed from Li-ion in the principle storage mechanism. Instead of flowing Li$^+$ ions back and forward between the electrodes, these new systems rely on reversible redox reactions where the electrode changes from one chemical compound into another during the charge-discharge cycle. This system can store more Li resulting in higher energy densities. Figure 3a shows the practical energy densities for some rechargeable battery systems and their comparison with gasoline. Although the energy densities do not surpass gasoline, the next generation of Li-based batteries delivers higher energy densities. Figure 3b presents the same information, but it includes the driving range that can be delivered with each system. Two technologies have been particularly pop-
ular, the lithium-sulfur (Li-S) and the lithium-oxygen (Li-O₂) batteries. Table 1 shows a comparison of some of the different battery technologies.\textsuperscript{9, 11, 25-26}

<table>
<thead>
<tr>
<th>Battery technology</th>
<th>Cell voltage (V)</th>
<th>Theoretical specific energy density (Wh kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-ion</td>
<td>(\frac{1}{2}C_6Li + Li_{0.5}CoO_2 = 3C + LiCoO_2)</td>
<td>3.8</td>
</tr>
<tr>
<td>Li-S</td>
<td>(2Li + S = Li_2S)</td>
<td>2.2</td>
</tr>
<tr>
<td>Li-O₂</td>
<td>(2Li + O_2 = Li_2O_2)</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Figure 4 shows the schemes for the Li-S and Li-O₂ technologies. For both systems, the ideal anode is lithium metal (Li-metal) and the cathode either sulfur or oxy-
In the case of the Li-O\textsubscript{2} systems, during the discharge cycle, Li-metal is oxidized to \(\text{Li}^+\) ions, which are released into the electrolyte and flow towards the cathode, whereas the electrons travel from the anode to the cathode. In the cathode, \(\text{O}_2\) flows inside the porous cathode and reacts with the \(\text{Li}^+\) ions, forming \(\text{Li}_2\text{O}_2\) as the final product. During the charge cycle, the reverse process occurs. For the Li-S system, during the discharge cycle, Li-metal is also oxidized to \(\text{Li}^+\) ions that flow to the cathode, where they react with sulfur in a series of redox reactions until the final product, \(\text{Li}_2\text{S}\). During the charge cycle, the reverse process occurs.\textsuperscript{25,27-29}

Li-S batteries have been in development longer than Li-O\textsubscript{2}, and they are predicted to reach the market first. Thus, for this work, I focused on Li-S systems, which present challenges in both the cathode and the anode. Briefly, the ideal anode is metallic Li, a reactive metal that forms an inhomogeneous solid electrolyte interface (SEI layer). The SEI layer is a product of the decomposition of the electrolyte on the electrodes (cathode or anode) in the first charge/discharge cycles of the battery. The SEI layer acts as a passivation layer that prevents further decomposition of the electrolyte on the electrode surface. In the case of metallic Li, during the charge and the discharge cycle, Li undergoes reduction reactions, or plating, and oxidation reactions, or stripping. Because the SEI layer is not homogenous, Li tends to plate in specific areas that give rise to the growth of needle-like structures, or Li dendrites. These structures can penetrate the separator, causing short-circuits and safety hazards (such as fires), or they can lead to the gradual consumption of the anode, causing the failure of the battery.\textsuperscript{26,30} In the case of the cathode, the insulating properties of sulfur require the addition of conductive materials that do not participate in the reaction with Li; therefore, these additives represent extra weight that decreases the energy density of the battery. In addition, lithium and sulfur react in a series of steps, where sulfur chains or lithium polysulfides are formed. The longer lithium polysulfide chains are very soluble in the electrolyte and move between the cathode and anode, decreasing the amount of active material available for reactions.
and promoting parasitic reactions in the anode. These issues considerably decrease the life of the battery, lowering the capacity of the cathode and making the system inefficient.\textsuperscript{31-33}

![Image]

**Figure 4** Graphic representation of a) Li-O\textsubscript{2} and b) Li-S battery. Image reproduced from reference 25, © 2012 Nature.

### 1.2 Electrochemical capacitors

The storing energy mechanism of electrochemical capacitors gives them the advantages of fast charging and discharging, unlike batteries, without affecting the stability of the device. Electrochemical capacitors (ECs) are also known as supercapacitors or electrochemical double-layer capacitors. An EC results from the modification of a conventional capacitor to increase the energy density. A typical capacitor stores energy by the separation of positive and negative charges that accumulate on the opposite charged-conductive plate when it is connected to a power source (charge cycle of the capacitor); between the conductive-plates, there is a dielectric layer made of insulating materials such as glass or paper. When the capacitor is discharged, the power supply is removed, and the charges are released, which is a fast process. An EC differs from a conventional capacitor in that they are composed of high surface area porous materials that are separated by an electrolyte, where the ions in the electrolyte are adsorbed in
the surface of the electrodes forming an electric double-layer that allows them to store more energy (Figure 5).\textsuperscript{34-35}

The first capacitor dates back to 1745 when the German Ewald Georg von Kleist used a Leyden jar, a glass jar where metal foils covered the interior and exterior and the glass acted as the dielectric layer. Then in 1876, Fitzgerald used a wax-impregnated paper as the dielectric layer with metal foil electrodes and used radio receivers as filter chokes. Many configurations and materials were explored for capacitors, but everything changed when the first EC was patented in 1957 by Howard Becker of General Electric. The first EC consisted of porous carbon electrodes and sulfuric acid as the electrolyte. However, they did not pursue further developments, and other companies started developing new versions, such as Panasonic and Maxwell Technologies. With the rapid growth of applications for ECs in the 1950s, two more technologies were born from EC: the pseudocapacitors and the asymmetric capacitors. The former combines an active redox compound with porous carbon; therefore, there is not only storage of ions in the electrode-electrolyte interface (non-Faradaic process), but also surface redox reactions occur (Faradaic process) giving rise to higher energy densities. The second one combines a battery-type electrode, governed by Faradaic processes, with a common capacitor-type electrode, governed by non-Faradaic processes. This combination allows an increase in the voltage window and considerably increases the energy density. Li-ion capacitors are part of the last category, as the name suggests, Li\textsuperscript{+} ions are used for the fast surface redox reactions.\textsuperscript{35, 37-39}

ECs are thought to bridge the gap between capacitors and batteries since they have higher energy densities than capacitors and higher power capabilities than batteries. This property makes them attractive for high powered applications, such as energy recovery in electrical transportation applications.
Figure 5 | Scheme for an electrochemical capacitor. The device is fully charged when a potential is applied and the electrodes become positively (pink) and negatively (blue) charged, then the electrodes attracts the ions of the opposite charge from the electrolyte, forming the electric double-layer. Image reproduced from reference 36, © 2005 IEEE Spectrum.

1.3 Bibliography


31. Dong, C.; Gao, W.; Jin, B.; Jiang, Q. Advances in Cathode Materials for High-Perfor-


Chapter 2

Materials and Methods

“All life is an experiment. The more experiments you make the better.”

- Ralph Waldo Emerson
The purpose of this chapter is to describe the methods and materials pertinent to this research. Therefore, the experimental details of the procedures significant to the projects described in this thesis are found here. In the following chapters, I will refer to this chapter and the specific methods used.

2.1 Graphene growth on nickel

The graphene growth on Ni foams was based on prior publications.\(^1\)\(^-\)\(^3\) For the growth, chemical vapor deposition (CVD) was used, where a Ni foam (Heze Tianyu Technology Development Co., 1.2 mm of thickness, and areal density of 320 g/m\(^2\)) was cut into pieces of the desired size; typically, the foams were cut into rectangles of 2 cm x 4 cm. Then, each piece was sonicated (Cole Parmer bath sonicator, model 08849-00) for 15 min in ethanol (200 Proof, Decon Labs, Inc.) and dried with N\(_2\) flow (high purity 4.8 grade, Airgas). After the foam was cleaned, it was placed in a quartz tube (22-mm ID, 25-mm OD, Technical Glass Products), which was inside a horizontal tube furnace (Lindberg Blue M). A magnet-on-a-rod sample retrieval system was used to move the samples to the heating area. Figure 6 shows a scheme of the set-up. Once the system was closed, Ar (500 SCCM, ultra-high purity 5.0 grade, Airgas) and H\(_2\) (200 SCCM, ultra-high purity 5.0 grade, Airgas) flowed continuously into the system, which was purged to remove O\(_2\). In the meantime, the furnace was heated up to 1,000 °C. Once the temperature was reached, the main valve connecting the system to the vacuum pump was closed, and the pressure was increased and controlled to 760 Torr using a needle valve.

The surface of the Ni foam was cleaned by annealing the pieces for 15 min under Ar and H\(_2\) flow. Then methane (10 SCCM, CH\(_4\), ultra-high purity 4.0 grade, Airgas) was introduced into the system, and the gas-reaction was maintained for 30 min. After the reaction time, the Ni pieces were rapidly cooled down to room temperature; this was done by placing the samples to the side of the quartz tube that was at room temperature outside of the furnace, and Ar and H\(_2\) were flowed to cool down the system. After all
this process, the Ni foam gets a darker gray color indicating the growth of graphene is visible.

Figure 6 | Photographs of the CVD system for graphene growth. The photos show the main parts of the setup, for example, the tube furnace, the magnet-on-a-rod sample retrieval system, and the connections to the vacuum pump and the needle valve. The inlet connections of the gases are not visible; they are positioned toward the other side of the tube furnace.

2.2 Synthesis of the Fe$_3$O$_4$/AlO$_x$ binary catalyst

The synthesis of the catalyst nanoparticles (Fe$_3$O$_4$/AlO$_x$) was based on a prior publication. The procedure was as follows, in a round bottom flask all the following chemicals were added and stirred until the majority of the solids were dissolved: iron(III)acetylacetone (0.15 g, 97%, Aldrich), aluminum(III) acetylacetonate (0.138 g, 99%, Aldrich), 1,2-hexadecanediol (0.616 g, 90%, Aldrich), oleyamine (0.62 mL, 70%, Aldrich), oleic acid (0.45 mL, 90%, Aldrich) and benzyl ether (20 mL, 98%, Sigma-Aldrich). Then the mixture was heated up to 200 °C, and this temperature was maintained for 20 min under magnetic stirring (500 rpm). The heating rate needs to be between 8 to 10 °C/min; otherwise there will be no formation of the Fe$_3$O$_4$/AlO$_x$ nanoparticles.

After the 20 min, the mixture was cooled to room temperature by removing the flask from the heating source. Then, methanol (20 mL, 99.8%, Sigma-Aldrich) was added and the new dispersion was shaken and centrifuged for 10 min at 4000 rpm. The su-
pernatant was decanted, and more methanol was added; this procedure was repeated three times. Finally, the Fe$_3$O$_4$/AlO$_x$ nanoparticles (dark brown) were dispersed in hexane (10 mL) to get a concentration of approximately 2 mg/mL.

### 2.3 Addition of the CNT catalyst

In order to grow carbon nanotubes (CNTs) seamlessly bonded to the graphene or any carbon source, such as carbon fibers, it is necessary to load the Fe-Al catalyst on the substrates. The addition of catalyst was done through two primary methods, the electron beam (e-beam) evaporation and the addition of the Fe$_3$O$_4$/AlO$_x$ nanoparticles. In the first method, 1 nm of Fe and 3 nm of Al$_2$O$_3$ were evaporated on the substrates using an electron beam evaporator. The sample needs to be flipped over, and another evaporation cycle is needed to grow CNTs on both sides of the substrate. In the second method, the substrate is immersed in a Fe$_3$O$_4$/AlO$_x$ nanoparticle solution (the synthesis has been described in section 2.2), then the substrate is dried using N$_2$ flow.

### 2.4 Carbon nanotubes growth over graphene or any carbon source

The growth of carbon nanotube carpets was based on prior publications. The carbon nanotubes were grown via chemical vapor deposition with a water-assisted hot filament furnace; Figure 7 shows the system. The furnace was heated to 750 °C before inserting the samples; once the temperature was stable acetylene (1 SCCM, C$_2$H$_2$, purified 99.6%, Matheson), H$_2$ (210 SCCM), and water vapor were introduced inside the quartz tube. The water vapor was produced by bubbling H$_2$ (200 SCCM) through ultrapure water. Then, the pressure inside the quartz tube was adjusted to 25 Torr, and the samples loaded with the Fe-Al catalyst were inserted inside the furnace using a sample retrieval boat system.

After the samples were inserted, the W filament was placed inside the furnace in
the heating area and turned on with a power of 30 W for 30 s. After that time, the pressure was reduced to 8 Torr, and the filament was turned off; the hot filament process is needed to reduce the catalyst. After the activation, the gas-reaction was left to run for 10 min, which typically gives carbon nanotubes carpets with a height between 60 and 120 μm. Finally, the samples were cooled down to room temperature by moving the boat outside the heating area in the furnace. The growth of carbon nanotubes is visible, the substrate (graphene on a Ni foam or a carbon fiber disk) acquires a black color.

**Figure 7** | Photographs of the CVD system for the carbon nanotube growth on graphene or any other carbon source.

### 2.5 Fabrication of elemental sulfur cathodes

The fabrication of the elemental sulfur cathodes was done via a melt-diffusion method. For my work, different substrates were used, among them the nickel foams coated with hybrid structures of graphene and carbon nanotubes (Ni-GCNT); multiwall carbon nanotubes (M-grade, NanoTechLabs), acetylene black (research grade, Soltex, Inc.), and graphene foams (produced from a prior publication). During this method, the substrate was covered with an excess of elemental sulfur (purified by sublimation, Fluka chemicals) typically in a weight ratio of 5:1 (sulfur: carbon). In the case of the Ni-GCNT and the graphene foams, the sulfur was dispersed throughout the entire substrate surface carefully to avoid damaging the carbon structures. For the carbon nanotubes and
the highly-conductive acetylene black, the sulfur was mixed through ball milling using a vacuum planetary centrifugal mixer (MSK-PCV-300-LD, MTI corporation); the mixing program was based on three cycles at 600, 1200 and 800 rpm with a two-minute duration each one.

Once the substrates were loaded with elemental sulfur, they were placed inside a quartz tube in a tube furnace, this was done using the magnet-on-a-rod sample retrieval system, similar to the system for graphene growth (Figure 8). The tube was left under vacuum with Ar (200 SCCM) flow for 15 min. After 15 min, the vacuum pump was closed, and the system was brought to atmospheric pressure using the Ar gas; the inert atmosphere was maintained throughout the reaction. Then, the sample was heated to 155 °C (10 °C min⁻¹) for 12 h. Once this step was completed, the temperature was increased to 250 °C (heating rate of 10 °C min⁻¹) and maintained between 5 and 30 min; the last step was done to eliminate the sulfur on the surface and that did not diffuse into the electrodes. When the heating was complete, the samples were quickly cooled to room temperature by moving the samples from the heating area to the area of the tube that was not in contact with the furnace.

2.6 Synthesis of sulfurized polyacrylonitrile cathodes

The synthesis of sulfurized polyacrylonitrile (SPAN) cathodes was based on a prior publication. In a typical synthesis, sulfur (550 mg), polyacrylonitrile (110 mg, research grade, Mw 150k, Sigma-Aldrich) and graphene nanoribbons (10 mg, GNR, research grade, EDM-Merck) were mixed using the vacuum planetary centrifugal mixer. The resulting powder was placed in a quartz tube in a tube furnace. The system was left under vacuum for 15 min with a constant Ar flow (200 SCCM). Then, the vacuum pump was stopped, and the system was allowed to reach atmospheric pressure. The Ar atmosphere was maintained, and the powder was placed in the heating area throughout the magnet-on-a-rod sample retrieval system. The mixture was heated to 450 °C for 6 h (heating rate
of 5 °C min⁻¹); after that time, the powder was cooled to room temperature. The final product is a fine green-black powder with approximately 60 wt% of sulfur.

2.7 Synthesis of lithium polysulfides (Li₂S₆)

The lithium polysulfides are composed of different S to Li ratios, where the most stable species are Li₂S₂, Li₂S₄, Li₂S₆, and Li₂S₈; for this thesis the species used was Li₂S₆. The solution of Li₂S₆ was prepared by reacting sublimed S (1.6 g) with lithium sulfide (0.46 g, Li₂S, 99.98%, Sigma-Aldrich) in dimethoxyethane (5 mL, DME, anhydrous, 99.5%, Sigma-Aldrich) and 1,3-dioxolane (5 mL, 99.5%, Sigma-Aldrich); the mixture was stirred at 50 °C for 24 h. Since Li₂S hydrolyzes when it is in contact with moisture, everything was performed inside an Ar-filled glove box. The reaction is complete when there are no solids remaining and the solution becomes a brownish-red color.

2.8 Electrolyte solutions

The electrolyte solutions used in this thesis were made inside an Ar-filled glove box. The solutions consisted of a lithium salt dissolved in DME and DOL (1:1 ratio). The lithium salts used were either lithium bis(fluorosulfonyl)imide (LiFSI, Oakwood Chemicals) or lithium bis(trifluoromethane)sulfonimide (LiTFSI, Sigma-Aldrich). In some works, lithium nitride (LiNO₃, 99.99%, Sigma-Aldrich) was used as an electrolyte additive (0.16 M concentration). Typically, the solutions had lithium salt concentrations of 1 M and 4 M; the weight of the salts was calculated to make a solution of 2 mL.

The electrolyte solution of 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate and diethyl carbonate (1:1) was purchased from Sigma-Aldrich.
2.9 Fabrication of freestanding MWNCT and GNR films

The freestanding MWCNT and GNR films were prepared by dispersing the MWCNTs or the GNRs in n-methyl-2-pyrrolidone (NMP, 97%, Sigma-Aldrich) via tip sonication (Misonix - 550 Watts, 10 min with 10 s off intervals). Enough MWCNT or GNR were added to obtain the desired mass loading per area, knowing that the effective filtration area was 44.18 cm$^2$, and with a typical weight ratio C to NMP of 1:2.5. After the sonication, the dispersion was vacuum filtered through a porous Al membrane. The MWCNTs or the GNRs were trapped and stacked on the membrane surface, which resulted in the formation of a compact film. The film was rinsed with methanol five times and dried overnight at 70 °C in a vacuum oven (Isotemp 281A, Fisher Scientific). The Al film was later dissolved using an aqueous etching solution of hydrofluoric acid (HF, 2.5 v/v%) and hydrochloric acid (HCl, 2.5 v/v%) at room temperature. After the Al foil was entirely dissolved, the MWCNT or the GNR film was removed from the solution, rinsed with water and methanol, and dried overnight at 70 °C.

The porous Al membrane was prepared by etching a commercial Al foil (60 µm thickness, Fisher Scientific Inc.) in the aqueous etching solution mentioned above for approximately 10 min. The membrane is ready when the light can penetrate the membrane, and small pores are visible. Otherwise, the membrane must be immersed for a more extended time. It is important to notice that Al etching is highly exothermic and can cause local heating, therefore, the solution must be stirred carefully. Because HF is being used the following safety precautions need to be addressed, a calcium gluconate gel and a spill kit must be nearby the working area, and the etching should always be handled inside of a fume hood.
2.10 Fabrication of GNR coated separators

For the coated separators, the same procedure from section 2.9 was used, the difference is that the GNRs were dispersed in ethanol via tip sonication, and the dispersion was vacuum filtered through a battery separator (polypropylene monolayer, Celgard® 2500). The coated separator was dried overnight at 50 °C in a vacuum oven and carefully cut to the desired size.

2.11 Fabrication of the protected Li metal anode with a Li-MWCNT interface

The lithiated MWCNT interface (Li-MWCNT) was produced by placing a freestanding MWCNT film between two Li foils, one that constitutes the anode and another one that will be sacrificed; all the preparation was performed in an Ar-filled glove box. The Li metal foil (1.6 cm diameter, 230 µm thickness, MTI corporation) was cleaned before its use by scraping the surface until a shiny metallic surface appeared. First, the Li metal anode was wetted with 30 µL of a 4 M LiFSI in DME electrolyte solution. Then, the MWCNT film was placed on the wetted surface covering it all. The film became soaked with the electrolyte, and a sacrificial Li foil was placed on top. A small pressure with the fingers was applied to ensure the three layers were in intimate contact. The interaction was maintained for 10 min; after that time, the sacrificial Li foil was carefully removed, leaving only the Li metal anode covered by the Li-MWCNT film. If the Li-MWNCT film acquires a red color, the lithiation is complete; otherwise, the sacrificial Li foil is again applied until the red color appears.

2.12 Electrode preparation for coin and pouch cells

In order to assemble coin and pouch cells, the self-standing electrodes were used without further modifications. However, the cathodes that were in powder form, such as
SPAN, required an additional step to be spread onto an Al foil for the assembly. The powders containing the active materials were mixed with conductive additives and binders using the vacuum planetary centrifugal mixer. The first ones were used to increase the conductivity of the electrode, the second ones were used to increase the elasticity and viscosity of the composite. In my work acetylene black was used as the conductive additive and polyvinylidene fluoride (PVDF, 99.5%, MTI corporation) as the binder. The typical weight ratio used of the powders containing the active material, conductive additive and binder was 8:1:1, but these numbers were modified to obtain the desired percentage of the active material in the whole electrode.

Once the powders were mixed, NMP was added to make the slurry. First, enough NMP was added to have a weight NPM: powder ratio of 1:1, followed by the mixing program in the centrifugal mixer. For the next round, more NMP was added to increase the NMP: powder ratio from 1:1 to 2:1 and so on. Typically, a good slurry needs an NMP: powder ratio of 4:1. The slurry should be as viscous as oil; this is important to obtain an acceptable coating of the current collectors with the slurry.

After the slurry was ready, a large piece of carbon coated aluminum foil (MTI Corporation) was washed with isopropanol (99.5%, Sigma-Aldrich), then the slurry was spread over the metal foil using a doctor blade (MTI corporation). To evaporate the NMP, the metal foil coated with the slurry was dried in a vacuum oven at 60 °C for 12 h.

The final electrode could be further pressed by passing it through a roller press to produce more uniform contact. Lastly, the electrode was cut into smaller pieces by using a sharp punch, this process has to be done with a sudden movement. For coin cells the electrodes were typically disks of 2 cm².

The amount of active material was determined by weighing the disks of the carbon coated aluminum foil and subtracted the average mass from the mass of the foil with the electrode material. The difference in weight corresponded to the electrode material present. Lastly, the mass of the electrode was multiplied by the percentage of the
active material in the slurry composite, which determined the total amount of the active material in the electrode.

### 2.13 Coin cell assembly

Coin cells are commonly used to test the electrochemical performance of active materials. These cells are easy to assemble and have the feasibility of using small amounts of active material and electrolyte. Therefore, they quickly provide information about the high-performing active materials and the best electrode composition. In this work, stainless steel CR2032 coin cells (MTI Corporation) were used, which are cells with a 23 mm diameter and a 2.5 mm thickness. Figure 8 shows a schematic representation of a typical coin cell configuration.

![Figure 8](image)

**Figure 8** | Schematic representation of the coin cell assembly.

In summary, the coin cell was assembled by stacking and aligning all of the battery components. The electrode with the active material was placed in the bottom cap and wetted with the electrolyte (20 to 30 μL); then, the separator was placed, usually Celgard® 2500 (polypropylene) or Celgard® K2045 (polyethylene). More electrolyte was
added (20 to 30 μL) and finally a Li metal disk was placed; prior to placement the surface of the Li metal was cleaned by scratching the surface until it was completely shiny. The Li metal and electrode disk had an area of 2 cm$^2$, and the separator area was 3.8 cm$^2$. After the anode, a spacer and a spring were placed to fill the space in the cell, providing better contact between all the components. The coin cells were sealed once all the components were stacked using a crimping machine (MTI Corporation) in an Ar-filled glove box. The cells should rest 3 h before testing to enable good wetting of the electrodes and separator by the electrolyte.

2.14 Pouch cell assembly

For the pouch cell assembly, the first step was to cut the electrodes to the desired size, typically the electrodes used had an area of 2 cm$^2$. Then, the package was prepared; the Ni tab (for the anode side, MTI Corporation) and the Al tab (for the cathode side, MTI Corporation) were welded to the supporting metal for the electrode, for example for the 2 cm$^2$ electrodes a stainless-steel foil of the same size was used. After the welding was finished, a bag was made using an Al laminated film (MTI Corporation) for pouch cells, which was folded and sealed on two opposites sides with a heating sealer (MTI Corporation). Inside an Ar-filled glovebox, all of the components of the cell were stacked (tab-supporting metal, electrode, separator, electrolyte), see Figure 9. The electrolyte was added between the separator and the electrodes.

After all the components were aligned, they were placed inside the pouch cell bag, making sure that the heatable polymer on the tab was right between the Al laminated film of the open sides; placing the heatable polymer of the tab is extremely important, since the tabs cannot be sealed directly in between the Al laminated film. Finally, using a vacuum sealer (MTI corporation) inside the glovebox, the open sides with the tabs are sealed.
2.15 Electrochemical performance evaluation

The most crucial experiment to determine the high-performing active materials is to electrochemically charge and discharge the material in a coin cell or a pouch cell configurations. The tests were done in a two-electrode setup, where the active material was the working electrode and Li metal served as the counter and reference electrode. A charge and a discharge step compose a cycle. In this work, the characterization was done using a battery analyzer (MTI corporation). The typical program was constant current until the cell reached a particular potential. The amount of current was calculated based on the desired C-rate, which corresponds to the expected capacity of the active material/working electrode divided by the desired time. For example, 1C corresponds to a charge/discharge step of 1 h each one, 2C corresponds to a time of 30 min and 0.5C a time of 2h. The cyclic voltammograms and the electrochemical impedance spectra were carried out using a battery station (Arbin instruments) at room temperature.
2.16 High-pressure testing

For the high-pressure testing of capacitors, a 400 mL high-pressure reactor (American Instrument Co., Silver Spring MD) was used, see Figure 10. The reactor consisted of the body (3" ID, 4-1/4" OD and 12" tall), a cap with a central opening (2" ID, and 10 1/2" bolts that form a 3-1/4" circle around the opening), a head in a shape of an inverted "T", and a copper gasket (0.025" thick) used as a seal between the "T" head and the body. The reactor was factory tested to 8,500 psi and hydrostatically tested to 6,000 psi. All the valves, fittings and tubing used were rated at 6,000 psi or higher. A PVC plastic cylinder 3" diameter and 8" tall was inserted into the HP reactor to reduce the volume and limit gas consumption from the high-pressure cylinder.

The head had three ports, the first port was blanked off, the second one was connected to a 0.035" thick wall stainless steel tubing for the gas, and the third one was used to install an electrical feedthrough. A standard computer cable with a nine-pin D connector was adapted to connect the battery and capacitors placed inside the reactor with an exterior protoboard circuit connected to the battery analyzer.

For the high-pressure tests, the copper gasket was placed on the reactor, then the battery or capacitor where connected to the head and placed inside the reactor. The cap was mounted, and the 10 bolts were tightened. The reactor was then placed inside a shielded enclosure. The enclosure was constructed from a 1/4" thick aluminum plates bolted top and bottom and eight solid high-density concrete blocks, which were placed inside the frame and overlapping at the corners. To supply the pressure a 6,000 psi N₂ (AirGas) cylinder was used with a 4,000 psi rated CGA gas regulator.
2.17 General characterization

The elemental composition of the electrodes was determined using X-ray photoelectron spectroscopy (XPS) with a Phi Quantera SXM scanning X-ray microprobe with a 200 µm beam size, a 45° take-off angle, pass energy of 140 eV for the survey scan and 26 eV for the high-resolution elemental analysis. The morphology characterization was performed using a FEI Quanta 400 ESEM and a JEOL 6500 SEM; both operated at 12 kV. The crystal structure was analyzed with a Rigaku D/max Ultima II X-ray diffraction (XRD) configured with Cu Kα radiation. The study of the vibrational modes of the materials was done using a Renishaw Raman RE01 scope with 514 and 633 nm Ar⁺ excitation line, and a Nicolet Nexus 6700 Fourier transform infrared spectrometer (FT-IR) equipped with an attenuated total reflectance system and an MCT-A detector. The thermogravimetric analysis (TGA) to evaluate the mass loading of sulfur on the electrodes was done using a Q-600 simultaneous TGA/DSC from TA Instruments, alumina pans and a Ar atmosphere were used.
2.18 Bibliography


Chapter 3

Sulfur cathodes based on hybrid carbon structures

"About eight days ago I discovered that sulfur in burning, far from losing weight, on the contrary, gains it…"

- Antoine-Laurent Lavoisier
As discussed in chapter one, in order to meet the demands for the transition to a carbon-neutral society, it is necessary to develop energy storage devices with higher energy densities. One of the most promising systems is the lithium-sulfur (Li-S) battery, in which the energy storage mechanism differs from one of current lithium-ion (Li-ion) batteries. An ideal Li-S battery is composed of two conversion electrodes that will go through phase changes, unlike the intercalation electrodes used in Li-ion batteries. If we take a look at the different mechanisms, Li\(^+\) ions reversibly intercalate back and forward between the layers of the electrode materials and this process does not significantly compromise the physical state of the electrodes, bringing superior stability. However, there is limited space for the ions that can be stored, yielding batteries with lower energy densities than those of conversion materials. Unlike Li-ion batteries, the whole active material reacts forming a new compound in conversion electrodes. Hence Li-S batteries can offer up to 5 times the energy density of commercial Li-ion batteries, but they have poor lifecycle and additional stability issues that have hindered their commercialization. In this chapter, I will discuss the principles of Li-S batteries, the main challenges and my work towards better S cathodes by using hybrid carbon structures based on graphene, carbon nanotubes, and graphene nanoribbons.

### 3.1 Why Li-S batteries?

The history of Li-S batteries started in the early 1960s\(^1\) when Herbert Danuta and Ulam Juliusz introduced the combination of lithium metal as the anode and sulfur as the cathodes. They recognized the reversible reaction between these two elements as shown in the following reaction:

\[
\text{Discharge} \\
2 \text{Li}^+ + 2e^- + xS \rightarrow \text{Li}_2S_x \quad 1 < x < 8 \\
\text{Charge}
\]

Nevertheless, the development of Li-S batteries was slow and stopped in the 1990s when the first Li-ion battery was commercialized, which was being developed
at the same time, see Figure 11. The triumph of the Li-ion over the Li-S battery was a consequence of the difference in energy storage mechanisms. Almost ten years later, the accelerated development for new applications in transportation, military devices, and stationary storage placed demands on higher energy densities, beyond the Li-ion theoretical values. These demands provided the environment for the resurgence of Li-S batteries as one of the candidates in the race for the ultimate energy storage device. This phenomenon can be seen in Figure 11, where the number of publications on Li-S systems increased considerably after 2002.

**Figure 11** | Number of publications per year regarding Li-S batteries. The topics searched in the database of SciFinder Scholar were lithium, sulfur, and rechargeable battery.

The appeal of Li-S batteries lies in their high energy density, which has a theoretical value of 2600 Wh kg\(^{-1}\), five times larger than the one for commercial Li-ion batteries (LiCoO\(_2\)/graphite, 387 Wh kg\(^{-1}\)), and practical values between 400 to 600 Wh kg\(^{-1}\) (where the whole weight of the battery is considered). In addition to the improvement in energy density, Li-S batteries offer additional advantages.\(^2\)\(^4\) Almost all of the cathodes in commercial Li-ion systems are based on transition metal oxides with low abundance on the Earth’s crust and high costs. In the case of Li-S, elemental sulfur is the cathode ac-
tive material, the 17th most abundant element on Earth and one of the least expensive (US$60–200 per ton).\textsuperscript{5,7} Therefore, sulfur has significant advantages but does not have the necessary characteristics for an ideal electrode, which has hindered its development. First, sulfur is an insulating material, and the products formed during its reaction with lithium cause the degradation of the battery.

### 3.2 How does a Li-S battery work?

A Li-S battery consists of a lithium metal anode, a sulfur cathode, a polymer separator, and an organic electrolyte, see Figure 12a. When assembled, the battery is found in the charged state, since there are no $\text{Li}^{+}$ ions in the cathode. During the discharging process, lithium is oxidized to $\text{Li}^{+}$ ions, releasing electrons. The ions move to the cathode through the electrolyte, while the electrons travel to the cathode through an external electrical circuit, thus generating an electrical current. In the cathode, sulfur is reduced to lithium sulfide ($\text{Li}_2\text{S}$) by a two-electron reduction reaction. During the charging process, an external potential is applied, and the backward reactions occur. In such process, the sulfur is oxidized from $\text{Li}_2\text{S}$ to elemental sulfur, and the $\text{Li}^{+}$ ions travel back to the anode where they are reduced to Li metal, Figure 12b.\textsuperscript{3-4}

![Figure 12](image-url) A Li-S battery is composed of a Li metal anode and a S cathode, a) typical cell configuration, and b) scheme of the redox reactions that occur.
The typical voltage profile of the redox reactions between lithium and sulfur presents two plateaus, one at ~2.3 V and the other one at ~2.1 V, which indicates that this reaction is not a one-step process. When lithium reacts with sulfur (cyclo-S₈), it opens the S₈ ring, which results in the formation of high-order lithium polysulfides Li₂Sₓ (6 < x ≤ 8). As the reaction continues, the long chains of polysulfides are reduced to low-order lithium polysulfides Li₂Sₓ (2 < x ≤ 6) and finally to Li₂S. As shown in Figure 13, in the first plateau, there is a phase transition where sulfur (solid) is transformed into the high-order polysulfides (liquid) that are soluble in the electrolyte. In the second plateau, there is a liquid-liquid single-phase reaction where the lithium polysulfides chains are being shortened. At the end of the second plateau, the polysulfides chains are further reduced to Li₂S₂ and Li₂S, which are insoluble in the electrolyte, promoting a two-phase reaction (liquid-solid) again. Then, there is a single-phase reaction (solid) of the reduction of Li₂S₂ to Li₂S.

Figure 13 | Typical galvanostatic charge-discharge profile for a Li-S battery. Image reproduced from reference 10, © 2012 Nature.
3.3 What are the challenges in a Li-S battery?

Despite the significant advantages of Li-S batteries, there are important challenges in the cathode and anode that still need to be addressed for a functional system. In this chapter, we will focus on the sulfur cathode.

The sulfur cathode has three main challenges. The first one is the electrical and ionic insulating properties of sulfur, which is one of the best insulating materials known with a conductivity of \( \sim 10^{-30} \text{ S cm}^{-1} \) (at 20 °C).\(^3\) In a battery, a series of redox reactions happen in the electrodes; therefore, they need to be electrically conductive to transfer the electrons needed for the reactions to occur. Generally, the materials used as cathodes and anodes are ionically conductive and in some degree electrically conductive; to further improve their electrical conductivity, they are usually mixed with highly conductive materials or additives, such as carbon black.\(^9\)\(^-\)\(^12\) The typical ratio of active material to conductive additive is 10:1. Because sulfur is highly insulating, it prevents the use of small amounts of conductive additives to solve the problem, resulting in electrodes that contain low percentages of the active material and decreasing the specific capacity of the entire electrode. For this reason, it has been challenging for Li-S batteries to be competitive against commercial Li-ion batteries as it is imperative to have sulfur cathodes with a weight percent of sulfur between 60 to 90%.\(^13\)

The second challenge is the diffusion and loss of lithium polysulfides. This process, also called the shuttle mechanism, results from the solubility of the high-order lithium polysulfides \( (\text{Li}_2\text{S}_x, 4 < x < 8) \) in the organic electrolyte. Once the lithium polysulfides are formed, they freely migrate to the Li metal anode reacting with it and creating low-order polysulfides, which travel back to the cathode and react with sulfur to form high-order polysulfides that diffuse back, and so on; therefore, creating the shuttle mechanism. This behavior causes low Coulombic efficiency (the efficiency of the battery) and short cycle life of the system since part of the active material (sulfur) is being
lost in every charge-discharge cycle.$^{14-18}$

In addition, the solubility of polysulfides can cause severe self-discharge behaviors with an approximate 50% specific capacity fading in a month or less.$^{19-20}$ When the Li-S battery is completely charged and resting, the sulfur in the cathode gradually reacts with the electrolyte forming the high-order polysulfides; these polysulfides diffuse to the anode since there is a concentration gradient in the electrolyte, where more reduction reactions occur. This phenomenon leads to the discharge of the battery when it is not being used.$^{18}$

The third challenge is the volume expansion that occurs in Li-S batteries during their operation. During the discharge step, the sulfur cathode (1.92 g/cm$^3$ at 25 °C) expands in volume when Li$_2$S is formed (1.66 g/cm$^3$ at 25 °C),$^{21}$ whereas the lithium metal anode contracts, since lithium is stripped from it to react with sulfur. Conversely, during the charging step, the opposite volume changes occur; the sulfur cathode contracts and the lithium anode expands. The volume changes are an essential factor to consider in batteries since drastic volume expansions or contractions cause capacity decays due to mechanical fractures in the electrodes.$^{22}$

### 3.4 Approaches for sulfur cathodes

Throughout the last two decades, multiple solutions to the Li-S challenges have been proposed. However, these solutions generally target only one or two issues at a time due to the complexity of this system. The most common route to solve the problem of the sulfur insulation properties has been the addition of conductive materials to ensure good electron and ionic transportation in the electrode. Typically, sulfur is mixed with conductive materials and polymers that serve as host materials or containers. Their conductivity allows the sulfur utilization in the redox reactions reaching specific capacity beyond 700 mAh g$^{-1}$, still far lower than the theoretical value, 1675 mAh g$^{-1}$. The use of host materials also allows room for the electrode volume expansion changes without
damaging the electrode. Among the conductive materials, carbon has been the favorite one so far, which can be categorized according to the type of carbon material used. Examples of this carbon materials are activated carbon, carbon nanotubes, graphene, carbon fibers, and polymers. Another advantage of the carbon-based materials is their ability to absorb the electrolyte, reducing the diffusion of lithium polysulfides.

The first approach of the utilization of carbon-based materials consisted of composites of sulfur with activated carbon or carbon black,23-25 which is a common conductive additive for Li-ion batteries. The resulting cathodes increased the cycle life and capacity of the cathode since the activated carbon coated the sulfur particles. The carbon black porosity gave rise to the introduction of micropore (D < 2 nm), mesopore (2 nm < D < 50 nm), macropore (D > 50 nm), and hierarchical porous carbon structures26-32 to encapsulate sulfur and allow good electrical and ionic transportation. As a result, this allows the creation of channels for the electrolyte and a conductive network in close contact with sulfur. This carbon materials reduced the polysulfide diffusion and therefore further improved the cycling life and capacities of the sulfur cathodes. The first discharge capacities obtained with these host materials ranged from 400 to 1400 mAh g⁻¹. Then, the introduction of carbon nanotubes,33-35 carbon fibers,36-38 graphene,39-41 and hybrid structures of these materials42-45 took place, obtaining even higher capacities, ranging from 800 to 1500 mAh g⁻¹. The introduction of polymers brought the possibility of creating C-S covalent bonds to trap the sulfur or the introduction of confined metastable species (S₂-S₄). The most popular polymers are polyacrylonitrile,46-48 polypyrrole,49-50 and polyaniline.51-52 These polymer-sulfur composites produce cathodes with exceptional cycle life, surpassing 500 cycles.

However, dissolution of lithium polysulfides was not completely solved for some of the cathode composites. This remaining issue evoked an interesting approach: the introduction of conductive carbon interlayers53-54 or coated separators55-56 to trap the polysulfides in the electrolyte. In the same fashion, metal oxides and inorganic salts57-59
were added to the cathode or to the interlayers\textsuperscript{60-61} to act as anchors for the polysulfides. In the case of the electrolyte, there has not been much research; one possible reason is the lack of stable and inert organic solvents in the working voltage window of the battery. For commercial Li-ion batteries, carbonate-based electrolytes have shown excellent stability, but they cannot be used in Li-S systems since they react with the lithium polysulfides, leading to irreversible loss of the active material. Therefore, ether-based combinations are typically used as electrolytes.\textsuperscript{62} The most popular electrolyte is a solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL) and dimethoxyethane (DME) with a volume ratio of 1:1. Solid electrolytes are more efficient since they block the polysulfides; however, they have lower ionic conductivities than liquid electrolytes, decreasing the utilization of sulfur and rate performance.

3.5 Seamless three-dimensional graphene/carbon nanotubes structure as a host material for sulfur cathodes

After the discovery of the buckyball by Rick Smalley, Bob Curl, and Harry Kroto, Rice University became a power in carbon research, where multiple carbon structures were atom-by-atom designed to create an endless number of nanostructures for energy storage, health, and other applications. In 2006, the growth of a vertical array of single-walled carbon nanotubes (SWCNT) was developed at Rice University by Smalley and Hauge.\textsuperscript{63}

As shown in Figure 14, the SWCNTs were grown as carpets on Si substrates. The growth was done via chemical vapor deposition (CVD), where hydrogen and hydrocarbons gases, such as acetylene or methane were activated at subatmospheric pressures (less than 30 Torr). The created atomic hydrogen and free carbon radicals react with the metal catalyst (Fe) deposited on the substrate, resulting in the tip growth of SWCNTs. The addition of water during the synthesis showed to enhance the catalyst’s activity and lifetime resulting in massive growth of SWCNTs carpets. Water also showed the capa-
bility of removing impurities from the nanotubes, such as amorphous carbon without damaging the SWCNTs.\textsuperscript{63-65}

Figure 14 | SEM images of the SWCNTs carpets grown at different growth times, a) 1.3 min, scale bar = 1 µm; b) 20 min, scale bar = 10 µm; c) 40 min, scale bar = 10 µm; d) 40 min, scale bar = 10 µm, and their inset with a scale bar = 1 µm. Image reproduced from reference 63, © 2006 JACS.

In 2009, Robert Hauge showed the possibility of growing the SWCNTs carpets on carbon substrates with high yields.\textsuperscript{66} Then, in 2012, the Tour group was able to bond the SWCNTs carpets covalently to graphene (GCNT).\textsuperscript{67} During the synthesis, the Fe catalyst was deposited on graphene followed by a thin layer of alumina, which acted as a support layer. Upon heating and hydrogen activation, the alumina layer cracked and the CNT growth starts, which lifts off the alumina layer, following in this manner a tip growth, or so-called Odako (Japanese Kite), mechanism. The synthesis of GCNT nanostructures opened up the extension of the graphene and SWCNTs to three dimensions, making it an attractive candidate for energy storage. Since graphene can be grown on either Cu or Ni, the structure can be tuned to be used as an anode or cathode, respectively.

The properties of GCNT made it a suitable host material for sulfur and formed the base of this work to fabricate high-performance sulfur cathodes. Figure 15 summa-
rizes the advantages of using GCNT as a host material. GCNT was found to exhibit high surface areas (>2,000 m$^2$ g$^{-1}$).\textsuperscript{57} This surface area provides room for high sulfur loadings. In addition, its nanostructure allows the accommodation of strain during the volume changes, preventing the fracture and damage of the electrode. GCNT also possess an excellent electrical conductivity due to the C-C bonds between the graphene and CNTs, which creates a 3D network. The excellent electron conductivity allows more sulfur utilization during the redox reactions with Li, resulting in high specific capacities. Finally, the high-surface-area of GCNTs shortens the distance for the electronic and ionic transportation, allowing high-rate performance cathodes, with a capacity that does not considerably decrease when the current is high.

![Figure 15](image)

**Figure 15** | Scheme of the S-GCNT cathode. The properties of GCNT, such as high surface area and electrical conductivity make it a promising host material for sulfur, enabling high sulfur contents and specific capacities.

### 3.5.1 Fabrication of covalently bonded graphene/carbon nanotubes

The fabrication of the S-GCNT cathodes was done via the melt-diffusion method for which detailed experimental procedure is found in the sections 2.1, 2.3, 2.4 and 2.5 of chapter 2. Briefly, S-GCNT was fabricated (Figure 16) by growing graphene on a Ni foam, which is more stable than Cu in the cathode voltage window (up to 3 V). Then the Fe catalyst and the alumina layer were deposited by e-beam, following by the CVD growth.
of CNTs. Once the Ni-GCNT structure was made, elemental sulfur was placed on top of the structure, and it heated to 155 °C for 12 h. Above 95 °C, the orthorhombic α-sulfur, the most stable form of sulfur, is transformed into other allotropes, resulting in different viscosities of the liquid sulfur. The lowest viscosity is found at 155 °C; therefore, this temperature is typically selected to ensure good diffusion of sulfur on the host material. After heating for 12 h, the electrodes are heated to 250 °C to remove the sulfur that did not diffuse between the walls of the CNT; this temperature is known to make sulfur extremely reactive (S₃-S₅), thus boiling off the material.⁶⁸

**Figure 16** | Scheme of the fabrication of the S-GCNT cathodes using a hybrid structure of GCNT as a host material. Graphene is grown on a Ni foam by chemical vapor deposition, then iron and alumina are deposited to grow the CNTs carpéd directly on the graphene surface. Sulfur is deposited on top of the GCNT and melted at 155 °C for 12 h; the excess sulfur is removed by heating the electrode at 250 °C.

### 3.5.2 Characterization of the S-GCNT cathodes

The details of the instruments used for the characterization of the S-GCNT cathodes are described in section 2.17 of chapter 2. The scanning electron microscopy (SEM) images in Figure 17 reveal that the growth GCNT on the Ni foam is uniform over the entire metallic structure. As shown, the CNTs grew in the form of bundles, typical of a tip growth mechanism, which can be demonstrated by looking at the tips, where the alumina flakes visibly cap the exposed ends of the CNTs. The alumina plays a crucial role in the formation of bundles instead of bulk arrays since they crack and break during the CNT
growth. After the sulfur deposition, the morphology of the GCNT structure is preserved, as shown in Figure 17. There is no evidence of bulk sulfur since no large particles are observed. The whole GCNT structure possesses the same contrast in the SEM images, suggesting that sulfur is homogeneously distributed in the entire carbon matrix.

Figure 17 | SEM images of the GCNT structure before and after sulfur incorporation (S-GCNT) at different magnifications.
The presence of S in the GCNT structure was also corroborated by Raman and X-ray photoelectron (XPS) spectroscopy. Figure 18 shows the XPS spectra of GCNT and S-GCNT. As expected, the S-GCNT spectrum shows the S 2s and S 2p core-level peaks, while the GCNT spectrum did not show them. The binding energies of the S 2p peak split into two components (S 2p$_{1/2}$ and S 2p$_{3/2}$) at 164 and 165 eV, which correspond to the presence of elemental sulfur ($\alpha$-S$_8$). Both spectra have the C 2s core-level peak at 284.4 eV that corresponds to the binding energy of the sp$^2$ bonded carbon atoms in the CNTs. After the sulfur incorporation, the binding energy did not change. This result suggests the superficial coating of the CNTs with sulfur, and not the creation of covalent bonds between C and S. There is also a decrease in the intensity of the shoulder peaks at 286 and 290 eV, which can correspond to the desorption of C-O functional groups attached to the CNTs surface during the heating process.

**Figure 18** | Elemental composition of GCNT and S-GCNT; a) XPS survey spectra of GCNT and S-GCNT; b) high-resolution C 1s XPS spectra in GCNT, the peaks binding energies are 284.4 eV
(C=C), 282.2 eV (C-O), and 290.2 eV (π-π* satellite); c) high-resolution S 2p XPS spectra in S-GCNT, the peaks binding energies are 163.9 eV (S 2p_{3/2} S-S), and 165.0 eV (S 2p_{1/2} S-S); d) high-resolution C 1s XPS spectra in S-GCNT, the peaks binding energies are 284.4 eV (C=C), 282.1 eV (C-O), and 290.2 eV (π-π* satellite).

Figure 19 shows the Raman spectra for elemental sulfur, GCNT, and S-GCNT measured with a 514 nm excitation wavelength. The characteristic Raman peaks of CNTs and graphene were observed in GCNT and S-GCNT, indicating the preservation of the carbon matrix after the sulfur impregnation. The D, G and 2D peaks in the GCNT spectrum were present at 1334 cm\(^{-1}\), 1580 cm\(^{-1}\), and 2656 cm\(^{-1}\), respectively. In the S-GCNT spectrum, they were present at 1345 cm\(^{-1}\), 1593 cm\(^{-1}\), and 2680 cm\(^{-1}\). It is known that the 2D peak (an overtone of the D mode) is sensitive to structural constraints. From GCNT to S-GCNT there is a blue shift of 24 cm\(^{-1}\) in the 2D peak caused by the incorporation of sulfur between the CNT bundles. The presence of sulfur can be corroborated by the appearance of peaks in the range from 100 to 500 cm\(^{-1}\), which corresponds to sulfur vibrations. The G/D ratio did not change after the sulfur impregnation; the ratio was 3 for both GCNT and S-GCNT spectra.

TGA was performed in the S-GCNT samples under Ar atmosphere. Figure 20 shows the TGA spectra; it can be seen that the release of sulfur starts around 170 °C and completely evaporates at 350 °C, indicating that sulfur is present in its elemental form in the CNTs surface. When sulfur is wholly trapped, it starts being released above 300 °C. The TGA analysis was not used to determine the total content of sulfur in the cathode since it is destructive for the sample. The determination of the sulfur content is explained in section 2.12 of chapter 2, where the Ni foam was weighed before and after the GCNT growth to obtain the GCNT weight and then weighed again after sulfur impregnation to obtain the sulfur content in the cathode. The GCNT structure can have sulfur content between 60 to 90 wt% (considering total mass as the mass of sulfur and
carbon). For consistency in this study, the sulfur content was kept ~60 wt%, which corresponds to a density of 2 mg/cm$^3$ of sulfur.

**Figure 19** | Raman spectra of sulfur, GCNT, and S-GCNT using an excitation wavelength of 514 nm and 1% power.

**Figure 20** | TGA spectra of sulfur, GCNT and S-GCNT at a heating rate of 10 °C min$^{-1}$; a) complete spectra and b) expansion of the TGA spectra.
3.5.3 Electrochemical analysis of the S-GCNT cathodes

The purpose of using GCNT as a host material for sulfur was to obtain S cathodes with high capacities, good rate performances, and high sulfur loadings by taking advantage of the 3D GCNT structure and its high surface area. It was demonstrated that we could make cathodes with sulfur loadings above 60 wt% (total mass of carbon and sulfur), where sulfur coated the carbon nanotubes in thin layers since no bulk particles were observed. The structure of the S-GCNT cathodes brings properties that predict high capacities and good rate performances. The contact of sulfur with the conductive carbon matrix allows a significant utilization of sulfur during cycling, which can be translated in achieving capacities above 900 mAh g\(^{-1}\). The high surface area provides more contact between the sulfur and the electrolyte, which facilitates the ion transport, thus improving the rate capability of the cathode. In the following sections, the performance of the S-GCNT cathodes will be described. Figure 21 shows the typical voltage profile obtained for the S-GCNT cathodes, where the two distinct plateaus are present. In the discharge cycle, the first plateau appears around 2.3 V and the second one at 2.1 V. All of the electrochemical analyses were made using a 600 µm Li foil, but for practical applications, the performance will need to be reanalyzed using thickness <30 µm.

Another essential feature of the S-GCNT cathode is that the binder and extra conductive materials are not necessary, making S-GCNT a binder-free and additive-free cathode, which implies the elimination of additional weight that does not participate in the redox reactions, decreasing the energy density.
3.5.4 Selection of electrolyte and rate performance

For the electrochemical analysis of the S-GCNT cathodes, the optimal electrolyte was a 1 M solution of lithium bis(fluorosulfonyl) imide (LiFSI) and 0.16 M of lithium nitrate (LiNO₃) in dimethoxyethane (DME) and 1,3-dioxolane (DOL), in a ratio of 1:1. The most common salts for Li-S batteries are LiFSI, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in ether-based solvents (Figure 22). The performance was studied by cycling the S-GCNT cathodes at different rates using each lithium salt to determine the ideal electrolyte for the S-GCNT cathode, (the detailed experimental procedure of the battery assembly and evaluation is described in sections 2.13 and 2.15 of chapter 2). Figure 23a and b show the rate performance and Coulombic efficiency for LiFSI and LiTFSI in DME: DOL and 0.16 M of LiNO₃. The average specific capacities and Coulombic efficiencies of using 1 M LiTFSI and 1 M LiFSI at different C-rates (1C = 1675 mA g⁻¹) are shown in Table 2. Both salts resulted in similar specific capacities. However, LiFSI had a better rate performance since the capacity did not change considerably when the cathode was exposed to high currents (1-2C). For example, from 0.1C to 2.0C the capacity changed...
by 67.7% when LiTFSI was used, and 35.7% when LiFSI was used. Also, the Coulombic efficiency was more stable (~98.7%) with LiFSI; in contrast, for LiTFSI there were more fluctuations throughout the different rates, Figure 23c. Therefore, LiFSI was selected as the ideal salt for the electrolyte in the S-GCNT cathodes. The size of LiFSI explains the better rate performance: even though it has a similar structure to LiTFSI, it is smaller, and therefore it has higher ionic conductivity, which plays a significant role during the movement of ions at high current rates when a large amount of charge has to be used in short periods of time.

Figure 22 | Structure of a) lithium bis(trifluoromethanesulfonyl)imide, or LiTFSI, and b) lithium bis(fluorosulfonyl) imide, or LiFSI.

Figure 23d shows the galvanostatic discharge-charge voltage profiles at the different C-rate currents using LiFSI (from Figure 23a). Both plateaus were present even at high current rates; the first one decreased from 2.4 V to 2.3 V; the second one from 2.1 V to 1.9 V. This voltage drop is normal in electrodes since the internal resistance increased at higher currents. GCNT possesses a 3D electric network that helps the electrical conductivity of the cathode. Therefore, the electrode can still achieve high capacities (>600 mAh g⁻¹) at high currents. Another critical factor in the rate performance is the high surface area of the GCNT; it is known that the mass transfer is more important than the charge transfer in the rate capability of S cathodes. GCNT provides accessible diffusion pathways for the electrolyte to transport the ions and utilizes almost all the sulfur available when the current increases, resulting in a high-rate capability.
Figure 23 | Rate performance from 0.1C to 2C for the S-GCNT cathodes using as electrolyte a) 1 M LiFSI in DME: DOL - 0.16 M LiNO₃; 1 M LiTFSI in DME:DOL - 0.16 M LiNO₃; c) Coulombic Efficiency for the rate performance from a and b; d) galvanostatic charge-discharge profiles for the rate performance in a.

LiNO₃ is necessary for the electrolyte. Its role was studied and shown in Figure 24. When LiNO₃ is not added to the electrolyte, the Coulombic efficiency decreased considerably, below 90%. LiNO₃ is necessary to create a passivation layer on the Li metal anode which suppresses the parasitic reaction with the dissolved lithium polysulfides enabling a better efficiency of the S-GCNT cathode.
Table 2 | Values of the average specific capacities of the charge and discharge cycle and their Coulombic efficiencies at different rates (0.1, 0.2, 0.5, 1.0, 1.5, and 2.0C) using as electrolyte LiTFSI or LiFSI.

<table>
<thead>
<tr>
<th>Electrolyte salt</th>
<th>Rate (C)</th>
<th>Specific charge capacity (mAh g⁻¹)</th>
<th>Specific discharge capacity (mAh g⁻¹)</th>
<th>Coulombic Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LITFSI</td>
<td>0.1</td>
<td>1158</td>
<td>1065</td>
<td>91.9</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>999</td>
<td>968</td>
<td>92.8</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>863</td>
<td>855</td>
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<tr>
<td></td>
<td>1.0</td>
<td>770</td>
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<td>99.1</td>
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<tr>
<td></td>
<td>1.5</td>
<td>735</td>
<td>730</td>
<td>99.4</td>
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<tr>
<td></td>
<td>2.0</td>
<td>317</td>
<td>312</td>
<td>98.6</td>
</tr>
<tr>
<td>LiFSI</td>
<td>0.1</td>
<td>1031</td>
<td>980</td>
<td>95.7</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>885</td>
<td>872</td>
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</tr>
<tr>
<td></td>
<td>0.5</td>
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<td>779</td>
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</tr>
<tr>
<td></td>
<td>1.5</td>
<td>681</td>
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<td></td>
<td>2.0</td>
<td>638</td>
<td>630</td>
<td>98.8</td>
</tr>
</tbody>
</table>

Figure 24 | Coulombic efficiency for the S-GCNT cathodes using as electrolyte 1 M LiFSI in DME:DOL with and without the addition of LiNO₃, the current rate was 0.5C.

3.5.5 Cycle life of the S-GCNT cathodes

An essential aspect of determining the viability of a S cathode is the cycle performance. The cycle performance of the S-GCNT cathodes was tested at two different current densities (0.2C and 0.5C); generally, the current rate used in commercial batteries is 0.2C.
Figure 25 shows the cycle performance and Coulombic efficiency. The initial discharge capacities were 1016 mAh g$^{-1}$ (0.2C) and 977 mAh g$^{-1}$ (0.5C) with efficiencies above 90%. These values are among the high range of values that are typically obtained for sulfur cathodes, indicating the high charge-discharge capability of the S-GCNT cathode. After 200 cycles the capacity retention is 67% for 0.2C and 50% for 0.5C. These results imply that the properties of GCNT facilitate a fast transfer of electrons and ions, resulting and high capacities and good rate performance, but the lithium polysulfides formed do not interact actively with the carbon matrix. For the long-term cyclic stability of the S-GCNT cathodes, we explored the use of coatings that will be described in the next sections. The Coulombic efficiency was maintained above 90% for both rates.

**Figure 25** | Characterization of the cycle life of S-GCNT cathodes, a) cycle performance and b) Coulombic efficiency of the cathodes at 0.2C and 0.5C.

### 3.5.6 Improvement of the cycle life of the S-GCNT cathodes

To further improve the cycle performance of the S-GCNT cathodes we explored the use of carbon coatings. One of the reasons for the decay in specific capacity is the diffusion of lithium polysulfides that are lost in the electrolyte, thus decreasing the amount of active material with every cycle. In the last years, Manthiram has studied the use of carbon-based interlayers to suppress the diffusion because these interlayers adsorb the polysulfides, and they also have electron pathways for the utilization of the trapped...
polysulfides, preventing the capacity loss.\textsuperscript{4,54-55} The carbon layers act as upper current collectors and as polysulfide-diffusion barriers.

The cycle life of the S-GCNT cathodes was improved through two different approaches. In the first approach, a separator coated with graphene nanoribbons (GNR) was used (Figure 26a), where the carbon interlayer was facing the S-GCNT cathode, the fabrication method is reported in section 2.10 of chapter 2. Figure 26b shows the second approach where the S-GCNT cathode was coated with a light CNT film (0.33 mg cm\textsuperscript{-2}). The film was composed of few-wall CNT (FWCNT) forests grown by CVD. The FWCNT (2 or 3 walls) forests are pulled into an aligned film and wound on a polytetrafluoroethylene sheet.\textsuperscript{71} In both approaches, the lithium polysulfides were adsorbed in the carbon layer, impeding their free migration. Moreover, the conductivity of the CNTs and GNRs offer electron pathways that make possible the reaction of the trapped polysulfides. Therefore, the carbon layers help to prolong the cycle life of the S-GCNT cathode.

**Figure 26** | Scheme of the modification for the S-GCNT cathodes with a) a GNR-coated separators, and b) a CNT coating.

GNRs are narrow strips of graphene, commonly obtained by the unzipping the sidewalls of multiwalled carbon nanotubes (MWCNTs) and with a subsequent chemical reduction, the graphene ribbons can restore the MWCNT electrical conductivity.\textsuperscript{70} Their
ribbon-like structure facilitates their stacking into a uniform film that can cover the entire separator. The high aspect ratios result in the intercalation of ribbons that provides tortuosity, complicating the diffusion of lithium polysulfides towards the lithium anode. Also, because they are conductive and in contact with the electrode, the trapped polysulfides are re-used, resulting in a lower capacity decay. The GNR-coated separator improved the capacity retention after 200 cycles from 50% to 59.5% (Figure 27a) with Coulombic efficiencies above 97% (Figure 27b). The effect of decreasing the polysulfide diffusion can also be seen in Figure 28, where lithium polysulfides (0.5 M) were added in the electrolyte and where facing the GNR layer, in the other side just the electrolyte was added. The synthesis of the lithium polysulfides is described in section 2.7 of chapter 2.

![Figure 27](image.png)

**Figure 27** | Evaluation of the GNR-coated separator, a) cycle performance and b) Coulombic efficiency of the S-GCNT cathodes with and without a GNR-coated separator at 0.5 C.

The FWCNT coating on the S-GCNT cathode also improved the capacity retention after 200 cycles from 67% to 86.5% (Figure 29a) with Coulombic efficiencies above 97% (Figure 29b). As mentioned previously, the FWCNT film is exceptionally light (0.33 mg cm\(^{-2}\)) and produced a better performance than the GNR-coated separator, which has a density of almost eight times larger (2.6 mg cm\(^{-2}\)). The better performance can be attributed to the close contact with the S-GCNT electrode since the FWCNT film is directly coating it, keeping the polysulfides in a shorter distance to the cathode and conductive
pathways. This improvement of electrical conductivity is reflected in the higher specific capacity achieved of almost 32.5% compared with the pure S-GCNT cathode at the same rate.

![Figure 28](image)

**Figure 28** | Photographs of the diffusion process of polysulfides thorough the Celgard separator and the GNR-coated separator at different times.

![Figure 29](image)

**Figure 29** | Evaluation of the CNT coating, a) cycle performance and b) Coulombic efficiency of the S-GCNT cathodes at 0.2C with and without a FWCNT coating.

### 3.6 Sulfurized polyacrylonitrile composites for long-cycle life sulfur cathodes

Commercial Li-ion batteries have cycle durabilities from 500 to more than 1000 cycles at 0.2C. Traditionally, the battery is assumed to reach the end of its life when the capacity that delivers is 80% of its initial discharge capacity. Since the ultimate goal for
S cathodes is their commercialization, the goal is to develop S cathodes that can compete commercially. It was demonstrated in the last sections that the properties of the GCNT structure result in S cathodes with high specific capacities (above 900 mAh g\(^{-1}\)), excellent rate capability (capacity change of 35.7% from 0.1C to 2.0C), and high sulfur loadings (>60 wt%). However, the cycle life was limited (<200 cycles). Only when the S-GCNT cathode was coated with a FWCNT film, the capacity retention was above 80% at the 200\(^{th}\) cycle. This limited cycle life comes from the nature of the cathode. Sulfur is infiltrated in the surface of the GCNT in the form of S\(_8\), which means that it will form the high order polysulfides. The formation of the high order polysulfides can be seen in the galvanostatic voltage profile of the S-GCNT cathode, where the upper plateau appears ~2.3 V. Therefore, there will always be a dissolution of polysulfides, which affects the cycle life of the battery. Hence, we explored the fabrication of S cathodes where the formation of high order polysulfides was limited to make competitive cathodes.

In 2002 Wang and co-workers introduced the preparation of organosulfur-based cathodes using polymer-sulfur composites. Because sulfur is a well-known dehydrogenating reagent when it is heated with conductive polymers such as polyacrylonitrile (PAN) the sulfur creates disulfide bonds on the polymer side chain. It was also found that sulfur tends to form small metastable sulfur particles (S\(_x\), x = 2-3) that are embedded in the polymer matrix. Thus, during cycling, the high-order polysulfides are not formed, and the small S chains are maintained. These properties result in S-PAN cathodes with long cycle life and slow capacity decay.\(^{23, 46, 72}\)

### 3.6.1 Fabrication of the S-PAN cathodes with GNRs

Unlike the past works, where S-PAN is made and then mixed with acetylene black for the electrode preparation, we explored the addition of GNRs during the synthesis to improve the specific capacity of the cathode. The cathode was fabricated by heating elemental sulfur with PAN and GNRs at 450 °C in a 55:11:1 ratio, respectively; experimental
details are described in section 2.6 of chapter 2. Figure 30 shows a scheme of the S-PAN cathode fabrication.

Figure 30 | Scheme of the fabrication of S-PAN cathodes with GNRs.

We explored the ideal heating time for the reaction; Figure 31 shows the TGA spectra of different mixtures that were heated at 450 °C for 3, 6 and 15 h. As shown, the sulfur was well trapped and bonded with the PAN backbone. The release of sulfur started occurring above 500 °C. All the mixtures have approximate sulfur content between 55 and 65 wt%. The weight loss should indicate a small amount of nitrogen loss at high temperatures. However, it is difficult to determine the amount of nitrogen that is lost since it overlaps with the sulfur loss. Therefore, we assumed all the mass loss corresponded to sulfur.

Figure 31 | TGA spectra of different S-PAN composites fabricated at different heating times (three, six and 15 h). The heating rate for the measurement was 10 °C min⁻¹ in nitrogen atmosphere.
Since the sulfur content does not change significantly, we tested the electrochemical performance of the different composites. The reason behind this is that the different heating treatments result in different structures and sulfur confinement that affects the overall performance of the cathodes. The preparation and the electrochemical characterization of the S-PAN cathodes are described in sections 2.12, 2.13, and 2.15 of chapter 2. The sulfur loading percent decreased to 50 wt% because conductive additives and binders needed to be added to prepare the electrodes. Figure 32 shows the galvanostatic charge-discharge profiles for the composites heated at the three different times. Unlike the profile for S-GCNT cathodes, the S-PAN cathodes have one plateau, indicating the absence of high order polysulfides during the redox reactions. The tests were conducted using 4 M LiFSI in DME as the electrolyte. LiNO$_3$ did not need to be added because there is no formation of polysulfides that create parasitic reactions with the Li metal anode. The specific capacity based on sulfur was lower than that of the composite with a heating time of 15 h (~600 mAh g$^{-1}$); the samples with 3 and 6 h of heating presented similar capacities (~1000 mAh g$^{-1}$). This result could indicate that in 15 h PAN undergoes more carbonization and removal of nitrogen, leading to more sulfur being bonded to carbon; this decrease of metastable S species (S$_2$-S$_3$) and results in less active material available to react with the Li$^+$ ions.

In order to thoroughly explore the effect of the heating times, the cathodes were cycled. Figure 33a shows the cycle performance. As expected, the cycle performance is more stable (sulfur is more bonded) at 6 and 15 h than at 3 h, but at 6 h the capacity is higher, indicating the presence of more reactive sulfur species for the redox reactions. Since the Coulombic efficiency was similar for the three different heating times (Figure 33b), we found that the S-PAN composite heated for 6 h presents the best trade-off between cycle life stability, Coulombic efficiency, and specific capacity. Thus, this fabrication condition was used to characterize the electrochemical performance of the S-PAN cathodes.
Figure 32 | Galvanostatic charge-discharge profiles for the S-PAN composites prepared at different heating times.

Figure 33 | Electrochemical characterization of the S-PAN cathodes prepared at different heating times, a) cycle performance and b) Coulombic efficiency. The current rate is indicated in the graphs.

The S-PAN composite heated for 6 h was further analyzed by Raman spectroscopy. The Raman spectrum of S-PAN (Figure 34) showed the presence of C-S bonds at 174, 311 and 368 cm⁻¹. It also implies the presence of S-S bonds at 472 and 933 cm⁻¹. The G, and D bands (1331 and 1527 cm⁻¹) confirm the formation of a turbostratic carbon structure from the dehydrogenation of PAN.
3.6.2 Cycle life of the S-PAN cathodes

Figure 35a shows the cycling performance of the S-PAN cathodes at 0.5C. The cathode exhibits exceptional long cycle stability, considering the specific capacity of the second cycle (the first cycle has a contribution of parallel reactions that will be discussed later), the capacity retention after 700 cycles was 96.3%, which implies a capacity loss per cycle of 0.005%. The second discharge cycle delivers a capacity of 810 mAh g⁻¹, and after the 700th cycle, the capacity delivered is 780 mAh g⁻¹ (based on the mass of sulfur). In addition to the superior cycle performance, the Coulombic efficiency is in average 99.97% (Figure 35b); it is remarkable since LiNO₃ was not added to the electrolyte, proving that the polysulfide shuttle issue has been addressed in the cathode.

Figure 36 shows the galvanostatic charge-discharge profiles of selected cycles. All of them have just one plateau and not the typical two plateaus, implying that sulfur exists in small chains (S₂-S₃), preventing the formation of the high-order lithium polysulfides. This configuration decreases the polysulfide shuttle mechanism and improves the cycle life. It is also noticeable that the first discharge cycle has a lower voltage plateau.
and larger specific capacity, which can come from the formation of the SEI layer, and the cleavage of S-S bonds in the polymer matrix. The subsequent cycles have negligible changes in the voltage profiles that exhibit the excellent long-term stability of the S-PAN cathodes.

**Figure 35** | Electrochemical characterization of the S-PAN cathode, a) cycle performance and b) Coulombic efficiency at 0.5C.

**Figure 36** | Galvanostatic charge-discharge profiles for the S-PAN cathode at different cycles. Current rate was 0.5C.
3.6.3 Rate performance of the S-PAN cathodes

Figure 37a shows the rate performance of the S-PAN cathodes from 0.1C to 3.0C. Because of the conductivity of the PAN and the addition of GNRs, we could observe a capacity decay of only 29 from 0.1 to 3.0C, and when the rate was again 0.2C the difference in capacity was negligible, meaning that it completely recovered its original value. The Coulombic efficiencies of the rate performance averaged of 99.8%. (Figure 37b). Table 3 shows the average values for each current rate. Figure 38 shows the galvanostatic charge-discharge curves at the different rates, which present similar profiles implying good sulfur utilization at high currents.

![Graphs showing rate performance and Coulombic efficiency](image)

**Figure 37** | The S-PAN cathodes has excellent rate capabilities, a) rate performance from 0.1C to 3C and b) Coulombic efficiency of the rate performance.
**Figure 38** | Galvanostatic charge-discharge profiles for the S-PAN cathode at different current rates.

**Table 3** | Values of the average specific capacities of the charge and discharge cycle and their Coulombic efficiencies at different rates (0.1, 0.2, 0.5, 1.0, 2.0, and 3.0C).

<table>
<thead>
<tr>
<th>Rate (C)</th>
<th>Specific charge capacity (mAh g⁻¹)</th>
<th>Specific discharge capacity (mAh g⁻¹)</th>
<th>Coulombic Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>760</td>
<td>760</td>
<td>99.9</td>
</tr>
<tr>
<td>0.2</td>
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<tr>
<td>0.2</td>
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</table>
3.7 Conclusions

Li-S batteries are undoubtedly one of the favored battery candidates in the race for the ultimate energy storage device. However, the problems inherent to the sulfur cathode and the lithium anode have prevented their application. This work presents two main approaches towards the fabrication of sulfur cathodes with high sulfur loadings, high specific capacities, excellent rate performances, and high Coulombic efficiencies.

In the first approach, hybrid structures of the graphene-carbon nanotube (GCNT) were used as a host material for sulfur. The GCNT structure was developed in the Tour group in 2012, where CNTs carpet were grown over graphene bonded covalently. The GCNT is a 3D conductive carbon network with a high-surface-area able to store more than 60% in weight of sulfur. Once the GCNT is coated with sulfur, it provides electrons, and ion pathways for high utilization of sulfur resulting in capacities above 900 mAh g\(^{-1}\) and less than 36% capacity changed when the current is 20 higher. However, sulfur remains in the surface, and the GCNT is not able to absorb the lithium polysulfides that are being formed, which decreases its cycle life. Therefore, to further improve the cycle stability, a modified separator coated with GNRs was used as a barrier to the diffusion of polysulfides. The aspect ratio of GNRs allows the fabrication of dense films that have tortuous pathways slowing the diffusion of the lithium polysulfides. Also, the conductivity of GNRs enables the re-use of the trapped polysulfides by supplying electrons for the redox reactions. All the above properties result in S-GCNT cathodes with improved cycle life. A coating of the S-GCNT cathode with a thin FWCNT film was also explored since it has a lower density than the GNR film, decreasing the mass of extra material in the cathode. The FWCNT film does the same as the GNR-coated separator, where it acts as a barrier for lithium polysulfides and provides electrons for the re-utilization of the lithium polysulfides. The FWCNT film showed an improvement of the S-GCNT cathode, which can be attributed to the better contact with the cathode and its encapsulation.
This idea opens the door to new designs for sulfur cathodes that are far from conventional designs. Current Li-S batteries still have the same configuration as Li-ion batteries, but the energy storage mechanism is entirely different. Future work should focus on configurations where the cathodes encapsulate the sulfur and its species such as lithium polysulfides, or the design of separators able to keep the electrolyte in the cathode and anode apart from each other.

The second approach was the modification of polyacrylonitrile sulfur cathodes (S-PAN) with the addition of GNRs in the composite mixture. The resulting cathode performed as expected with exceptional cycle lives and capacity loss per cycle of 0.005%, and <30% capacity decay when the current was 30 times higher. The only limitation for S-PAN cathodes is that the sulfur content is not >60%. New configurations should be tried where S-PAN composite can be mixed with elemental sulfur to increase the sulfur content, keeping the electrode encapsulated to maintain the excellent cycle life.

3.9 Bibliography


Chapter 4

Suppressing dendrites through a solid Li-ion backup layer

"We've named it lithion, in order to allude thereby to its first discovery in the mineral realm, since the two others were first discovered in organic nature. Its radical will then be named lithium"

- Baron Jöns Jacob Berzelius
Since their commercialization in 1991, rechargeable lithium-ion batteries (LIBs) have revolutionized global communications. Almost three decades later, they are on pace to revolutionize the energy and transportation sectors by adoption into off-grid energy storage and electric vehicles. However, this transformation demands energy storage capabilities that today's state-of-the-art LIBs are unable to meet, even if practical efficiencies reach theoretical limits. Therefore, the next-generation of batteries, so-called post-LIBs, require a transition from intercalation electrodes to conversion electrodes, which have higher theoretical energy densities thanks to their large lithium (Li) to host material ratio.\(^1\)\(^-\)\(^5\) For example, replacing conventional metal oxide cathodes with sulfur or oxygen, and the graphite anode with Li metal can double the energy density of traditional LIBs.\(^6\)\(^,\)\(^7\)

### 4.1 Why Li metal anodes?

Among all the anode materials available for the post-LIBs, Li metal is the ultimate choice since it possesses a high theoretical specific capacity (3860 mAh g\(^{-1}\)) and the lowest electrochemical potential (-3.04 V vs standard hydrogen electrode). Li metal has been extensively investigated as an anode for LIBs since the 1960s, but the poor stability and safety concerns of the resulting batteries hampered its commercialization. Nevertheless, the growing demand for energy storage has revived attempts to use Li metal in the next generation of batteries.\(^7\)\(^,\)\(^8\)
4.2 What are the challenges of Li metal anodes?

The primary challenge of Li metal is its high reactivity, which leads to the spontaneous formation of an inhomogeneous and fragile solid electrolyte interphase (SEI). During cycling, the SEI inhomogeneities can provide nucleation sites for the preferential growth of whisker and needle-like structures, also known as dendrites. Additionally, the fragility of the SEI structure can cause it to rupture (dead Li), exposing fresh Li for continuous side reactions with the electrolyte (Figure 39). As a consequence, the resulting batteries exhibit short lifetimes, low Coulombic efficiency, and safety hazards caused by internal short circuits triggered by the Li dendrites.8,9

![Figure 39](image-url) Scheme of Li dendrite growth; during the Li plating there is a volume expansion that cracks the SEI layer, where Li deposition tends to concentrate. The concentration in Li plating causes the growth of dendrites and some parts to become isolated, called dead Li since it does not participate in the reaction anymore. After long cycling, the SEI layer becomes thicker and the anode porous.
4.3 Approaches for Li metal anodes

Previous approaches towards the Li metal anode stabilization can be divided into three main groups. The first utilizes additives to the electrolyte to improve the Li$^{+}$ ion transportation and/or passivate the metal surface.\textsuperscript{10-13} The second involves the development of solid electrolytes that act as physical barriers to stop the dendrite propagation without compromising the ion transportation.\textsuperscript{14,15} The third focuses on fabricating interfaces or 3D structures that control the Li deposition by manipulating the Li$^{+}$ ion flux and distribution.\textsuperscript{16-21} Recent reports of interface fabrication involve the exploitation of the inherent reactivity of Li to self-produce protective interlayers.\textsuperscript{22} Examples include the reduction of metal layers (In, Zn, Bi, As) over the Li surface\textsuperscript{23} and the conversion of inorganic/organic precursors (such as AlI$_3$,\textsuperscript{24} CuN$_3$,\textsuperscript{25} polyphosphoric acid,\textsuperscript{26} and methyl viologen hexafluorophosphate\textsuperscript{27}) to produce new interfaces between the Li and the newly-formed layer (Li$_x$Al, Li$_3$N, Li$_3$PO$_4$ and methyl viologen, respectively).

4.4 Suppression of Li dendrites through a lithiated multiwall carbon nanotube diffusion interface

In this work, we report the fabrication of a Li diffusion interface based on lithiated multi-walled carbon nanotubes (Li-MWCNT) to suppress dendrite formation and allow its use in full Li-S batteries. MWCNT possess excellent chemical stability, are readily processed into thin-films, and can effectively intercalate Li$^{+}$ ions between the nanotubes walls, making MWCNTs an ideal material for this application. In this approach, the MWCNT film is electrostatically drawn to the Li during lithiation, resulting in intimate contact with the metal surface. This Li diffusion interface is capable of suppressing the Li dendrite formation by mediating the Li plating/stripping since it supplies the Li$^{+}$ ions during these processes while being refilled to maintain the equilibrium (Figure 40). It also acts as a physical barrier that protects the Li anode from side reactions with the electrolyte.
and other species, such as lithium polysulfides, intermediate products in Li-S batteries. These improvements in the Li anode stability allowed us to fabricate a full Li-S battery with excellent rate capabilities.

Although the use of carbon nanotubes, graphene and graphite has been explored for Li dendrite suppression, less attention has been paid to the role that the interface between Li and carbon plays in the stabilization, since these works focus on the control of the morphology,\cite{28-31} hybrid designs,\cite{16} or the use of 3D systems as host materials for Li.\cite{20,22} Here, the Li-C interface is used to promote the dendrite suppression effect by exploring the heterojunction between Li and MWCNTs. The use of graphitic-type structures as intermediate layers is also beneficial because of the selective intercalation of Li$^+$ ions.\cite{32,33} The intercalation of larger anions (PF$_6^-$, FSI$^-$, TFSI$^-$) is prevented since this reaction is only activated at very high potentials.

**Figure 40** | Scheme of the mediation of the Li$^+$ ion flux through the MWCNT and the comparison with bare Li metal.

### 4.4.1 Fabrication and characterization of the Li-MWCNT diffusion interface

The spontaneous reaction of Li metal with different materials when no potential is applied is the basis of several studies on the passivation of Li anodes.\cite{34} Upon physical contact with metals and non-metals, Li can either form alloys (such as Li-Si and Li-Al)\cite{35,36} or
reduce the layered material by intercalating Li\(^+\) ions to maintain charge neutrality.\(^{37}\) In this work, we take advantage of Li\(^+\) ion intercalation to form an \textit{in situ} protective coating for Li anodes. The Li metal modification is shown in Figure 41 (see sections 2.9 and 2.11 in chapter 2), in which a free-standing MWCNT film with low mass density (from 0.6 to 1.5 mg cm\(^{-2}\)) was wetted with a highly concentrated electrolyte: 4 M lithium bis(fluorosulfonyl)imide (LiFSI) in 1,2-dimethoxyethane (DME). The MWCNT film was then placed on top of a Li metal foil. The physical contact between Li and the MWCNT film gives rise to a spontaneous reduction of the MWCNTs, counterbalanced by the intercalation of Li\(^+\) ions (Li-MWCNT). The hypothesis is that the Li-MWCNT diffusion interface functions as a mediator that controls the Li plating/stripping, preventing the growth of dendrites. During the charge in a full battery, Li\(^+\) ions from the MWCNTs are plated or deposited first on the Li surface, and then refilled from the Li\(^+\) ions in the electrolyte, as will be further discussed.

![Figure 41](image)

\textbf{Figure 41} | Schematic of the fabrication method of the Li metal protected by the Li-MWCNT. The final structure of the electrode is composed of Li metal coated with a lithiated MWCNT film (Li-MWCNT). The fabrication process of the Li-MWCNT electrode consisted in wetting a MWCNT film with a highly concentrated electrolyte and pressing it against a Li foil.

The spontaneous lithiation completes in less than 30 min and can be visualized by a color change of the MWCNT film from black to red (Figure 42b) only in the areas where there is intimate contact with the Li metal. The driving force for the lithiation comes from the difference of the Fermi levels of the two materials, as shown in Figure 42b. The work functions of Li (~2.9 eV) and C (5.0 eV)\(^{38-39}\) yield an electrochemical po-
tential between the two conductors, also known as Volta or contact potential. This difference in potentials promotes the reduction and lithiation of the MWCNTs. The use of the Fermi level equilibrium to engineer batteries has also been recently employed; in that case it was used in solid, glass type electrolytes, to promote Li metal plating at the cathode.

![Image of MWCNT film](image)

**Figure 42** | When the MWCNT is lithiated it acquires a red color, a) photograph of MWCNT film after being lithiated; the lithiated area is red. b) Scheme of the spontaneous lithiation of MWCNTs and the corresponding redox reaction. Energy diagrams demonstrate the driving force for reduction of MWCNTs based on the difference of Fermi energy levels (work function) of Li (-2.9 eV vs vacuum) and C (-5 eV vs vacuum).

In our case, upon lithiation, the tubular structure of the MWCNTs did not change and no bulk deposits were observed, as shown in the SEM micrographs in Figure 43, indicating a homogenous lithiation process and the formation of a thin SEI layer. The composition of the SEI layer was determined by X-ray photoelectron spectroscopy (XPS), see Figure 44. The high-resolution region spectra peaks for F(1s), N(1s), S(2p) and Li(1s) suggest the presence of the typical breakdown products of the decomposition of the LiFSI salt (LiF, Li₂O, FSI⁻, SO₂F, and N⁺ containing species). The detailed chemical composition of the surface and inner layer after Ar⁺ ion etching is summarized in Table 4 and Figure 45.
Figure 43 | Morphology characterization of the Li-MWCNT, SEM images of a) the pristine MWCNT film and b,c) the Lithiated MWCNT film.

Figure 44 | XPS spectra of Li-MWCNT and pristine MWCNT highlighting the surface composition. Inset figures show Li(1s) and C(1s) edges of the Li-MWCNT.

Table 4 | Elements, their peak positions, and percentage from the XPS spectra in Figure 45. Each peak was assigned to species found previously in other published works.42-44 * First peak of the doublet.

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Figure 45 | High-resolution a) Li 1s, b) C 1s, c) N 1s, d) O 1s, e) F 1s and f) S 2p XPS spectra of the Li-MWCNT before and after 15 min or Ar$^+$ ion etching.

The average thickness for a ~0.7 mg cm$^{-2}$ MWCNT film is ~25 µm, as observed by the SEM images (Figure 46). After the lithiation process, the film expands from 25 to 35 µm (in a 0.7 mg cm$^{-2}$ film) that can be caused by the increase in the SEI layer.

Figure 46 | Morphology of Li metal and Li-MWCNT, a) SEM images of Li metal foil (150 µm),
b) SEM images of pristine MWCNT film with a mass density of 0.7 mg cm\(^{-2}\), c) SEM image of Li|Li-MWCNT; d-e) High magnification SEM images of the Li-MWCNT portion of the Li|Li-MWCNT anode.

The lithiation of the Li-MWCNT diffusion interface is essential for dendrite suppression. Knowing that conditions such as electrolyte composition affects the level of lithiation,\textsuperscript{37, 39, 45} we explored different concentrations of the electrolyte to maximize the amount of Li\(^+\) ions stored in the Li-MWCNT film. In these tests, only the Li-MWCNT film was used (no Li foil support). Half-cell measurements were conducted to compare the lithiation percent when 1, 2, 3, 4, 5 and 6 M LiFSI in DME were used. The degree of lithiation was measured by forcing the electrochemical lithiation of the Li-MWCNT films after the fabrication step. Figure 47a shows the results from the forced lithiation where the higher the concentration, the higher percent of lithiation that is achieved, as observed by the ratio of the charge and discharge areal capacities. In addition, the open-circuit potential (OCP) of the Li-MWCNT films were stable (Figure 47b) and as the concentration of the electrolyte increases, the OCP decreases. From the last results, we observed that there is a clear difference between the concentrations of 1, 2 and 3 M with the concentrations of 4, 5 and 6 M, where the latter achieved clearly the maximum amount of lithiation (smaller discharge capacity in Figure 47a) and OCP values below ~40 mV. Therefore, a concentration of 4 M is the lowest concentration that can be used to achieve a good lithiation percentage in the Li-MWCNT protective layer. Moreover, the red color of the Li-MWCNT film is achieved only when 4, 5 and 6 M electrolytes are used. Similar color changes have been reported in graphitic structures with a high percentage of lithiation (60-90%).\textsuperscript{45}
Figure 47 | Comparison of the a) galvanostatic discharge/charge of Li-MWCNT and pristine MWCNT; b) open-circuit potential (OCP) of the Li-MWCNT after lithiation using 1 to 6 M LiFSI/DME as electrolyte during the fabrication. The OCP values are measured for 5 h immediately removing the Li-MWCNT film from the Li metal foil and assembling a 2032-coin cell. The inset graph shows an enlarged area of the graph for the OCP evolution over time.

The Li-MWCNT film was lithiated to near saturation (~99%) as determined from the half-cell measurements and compared with a pristine MWCNT film (Figure 48a). The significant difference in the initial discharge capacity of the Li-MWCNT film (~4 mAh g\(^{-1}\)) and the pristine MWCNT film (~320 mAh g\(^{-1}\)) indicates that the lithiation in the Li-MWCNT film was already near saturation before the measurement. The total gravimetric capacity delivered by the pristine MWCNT (~320 mAh g\(^{-1}\)) accounts for the intercalation of Li\(^+\) ion and the SEI formation. The lithiation reaction can be reversed in both systems, as observed by the charge capacities in Figure 48a (~ 200 mAh g\(^{-1}\)), demonstrating that Li\(^+\) ions are mobile in the Li-MWCNT interface.

Electron paramagnetic resonance (EPR) spectroscopy was used to characterize the Li-MWCNT paramagnetic centers (Figure 48b). The spectrum of the Li-MWCNT presents a high-intensity peak (line width 8.6 G) with a Dysonian (asymmetric) line shape, corresponding to the presence of conduction electrons\(^{46}\). In the case of the pristine
MWCNT film, the spectrum showed a low-intensity peak. The increment in the intensity of the EPR signal is due to lower charge screening caused by the presence of Li\textsuperscript{+} ions.\textsuperscript{47}

Figure 48 | a) galvanostatic discharge/charge of Li-MWCNT (using as electrolyte 4 M LiFSI/DME) and pristine MWCNT at 0.05 A g\textsuperscript{-1}, the tests started with the discharging step, followed by the charging step; b) electron paramagnetic resonance (EPR) spectra of Li-MWCNT and pristine MWCNT (X band, 9.3 GHz).

X-ray diffraction (XRD) patterns (Figure 49a) also confirm the Li\textsuperscript{+} ion intercalation by the increased interlayer spacing. The vibrational structure of the carbon layer was investigated using Raman spectroscopy (Figure 49b). The pristine MWCNT film showed the characteristic D (defect induced mode), G (C=C stretch vibration) and 2D (second-order mode of D band) bands for sp\textsuperscript{2} carbon materials. The Li-MWCNT spectrum showed less intense D and G bands and absence of the 2D peak. The large red-shift of the G band, from 1585 cm\textsuperscript{-1} (MWCNT) to \textasciitilde1620 cm\textsuperscript{-1} (Li-MWCNT), and the lower intensity of the lithiated material are consistent with the spectra of lithiated graphitic structures.\textsuperscript{48} The spectrum of bare Li metal presents low-intensity modes from unidentified impurities on the metal surface. Electrical characterization was also performed over the Li-MWCNT films. As expected, the current-voltage curves indicate slightly lower conductivity of the Li-MWCNT than the pristine MWCNT (Figure 50), which can be attributed to the SEI formed on the surface after lithiation.
Figure 49 | a) X-ray powder diffraction of a MWCNT film, a Li-MWCNT film and a Mylar film; b) Raman spectra of Li-MWCNT, the Li metal surface and pristine MWCNT film (at 532 nm laser excitation).

Figure 50 | IV curves of MWCNT and Li-MWCNT; a) scheme of metal pad deposition over the
MWCNT/Li-MWCNT film; b) scheme for testing I (current) vs V (potential) through lateral and vertical testing; c,d) IV curves for vertical and lateral testing of MWCNT/Li-MWCNT; e-f) average vertical and lateral conductivity for MWCNT films; g-h) average vertical and lateral conductivity for Li-MWCNT films.

4.4.2 Study of the Li plating/stripping by Raman spectroscopy

In order to study the Li plating/stripping mediation process by the Li-MWCNT diffusion interface, operando Raman spectroelectrochemical methods were conducted. In this experiment, the Li-MWCNT on Li foil was used. The Raman laser was focused on the Li-MWCNT interface through a 2-mm diameter hole (Figure 51a) and the spectra were taken at different stages of the Li plating/stripping (Figure 51b). The shift and the splitting of the G-band (1585 to 1604 cm\(^{-1}\)) suggest a change in the Li-MWCNT composition during the plating/stripping processes (Figure 51c-d). The observed spectral changes are consistently distinct during the charging (stripping) and the discharging (plating) steps, which corroborates our proposed mechanism in which the Li-MWCNT acts as a mediator in the Li plating, thus preventing dendrite formation.

**Figure 51** Structural properties of MWCNTs and Li-MWCNT indicate the mediation of Li\(^+\) ion flux through the lithiated interface; a) scheme of the setup for the measurements; the laser was
focused on the Li-MWCNT layer through a small hole (2 mm diameter) in the Li foil; b) galvanostatic stripping/plating curves; the numbers indicate the stages of Li stripping/plating where the Raman spectra were recorded. Raman spectra at the D and G peak regions (1300 to 1700 cm\(^{-1}\)) during (c) stripping and (d) plating processes. The * indicates peaks from outside the cell (not related to the experiment, Figure 52a, b and c). The symbols rhombus and triangle indicate wavenumbers at \(\sim 1585\) and 1604 cm\(^{-1}\), respectively.

The spectra also presented some sharp peaks along the D and G band region (1200 to 1700 cm\(^{-1}\)), mainly at 1457, 1521 and 1562 cm\(^{-1}\). We investigated these peaks by comparing the Raman spectra of all components present in the electrochemical cell. Figure 52a shows the comparison of Raman spectra of the Li metal surface, the electrolyte (4 M LiFSI/DME), and the Li metal after the electrolyte passivation. The peaks found are consistent with the Raman spectrum of LiFSI salt and related electrolytes.\(^{49,50}\) Figure 52b shows a Raman spectrum obtained at the steel surface from the modified CR2032 coin cell, where sharp peaks were observed at 1457, 1521 and 1562 cm\(^{-1}\). By focusing the laser on the Li-MWCNT inside the cell, the same peaks are present along with the G-band of the Li-MWCNT (at 1604 cm\(^{-1}\)). The measurements were performed using a 532 nm excitation line and low laser power (1%, \(\sim 0.2\) mW) to prevent drying or local heating of the MWCNT. Although we could not find a definitive attribution to those peaks, we confirmed they were not related to the Li-MWCNT or the vapors generated inside the electrochemical cell, as originally proposed. To prove this, we performed a simple measurement of a Si wafer substrate in air (Figure 52c). It is possible to observe the intense peak at 520.5 cm\(^{-1}\) of Si. However, the magnified portion of the spectra between 1300 – 1700 cm\(^{-1}\) shows the same narrow weak bands at 1457, 1521 and 1561 cm\(^{-1}\), ruling out their contribution to the electrochemical experiment. Figure 52d and Figure 52e show the full spectra during plating/stripping. The region of interest (next to the G-band frequency) are highlighted and plotted in the Figure 52f and Figure 52g.
Figure 52 | a) Raman spectra of the pristine Li metal surface, the 4 M LiFSI/DME electrolyte and surface of Li metal pre-treated with the electrolyte. The main peaks are identified and show that they do not overlap with the D and G band frequency of the MWCNTs; b) Raman spectra focused on the steel case surface of the electrochemical cell and focused on the Li-MWCNT inside the cell. The narrow peaks at 1457, 1521 and 1563 cm\(^{-1}\) are present in the region of the Li-MWCNT; however, they do not overlap with the G band centered at \(~1600\) cm\(^{-1}\). c) Raman spectra of a Si substrate in air. Magnified spectrum (50x) shows the low intensity peaks located at 1457, 1521 and 1561 cm\(^{-1}\) (inset); d-e) Raman spectra of the operando experiment in their full range (300 – 2800 cm\(^{-1}\)) for charge and discharge, respectively; f-g) Magnified Raman spectra in the G band
region (1525 – 1650 cm\(^{-1}\)) for charge (stripping) and discharge (plating), respectively. Arrows indicate the progress in time for the charge and discharge processes; the asterisks indicate peaks measured outside the electrochemical cell (at \(\sim 1562\) cm\(^{-1}\)). The FWHM measurement is identified by orange double-ended arrows; h) FWHM (in cm\(^{-1}\)) of the G band measured by the progress in time of the charge and discharge processes. Lines represent the linear fit of the FWHM values.

In the plating process (Figure 52f), the G band has a single peak located at 1604 cm\(^{-1}\), while in the plating (Figure 52g) the band can be deconvoluted into two modes, at 1585 and 1604 cm\(^{-1}\). We expressed these spectral changes using the FWHM of the G-band modes, which is consistently higher for the plating process, as demonstrated in the Figure 52h. The spectral differences, such as the G-band shift and splitting, were previously observed as Raman signatures of the lithium content in carbon, by using a similar experimental setup.\(^{51,52}\) Therefore, it is possible to affirm that a composition change was measured by Raman spectroscopy especially during the plating process, which corroborates our proposed mechanism. During the plating, the Li-MWCNT acts as a solid reservoir of Li\(^+\) ions on top of the metal surface. The potential application during plating drives the reduction of these ions on the surface of both Li metal and possibly the Li-MWCNT surface. On the other hand, Li\(^+\) ions from the electrolyte are also intercalated between the MWCNT walls during this process because of the potential application. The band at 1585 cm\(^{-1}\) during plating indicates that there is a depletion of Li\(^+\) ions from the Li-MWCNT, showing that this material is not fully lithiated since there is a balance towards Li metal reduction, not MWCNT lithiation. Regarding the stripping process, we observed a single peak at 1604 cm\(^{-1}\) because the potential for Li metal oxidation is lower than the potential for Li-MWCNT delithiation, as measured in our half-cell measurements, Figure 47a and Figure 48a.

Also, a simple Li plating/stripping experiment demonstrates that the Li-MWCNT interface works as an intermediate in the Li\(^+\) ion flux, and not as the Li\(^+\) ion source per
In this anode configuration, Li metal acts as the source for Li$^+$ ions, and the Li-MWCNT film serves as a mediator. To provide evidence for this, a hole was made in the Li foil to eliminate the Li$^+$ ion source from the lithiated MWCNT film, and then Li was plated from this anode to a Li metal foil (Figure 53a shows the experimental scheme using a total areal capacity of 2 mAh cm$^{-2}$). These metal foils were identified as A and B. Li was plated from A to B only in the areas that had the Li metal source. Figure 53b and Figure 53c are photographs of the foil A from the back and front sides. Figure 53d is a photograph of the front side of foil B after plating. Figure 53e and Figure 53f are SEM images of the foil B showing the non-uniform Li plating.

**Figure 53 |** a) Experimental scheme using a total areal capacity of 2 mAh cm$^{-2}$. The metal foils used are identified as A and B; b-d) photographs of the A and B metals foils after the Li plating from A to B; e-f) SEM images of the metal foil B after the plating.
4.4.3 Electrochemical testing of modified Li metal anodes

As demonstrated above, the Li-MWCNT interface mediates the Li\(^+\) ion flux during the charge/discharge processes, opening the opportunity to stabilize Li metal anodes. To study the stabilization of Li anodes by the Li-MWCNT interface, repeated Li plating/stripping cycles were made in symmetrical cells using Li foil covered by the Li-MWCNT. The use of symmetrical cells can provide direct analysis of the Li anode stability and reversibility (Coulombic efficiency) by mimicking the charge/discharge cycling where dendrite formation and reactions between the electrolyte and the Li anode produce voltage fluctuations and variations in the cell polarization or overpotential.\(^{53,54}\) The behavior was compared to a control sample composed of unprotected Li metal.

Figure 54a shows the charge/discharge cycling at a constant current of 1 mA cm\(^{-2}\) and a capacity of 2 mAh cm\(^{-2}\) for both Li-MWCNT protected and unprotected Li metal anodes. For the symmetrical cells cycling, 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL)/DME (1:1 vol:vol) was used as the electrolyte. This commonly used electrolyte for Li-S batteries was chosen to demonstrate that the dendrite suppression effect results from the Li-MWCNT layer and not from the high concentration electrolyte condition, as will be further discussed and compared. The high concentration electrolyte was used to maximize lithiation and for the fabrication of the Li-MWCNT only. The voltage profile indicates a stable cycling performance for 2000 h (500 cycles) with minimal changes in the cell polarization, stabilized at \(\sim20\) mV (magnified curve in the inset, Figure 54a). Under the same conditions, the unprotected Li anode presented a higher cell polarization (\(\sim80\) mV) for the plating/stripping and more oscillatory/peaking behavior. The same cycling was conducted at higher areal current densities and capacities (2 mA cm\(^{-2}\), 4 mAh cm\(^{-2}\)) showing a more stable voltage profile and lower cell polarization for the Li-MWCNT protected Li anode (Figure 55). Similar lithiation processes during the fabrication step and protection of Li anodes could be
also observed with other carbon materials, such as graphene nanoribbons (Figure 56).

The ability to support higher current densities (for fast charge/discharge) was studied by increasing the current densities up to 5 mA cm\(^{-2}\) for a capacity of 2 mAh cm\(^{-2}\) in the Li plating/stripping, as shown in Figure 54b. The protected Li anode with the Li-MWCNT interface presented lower cell polarizations than the control Li-only electrode. This protection was also observed using SEM. After more than 580 cycles of repeated plating/stripping (2 mA cm\(^{-2}\), 4 mAh cm\(^{-2}\)), the Li-MWCNT interface had a smooth surface with the MWCNT mat visible (Figure 54c). In contrast, the control Li metal showed a roughened surface covered by Li dendrites (Figure 54d).

**Figure 54** | Electrochemical characterization of Li-MWCNT symmetric cells. Comparison of the cycling stability of Li-MWCNT and bare Li symmetric cells at a current density of a) 2 mA cm\(^{-2}\) for a total capacity of 2 mAh cm\(^{-2}\). The inset figure shows magnified plating/stripping cycles; b) rate performance test from 1 to 5 mA cm\(^{-2}\); SEM image of c) the Li-MWCNT and d) the bare Li surface after >500 cycles at 2 mAh cm\(^{-2}\) under current density of 2 mA cm\(^{-2}\); e) chemical resistance test.
at 2 mA cm$^{-2}$ for a total capacity of 4 mAh cm$^{-2}$, 2 mg of sulfur were added to the electrolyte in the form of Li$_2$S$_6$ for chemical resistance testing.

![Graph](image)

**Figure 55** | Comparison of the cycling stability of Li$\mid$Li-MWCNT and Li$\mid$Li symmetrical cells a) at 2 mA cm$^{-2}$ for a total capacity of 4 mAh cm$^{-2}$; b) at different current densities for a total capacity of 4 mAh cm$^{-2}$.
Figure 56 | Comparison of the cycling stability of symmetrical cells of Li metal protected with different carbon films; currents of 1 mA cm\(^{-2}\) for a total capacity of 2 mAh cm\(^{-2}\) were used. The graphene nanoribbons (GNRs) and MWCNTs have comparable behavior, graphene oxide (GO) and single walled carbon nanotubes (SWCNT) presented a larger overpotential and lack of mechanical integrity upon lithiation.

The composition of the SEI layer after cycling was determined by XPS. The high-resolution region spectra suggest the stability of the initial SEI, since the same LiFSI breakdown products were present in the inner layers with the addition of the LiTFSI breakdown products on the surface, such as \(-\text{CF}_3\) groups, as summarized in Table 5 and Figure 57. Also, the Li metal surface was analyzed by XPS (Table 6 and Figure 58); the spectra showed the same breakdown products found in the Li-MWCNT film, which suggests the homogeneity of the SEI layer across the Li-MWCNT and the Li metal, and their synergistic behavior as a single electrode.
Table 5 | Elements, their peak positions, and percentage from the XPS spectra in Figure 57. Each peak was assigned to species found previously in other published works.42-44 * First peak of the doublet.

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Figure 57 | High-resolution of a) Li 1s, b) C 1s, c) N 1s, d) O 1s, e) F 1s and f) S 2p XPS spectra before and after 15 min Ar⁺ ion etching of the Li-MWCNT in the symmetrical cell shown in Figure 55a.
Table 6 | Elements, their peak positions, and percentage from the XPS spectra in Figure 58. Each peak was assigned to species found previously in other published works.42-44 * First peak of the doublet.

<table>
<thead>
<tr>
<th>Etching time</th>
<th>Li1s</th>
<th>C1s</th>
<th>N1s</th>
<th>O1s</th>
<th>F1s</th>
<th>S2p</th>
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<tr>
<td>0 min</td>
<td>42.02%</td>
<td>3.12%</td>
<td>3.68%</td>
<td>29.54%</td>
<td>12.18%</td>
<td>8.78%</td>
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<tr>
<td>15 min</td>
<td>43.04%</td>
<td>3.95%</td>
<td>3.00%</td>
<td>22.31%</td>
<td>21.35%</td>
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</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak position (eV)</th>
<th>Assignment</th>
<th>Percent (%)</th>
<th>Peak position (eV) after 15 min Ar-ion etching</th>
<th>Assignment</th>
<th>Area Percent (%)</th>
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</thead>
<tbody>
<tr>
<td>Li (1s)</td>
<td>55.44 LiOH/ Li2O</td>
<td>LiF</td>
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<td>LiOH/ Li2O</td>
<td>30.23</td>
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<td></td>
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<td>LiF</td>
<td>56.19</td>
<td>LiF</td>
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<tr>
<td>C (1s)</td>
<td>284.88 C=</td>
<td>C=C-C</td>
<td>8.97</td>
<td>288.93</td>
<td>-</td>
<td>3.91</td>
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<td></td>
<td>286.01 -</td>
<td>63.76</td>
<td>286.13</td>
<td>-</td>
<td>64.70</td>
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<td></td>
<td>287.60 -</td>
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<td></td>
<td>293.43 -CF3</td>
<td>13.23</td>
<td>290.79</td>
<td>-CF3</td>
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<td>-CF3</td>
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<td>-CF3</td>
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<tr>
<td>N (1s)</td>
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<td>N^+</td>
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<td>N^+</td>
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<td>400.52 N</td>
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<td>404.96</td>
<td>-</td>
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<td>LiF</td>
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<tr>
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<td>S</td>
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<td>160.91</td>
<td>S</td>
<td>26.05</td>
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<td>25.81</td>
<td>169.80</td>
<td>SO2F</td>
<td>22.85</td>
<td></td>
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</tbody>
</table>

Figure 58 | High-resolution a) Li 1s, b) C 1s, c) N 1s, d) O 1s, e) F 1s and f) S 2p XPS spectra be-
fore and after 15 min or Ar+ ion etching of the Li metal surface in the symmetrical cell shown in Figure 55a.

Our testing conditions (2–4 mAh cm\(^2\), 1–2 mA cm\(^2\), >500 cycles) are comparable to the areal capacities delivered by commercial battery electrodes (2–3 mAh cm\(^2\) per side). The Li plating/stripping cycling in symmetrical cells is a conventional method used to test Li metal anodes in the literature. However, the conditions for the tests are generally below the commercial standard. A comparison of our performance metrics in terms of areal capacity during cycling, current per area, number of cycles and CE with the literature is shown in Figure 59. The Li-MWCNT interface enables good Li anode performance in all three parameters (areal capacity, current per area and number of cycles) compared to the recent literature which, in general, operate under shallow lithiation (< 2 mAh cm\(^-2\)) conditions. Considering the mass of the MWCNT film and the Li foil, the Li|Li-MWCNT anode can deliver specific capacities up to 2200 mAh g\(^{-1}\) full electrode at different areal capacities (2-4 mAh cm\(^{-2}\)) and using different Li foil thicknesses (40-200 µm). The calculation considered the extraction of Li from both sides of the foil (for example: at 2 mAh cm\(^{-2}\) per side, a total of 4 mAh cm\(^{-2}\) is extracted from the Li|Li-MWCNT). For the mass calculation, we considered the mass of Li per cm\(^2\) using a density of 0.534 g cm\(^{-3}\) and the Li-MWCNT mass from both sides of the Li foil (2 x 0.7 mg cm\(^{-2}\)).

The Li|Li-MWCNT anode can achieve gravimetric capacities up to 2200 mAh per gram of full electrode. For comparison, a graphite anode delivers only capacities of 212, 247 and 269 mAh g\(^{-1}\) of full electrode at 2, 3 and 4 mAh cm\(^{-2}\) per side. For the graphite anode calculation, it was assumed that graphite coats both sides of a 9 µm Cu foil (8.1 mg cm\(^{-2}\)) at a gravimetric capacity of 340 mAh g\(^{-1}\) with no binder addition (100% active material anode). The Coulombic efficiency was measured by a modified Aurbach method using a symmetrical cell with Li-MWCNT protected Li metal,\(^{55}\) resulting in an average Coulombic efficiency of 99.8% (Figure 60).
Figure 59 | A comparison of Li|Li-MWCNT anode performance with similar results in the literature considering the plating/stripping experiments in Li||Li symmetrical cells. The results were compared in terms of areal capacity (mAh cm\(^{-2}\)), current density (mA cm\(^{-2}\)) and representative number of cycles achieved with sharp voltage oscillations. Literature in reference 56.

Figure 60 | Coulombic efficiency (CE) of Li|Li-MWCNT anode. The CE was calculated by using a symmetrical cell with two Li-MWCNT protected Li metal foils (2 cm\(^2\)), one with 7.092 mg (measure by microbalance) and other with 62.5 mg. The plating/stripping was performed for 50 cycles at 1 mA cm\(^{-2}\) and total capacity of 0.5 mAh cm\(^{-2}\). The test finished by stripping up to 1 V (vs Li/Li\(^+\)).
Since it has been demonstrated that the use of highly concentrated electrolytes reduces the production of dendrites by increasing the Sand's time, a test was also conducted in which the 4 M LiFSI was used in the cycling of bare Li metal at 4 mAh cm$^2$. This test was compared to the cycling of bare Li and Li-MWCNT protected Li in 1 M LiTFSI in 1:1 (vol:vol) DOL:DME. The Li-MWCNT protected Li anode was able to outperform the bare Li testing in both electrolyte conditions (Figure 61), presenting lower overpotential. In addition, the voltage profile of the control samples (bare Li in 1 M LiTFSI and 4 M LiFSI) signals the presence of dead Li and dendrite formation. It is important to emphasize that the high concentration electrolyte (4 M LiFSI) was necessary during the fabrication of the Li-MWCNT, but it is not necessary in the cycling.

![Figure 61](image)

**Figure 61** | Comparison of the cycling stability of bare Li and Li|Li-MWCNT symmetrical cells using as electrolyte 1 M LiTFSI in DME:DOL with a bare Li symmetrical cell using as electrolyte 4 M LiFSI in DME, as shown in the figure. The tests were performed using a current of 2 mA cm$^2$ for a total capacity of 4 mAh cm$^2$.

The stability of the Li-MWCNT interface during the Li plating/stripping over different time periods was also studied (Figure 62). The smooth morphology in the Li-MWCNT interface is the result of a distributed Li plating and a stable SEI layer formed...
over the MWCNT mat. It is observed that MWCNT are not buried by the plated Li metal, but instead are observed through the top of the plated metal, showing the preference for Li metal deposition through and under the Li-MWCNT mat, supporting control of these processes by the Li-MWCNT interface.

Figure 62 | Voltage profiles of the Li|Li-MWCNT symmetrical cells using as electrolyte 1 M LiTFSI (DME:DOL) and the SEM images of the Li-MWCNT film at the different stages of the Li platting/stripping; each row of two images corresponds to the plating/stripping time shown in the first graph of the row. Plating/stripping time increases going down each column.
One of the goals of Li metal anodes is their use in Li-S batteries. However, these batteries present the problem of the solubilization of Li polysulfides ($\text{Li}_x\text{S}_y$), intermediate products formed in the charge/discharge that can leak to the electrolyte, thereby degrading the sulfur cathode and the Li metal anode. To study the chemical protection of Li by the Li-MWCNT interface against side reactions with $\text{Li}_x\text{S}_y$, Li plating/stripping experiments in symmetrical cells were performed with $\text{Li}_2\text{S}_6$ added in the electrolyte (at 4 mAh cm$^{-2}$ and 2 mA cm$^{-2}$) to simulate the chemical environment in a Li-S cell (Figure 54e). The cell polarization of the Li-MWCNT protected anode was lower, indicating enhanced chemical resistance and also showing that the $\text{Li}_2\text{S}_6$ could not penetrate the Li-MWCNT layer to reach the Li surface. The passivation of Li metal by $\text{Li}_x\text{S}_y$ can afford additional resistance for the Li-ion transport,$^{57}$ which is consistent with the increase in the cell polarization over time.

### 4.4.4 Fabrication of a full Li-S battery using a Li-MWCT$|$Li metal anode

To demonstrate the versatility of such an anode structure, we fabricated a full Li-S battery. The Li-MWCNT protected Li anode was paired with a sulfurized carbon (SC) cathode. SC is a type of sulfur cathode produced by the decomposition of sulfur and polyacrylonitrile (see section 2.6 of chapter 2).$^{58}$ Since the sulfur is covalently bonded with carbon, $\text{Li}_x\text{S}_y$ are not formed during the charge/discharge and only one-phase transition occurs; hence, just one voltage plateau is observed (Figure 63a). The stability of SC is better than elemental sulfur cathodes because sulfur is not lost to the electrolyte during cycling.$^6$ The capacity delivered by the SC cathode was between the range of 900-1000 mAh g$^{-1}$ sulfur. The power capabilities of SC were determined by studying the $\text{Li}^+$ ion diffusion coefficient. This coefficient was calculated by the galvanostatic intermittent titration technique, where a constant current was applied for 10 min and then interrupted for 2 h to equilibrate to OCP conditions, see Figure 63b. This test indicates a
high Li$^+$ diffusion rate at $\sim$10-9 cm$^2$ s$^{-1}$ in the solid structure of SC throughout the charge/discharge (Figure 64).

![Graphs and plots](image)

**Figure 63** | Electrochemical characterization of a full Li-S battery with Li-MWCNT/Li as the anode and SC as the cathode. a) Galvanostatic charge-discharge of SC at 0.2C; b) OCP values (V) and diffusion coefficients (cm$^2$ s$^{-1}$) vs normalized cathode composition variation ($\text{Li}_x\text{S}$) during charge-discharge; c) constant current discharge at different rates (0.05 to 3C); d) pulse discharge for SC||Li-MWCNT/Li and commercial LiCoO$_2$||C battery. Inset figures show the potential drop during a 10 s pulse; e) cycling stability of SC||Li-MWCNT/Li at different rates (0.4, 1 and 2C) at areal capacities of 1-1.5 mAh cm$^2$, applied for both charge and discharge; g) self-discharge after
1 month. Inset figure shows discharge curves before and after 1 month of resting.

The diffusion coefficient of the SC cathode was calculated following similar reports in the literature for cathode characterization.\textsuperscript{59,60} Equation 1 was used for calculating the coefficients:

\[
D = \frac{4}{\pi} \left( \frac{V_m}{AF} \cdot \frac{dE/dT}{dE/dt^{0.5}} \right)^2
\]  

(1)

\(D\) is the diffusion coefficient (in cm\(^2\) s\(^{-1}\)), \(V_m\) is the molar volume (in cm\(^3\) mol\(^{-1}\)), \(A\) is the area of the electrode (cm\(^2\)), \(F = (96485\) C mol\(^{-1}\)), \(dE/dT\) is the OCP change after each pulse, \(dE/dt^{0.5}\) is the voltage variation per root square of pulse time after iR drop.

The molar volume was calculated by the SC density and SC empirical mass. The empirical mass was estimated based on the atomic proportion given by XPS measurements (C\(_{0.68}\)N\(_{0.132}\)O\(_{0.067}\)S\(_{0.121}\)), resulting in 16 g mol\(^{-1}\). The density (1.3 g cm\(^{-3}\)) was calculated by volume displacement of SC in water using a graduate cylinder. The estimated molar volume is 12.3 cm\(^3\) mol\(^{-1}\).

Figure 64 | a) Voltage profile during galvanostatic intermittent titration technique experiment.
The current pulses were delivered for 10 min followed by 2 h of resting time. The test was applied for both charge and discharge. Blue and orange lines correspond to curves connecting the OCP values after 2 h of relaxation. The inset figure shows a single pulse (voltage vs time), showing the terms used in the equation 1 for diffusion coefficient calculation; b) OCP values expressed in terms of normalized Li$_x$[SC] composition.

The high rate capability of SC and Li metal anode can enable faster discharges in a full battery, as shown in Figure 63c, where the full Li|Li-MWCNT||SC cell was discharged at constant current with C-rates from 0.05 to 3C. The capacity retention at the highest rate is ~75% of the capacity obtained at the lowest rate. A rate testing cycling, from 0.4C to 5.0C (equivalent to 0.62 to 7.75 mA cm$^{-2}$) was also demonstrated to confirm the high-power capability of the Li|Li-MWCNT||SC cell (Figure 65). Also, the Li|Li-MWCNT||SC battery performance was compared with a commercial C||LiCoO$_2$ battery in terms of pulse discharge. The batteries were subjected to a single 0.1C discharge with pulses of high current discharge (20, 40 and 60 times the 0.1 C current) for 10 s every 10 min, as shown in Figure 63d and Figure 63e. The Li|Li-MWCNT||SC battery could withstand the pulses with a lower potential drop (~190 mV for a 60x pulse) than in the C||LiCoO$_2$ battery (~500 mV for a 40x pulse). Commercial batteries such as C||LiFePO$_4$ can also provide high power, however, they require long charging times (2-3 h).

In order to demonstrate the contribution of the Li-MWCNT film in the stabilization of the full Li|Li-MWCNT||SC cell, we paired a SC cathode with a bare Li metal anode. Although the SC is a stable cathode material, the cell with bare Li metal presented lower capacity retention through cycling (compared at 0.4C), and it was 5% less energy efficient, which is caused by the higher overpotential when compared with the cells with Li-MWCNT (Figure 66). The higher overpotential observed in the cells with bare Li metal corroborates our results in plating/stripping (discussed previously) in which lower and stable overpotentials were obtained with Li|Li-MWCNT through cycling. SEM character-
ization indicates no dendrites after the Li||Li-MWCNT||SC cycling (Figure 67).

**Figure 65** | Rate performance of Li||Li-MWCNT||SC cells. The initial test was conducted at 0.4C (0.62 mA cm\(^{-2}\)). The rate was progressively increased to 1C (1.55 mA cm\(^{-2}\)), 2 C (3.1 mA cm\(^{-2}\)), 3C (4.65 mA cm\(^{-2}\)), 4C (6.2 mA cm\(^{-2}\)) and 5C (~7.75 mA cm\(^{-2}\)), returning to 1C. The total area of the electrodes is ~ 2 cm\(^2\). The total areal capacity was ~ 1.6 mAh cm\(^{-2}\) measured at 0.4C.

**Figure 66** | a) Capacity retention of Li||Li-MWCNT||SC and Li||SC cells tested at 0.4C. Electrodes
with ~2 mAh cm\(^2\) were used in both cells; b) energy efficiency of Li|Li-MWCNT||SC and Li||SC. The inset images show the 30\(^{th}\) cycle for each cell displaying the overpotential for Li|Li-MWCNT||SC (~0.38 V) and Li||SC cell (~0.55 V).

**Figure 67** a-c) SEM images of the Li|Li-MWCNT||SC cell at three different magnifications. The surface of the Li-MWCNT is smooth and no visible dendrites are observed; d-f) SEM images of Li||SC cell at three different magnifications. Li dendrites are observed evenly throughout the Li metal surface. The anodes were opened after 70 cycles at 0.4 C testing. The cell was opened after finishing the battery in the charged state.

The Li|Li-MWCNT||SC was also tested for long-range stability at different C-rates, supporting over 450 cycles (Figure 63f) with Coulombic efficiencies close to 99.9% (Figure 68). The self-discharge, which determines the shelf life of the battery, was also tested (Figure 4g), the cell was charged at 0.5C and then stored for 1 month. The potential of
the battery stabilized at 2.3 V without changes in the voltage profiles before and after the self-discharge (inset in Figure 63g). These results demonstrate the reliability of the Li-MWCNT protected Li anode in a viable Li-S battery with high power capability. The MWCNT films had no observable delamination from the surface of the Li metal once the MWCNT film is lithiated, as observed in the symmetrical cells (used in the plating/stripping experiments) and in the full cells (when paired with sulfur cathodes). The stability of the adhesion may be caused by the combination of SEI formation in the Li and MWCNT interface and from their interaction, although the exact mechanism is currently under investigation. If one tries to peel off the lithiated MWCNT film from the Li metal surface, the film breaks instead of peeling off the surface.

Figure 68 | Coulombic efficiency (CE) of charge/discharge cycling at a) 1 C and b) 2 C; c) the first CE after initial discharge (1st step of the 1st cycle) is ~73%.
4.5 Conclusions

We have achieved the stabilization of Li metal anodes through a Li diffusion interface. The interface was engineered by equilibrating the Fermi energy levels of Li metal and a MWCNT film. A highly concentrated electrolyte was necessary to maximize the amount of Li\(^{+}\) ions stored on the Li surface. The resulting Li-MWCNT interface functions as a reservoir of mobile Li\(^{+}\) ions atop the Li anode that controls the Li plating/stripping. During the charge and discharge, the potential applied disrupts the equilibrium between the three different phases (Li, MWCNT and electrolyte) that is restored by the movement of Li\(^{+}\) ions. At the discharging step, Li\(^{+}\) ions are ejected from the MWCNT and refilled from the Li metal. At the charging step, the Li plating is mediated by the Li\(^{+}\) ions stored in the Li-MWCNT interface, which are readily available for reduction. Moreover, this interface acts as a physical barrier for the side reactions that occur in the Li surface, enhancing the anode chemical resistance.

This Li anode structure has been used in full Li-S battery, where the anode was matched with a high power SC cathode. The cycle life was comparable to a commercial LIB with the advantage that it was charged and discharged at high rates. This method could be used for future anode designs in which the charge exchange (and the reactions associated with it) of two or more materials in equilibrium are advantageously used for practical solutions in battery or capacitor technologies.

4.6 Bibliography


Chapter 5

High-pressure performance of all-carbon Li-ion capacitors

“No pressure, no diamonds”
- Thomas Carlyle
5.1 Why Li-ion capacitors?

Energy storage has become a keystone in the transition to cleaner energy systems and more efficient portable electronic devices.\textsuperscript{1-2} For practical applications, energy storage devices require a balance between energy density, power density, and cycle life. However, the two primary energy storage devices (Li-ion batteries and electrochemical capacitors) offer only one or two of these three properties. For example, Li-ion batteries are known for their high energy density; on the other hand, the electrochemical capacitors are known for their high-power density and long cycle life. As discussed previously, the different performances come from their different storage mechanisms. In the case of Li-ion batteries, the storage of energy is done via insertion of Li\textsuperscript{+} ions in the bulk electrode materials, which is controlled by the diffusion of the ions between the layers of the material and is generally slow. On the other hand, electrochemical capacitors store energy by the adsorption of the electrolyte ions in the surface of the electrode materials, which is a fast process that results in high power capabilities.\textsuperscript{3-4}

The need for devices with excellent performance in energy density, power density, and cycle life has focused attention on hybrid devices, such as Li-ion capacitors (LICs), which provide a bridge between Li-ion batteries and electrochemical capacitors. LICs have higher power densities than Li-ion batteries and higher energy densities than electrochemical capacitors. These properties result from the combination of a battery-type electrode as the anode and a capacitor-type electrode as the cathode. During charging, Li\textsuperscript{+} ions are inserted in the anode, while the electrolyte anions are adsorbed in the cathode surface; during the discharge, the opposite process occurs. Usually, activated carbon is used as the cathode and pre-lithiated graphite as the anode.\textsuperscript{5-8}
5.2 Why high-pressure studies in Li-ion capacitors?

Research in energy storage devices, such as capacitors and batteries, mainly focuses on the development of high-performance electrode materials and ways to improve the capacity and power capabilities of devices. These topics are relevant for future applications considering the demands on high-performance devices. However, some future applications also include the use of these devices in extreme conditions, such as low/high temperatures and low/high pressures. For example, one growing market is the subsea industry where new oil fields are being discovered in deep water and offshore areas with water depths of more than 3,000 m, pressures higher than 4,000 psi and temperatures of 4 °C. The idea is to have a power grid located in the seabed that will power of the electrical systems needed for the oil extraction and transportation undersea. Especially in transportation, there is a growing demand for autonomous underwater vehicles (AUVs) and unmanned underwater vehicles (UUVs). For both AUVs and UUVs, the use of capacitors is attractive for rapid charging stations and their integration in a circuit with batteries for high-power impulses during acceleration and breaking recovery. Ideally, the power sources will operate normally, independent of the water depth.\textsuperscript{9-12}

In the case of LICs, there are studies that have analyzed their thermal stability.\textsuperscript{13-15} The effect of pressure in the electrochemical performance has been explored on rare occasions, focusing mainly on rechargeable batteries.\textsuperscript{16-17} Therefore, this study aimed to analyze the effects of pressure on the electrochemical performance of an all-carbon LIC,\textsuperscript{18} and its integration in a circuit with a Li-ion battery.

5.3 All-carbon Li-ion capacitors

A modified LIC\textsuperscript{18} was used for this study. The cathode and anode of the LIC were comprised of two different carbon nanostructures. A carbon nanotube carpet connected to carbon fibers (CF-CNT) constitutes the cathode. The carpet, the structure of which was
discussed in chapter 3, was produced according to sections 2.2, 2.3 and 2.4 of chapter 2. The growth over a carbon fiber sheet produces a self-standing electrode where 100% of the weight corresponds to the active material since there is no need for binders or conductive additives to attach the CNTs to the current collector (carbon fiber sheet). The advantage of the CF-CNT structure is its high surface area and high conductivity that enables faster surface redox reactions and room for the adsorptions of PF$_6^-$ ions, acting like a capacitor-type electrode.$^{19-20}$ Conversely, the anode is constituted of a self-stand- ing film of GNRs$^{21}$ also discussed in chapter 3. GNR stacking forms a film upon dispersion in solvent and vacuum-filtration. The high conductivity makes a GNR film an electrode composed 100% of active material (no binders or additives), and it can also act as its current collector. Similar to other graphene-based materials, Li$^+$ ions can intercalate between the GNR layers, making the GNRs film a battery-type electrode.

For our LIC a solution of 1 M LiPF$_6$ in EC and DEC was used as the electrolyte. This solution is a common electrolyte for commercial Li-ion batteries because the combination of its properties makes it a well-balanced electrolyte with high ionic conductivity and chemical stability at high voltages (above 5 V).$^{22}$ In addition, all the LICs were assembled in a pouch cell configuration (see section 2.14 of chapter 2). The pouch cell configuration was adopted to make tests at high pressures; coin cells cannot be used since they start deforming at pressures above 1000 psi.

LICs have two different mechanisms for storing energy that depend on the state of the anode. In order to describe these mechanisms, we need to look into how electrons, cations, and anions move during the charge and discharge processes. For example, a LIC with an anode that is not pre-lithiated undergoes a Faradaic process. That is, during the charge cycle electrons move from the cathode to the anode, and simultaneously, Li$^+$ ions are intercalated in the anode and PF$_6^-$ ions are accumulated in the cathode. During the discharge cycle, the reverse processes occur (Figure 69a).

A pre-lithiated anode in the LIC results in lower redox potential ($\sim$0.2 V vs. Li/
Li$^+$) and a different mechanism. During the charge cycle, Li$^+$ ions are inserted in the anode (Figure 69b), and once the voltage is above the open circuit potential (or resting potential), PF$_6^-$ ions start being adsorbed on the surface of the cathode. During the discharge process, Li$^+$ ions are released from the anode and PF$_6^-$ ions are desorbed from the cathode. Additionally, below the open circuit potential, Li$^+$ ions are adsorbed on the cathode’s surface. The electrons move from the cathode to the anode during the charge cycle, and vice versa during the discharge cycle. These mechanisms explain the difference in energy density in comparison with electrochemical double-layer capacitors (EDLC; Figure 69c) and ECs, as discussed in section 1.2 of chapter 1. In such case, the energy density is lower due to separation and accumulation of the ions from the electrolyte onto the surface of the anode and cathode during the charge cycle; at the same time, electrons move from the cathode to the anode through an external circuit. During the discharge cycle, the ions are released from the surface of the electrodes to the electrolyte, and the electrons move the opposite direction, from the anode to the cathode.$^{23-26}$

For the all-carbon LIC used in this study, both electrodes where pre-lithiated before being assembled in a full cell configuration, and the GNR anode was used fully lithiated. Figure 70 shows the scheme for the CF-CNT/GNR LIC used for the study of the high-pressure effect on its electrochemical performance. The following sections will describe the characterization of each electrode, the performance of the CF-CNT/GNR LIC and the electrochemical performances under high pressures.
Figure 69 | Scheme of the charge and discharge processes in a) a Li-ion capacitor, b) a Li-ion capacitor with a pre-lithiated anode, and c) an electrochemical double layer-capacitor. The green area corresponds to the energy stored; A⁻ is the anion of the electrolyte, PF₆⁻ in our case; ad corresponds to adsorption; de to desorption; C⁺ is the cation of the electrolyte, Li⁺ in our case; Li⁺ in to insertion, and Li⁺ out to de-intercalation. Figure edited from reference 23.

Figure 70 | Scheme of the CF-CNT/GNR Li-ion capacitor used in this study. The GNR anode involves the intercalation/de-intercalation of Li⁺ ions, whereas the CF-CNT cathode involves the adsorption/desorption of Li⁺ ions and PF₆⁻ anions.
5.4 Structural and morphological characterization of the CF-CNT cathode and the GNR anode

Both the CF-CNT cathode and the GNR anode are sp² carbon materials that are characterized by Raman spectroscopy since it is highly sensitive to their morphology. Figure 71 shows the Raman spectra for both electrodes. The bands presented in the spectrum of CF-CNT confirmed the presence of SWCNTs and few-wall carbon nanotubes (FWCNTs), which is in agreement with the growth of CNT carpets over the carbon fibers. The spectrum shows the typical D, G, and 2D bands for sp² carbon materials. The D-band, or Raman signature of disorder, appeared at 1329 cm⁻¹, the G-band for C-C bond stretching at about 1593 cm⁻¹, and the 2D-band at 2596 cm⁻¹. The presence of SWCNTs and FWCNTs was additionally confirmed by the appearance of additional Raman features, the radial breathing mode (RBM) with three main peaks (191 cm⁻¹, 259 cm⁻¹, and 294 cm⁻¹), and the split of the G band into the G⁺ and G⁻ peaks due to the bending and uniaxial deformation of the nanotubes. G⁻ comes from the vibrations along the stretching direction, and G⁺ from the vibrations perpendicular to the stretching direction. The Raman spectra of GNRs shows the typical bands for defective graphene, a D-band at 1334 cm⁻¹, a G-band at 1583 cm⁻¹, and a 2D band at 2661 cm⁻¹.²⁷⁻²⁹

The morphology of the electrodes was characterized by SEM microscopy; Figure 72 shows the SEM images for the CF-CNT cathode and the GNR anode. As shown, CNTs grow as carpets from the carbon fiber paper used as the substrate. The carpet looks different from CNT carpets grown when the Fe-Al catalyst is loaded via e-beam evaporation. This difference comes from the loading of the Fe-Al catalyst via a solution of binary nanoparticles (see sections 2.2 and 2.3 of chapter 2). The advantage of using a solution of Fe-Al binary nanoparticles is that they cover the entire substrate since they absorb the nanoparticles when dipped in the solution. This result in a better coating in the internal layers than when e-beam evaporation is used.

The SEM images for GNRs show that they form a net after the film fabrication.
Their morphology is typical of that of GNRs from the unzipping of MWCNTs by potassium intercalation, where the edges are curled. The images also showed small particles (~100 nm) that are attributed to the catalyst used for the CNT’s growth, the majority of the material corresponds to the GNRs.

Figure 71 | Raman spectra of a) the CF-GCNT cathode where the inset is a zoom in of the region from 100 cm\(^{-1}\) to 400 cm\(^{-1}\); b) the GNR anode. The wavelength used was 514 nm with 1% of power.

Figure 72 | SEM images for the CF-GCNT cathode and the GNR anode after their fabrication.
5.5 Electrochemical characterization of the CF-CNT cathode

Before the fabrication of the full LIC, the electrochemical performance of each electrode was obtained separately in half-cell configurations (where Li metal was used as the counter electrode), see section 2.15 of chapter 2.

The energy storage mechanism of the CF-CNT cathode is based on surface redox limited reactions and double-layer capacitance (see chapter 1). The cathode was analyzed in a voltage window from 1.0 to 4.5 V at a current density of 0.1 A g⁻¹, Figure 73 shows the galvanostatic charge-discharge curves of the first three cycles of a CF-CNT cathode. The curves presented a sloping profile over the potential range, a typical profile for capacitors (see chapter 1). Also, the voltammograms at different scan rates did not show any visible redox peaks (Figure 74a), and the dependency of current obtained at 3.2, 3.6 and 4.0 V in the positive scan was linear (Figure 74b). These results indicate that the CF-CNT energy storage mechanism is based on surface-redox limited reactions and double-layer capacitance. At lower scan rates (1 mV s⁻¹) the CV voltammogram (Figure 75) showed a broadened peak-shaped response that became quasi-rectangular at higher scan rates (Figure 74a), indicating that at lower rates there is a dominance of the surface-redox limited reactions and a predominance of the double layer capacitance at higher scan rates.30-33

![Graph](image)

**Figure 73** | Galvanostatic charge-discharge profile for the CF-CNT cathode at 0.1 A g⁻¹.
Figure 74 | a) Current-voltage curves for the CF-CNT cathode at different scan rates, b) dependence of the current-voltage curves on the different scan rates where the currents were obtained at 3.2, 3.6 and 4.0 V.

Figure 75 | Current-voltage curve for the CF-CNT cathode at 1 mV s⁻¹.

The capacity of the CF-CNT cathode became stable at approximately 60 mA h g⁻¹. Figure 76a shows the cycling performance of the cathode at a current density of 0.1 A g⁻¹, where the initial discharge capacity was ~112 mA h g⁻¹ and then stabilized at ~60 mA h g⁻¹ after few cycles. The Coulombic efficiency was close to 98% (Figure 76b). The rate performance test (Figure 77a) showed that the capacity could be preserved at higher currents, when the current increased from 0.1 A g⁻¹ to 8 A g⁻¹ the specific capacity
decreased from ~90 mAh g\(^{-1}\) to 34 mAh g\(^{-1}\). Then, when the current was reduced back to 0.1 A g\(^{-1}\) the specific capacity came back to its original. The Coulombic efficiency for the cycling was above 95% in all the cycles, being close to 100% at high currents, which it is attributed to the dominance of the surface-redox reactions.

Figure 76 | a) Cycling performance and b) Coulombic efficiency for the CF-CNT cathode at 0.1 A g\(^{-1}\); the darker blue corresponds to the discharge cycle and the lighter blue to the charge cycle.

Figure 77 | a) Rate performance for the CF-CNT cathode at different current densities, the darker blue corresponds to the discharge cycle and the lighter blue to the charge cycle; b) Coulombic efficiency for the rate performance.

5.6 Electrochemical characterization of the GNR anode

The GNR anode performance was governed by the intercalation/de-intercalation of Li\(^+\) ions. The anode was also characterized electrochemically in half-cell configurations (Li metal as the current collector). Figure 78 shows the Galvanostatic charge-discharge profile at a current density of 0.1 A g\(^{-1}\), where the profile showed a low potential plateau
similar to the one found in graphite anodes for the reversible intercalation of Li$^+$ ions (battery-type electrodes). The first discharge cycle had a specific capacity of $\sim$470 mAh g$^{-1}$, and the capacity became stable in the following cycles at about 200 mAh g$^{-1}$, only 43% of the first discharge capacity. The capacity difference is attributed to the formation of the SEI layer. The higher capacity loss after the first cycle, compared to graphite anodes, is attributed to the larger surface area of GNRs (48-58 m$^2$ g$^{-1}$, BET), allowing for more electrolyte to decompose than in graphite anodes (10-20 m$^2$ g$^{-1}$, BET). The SEI formation can also be seen in the plateau $\sim$0.8 V of the first discharge cycle. The following cycles present a plateau below 0.2 V, a typical potential for the intercalation/de-intercalation of Li$^+$ ions.

The reversible capacity is 54% of the theoretical capacity for graphite (372 mAh g$^{-1}$) and much lower than the theoretical capacity for graphene (744 mAh g$^{-1}$). However, it is known that the capacity of graphene-based electrodes ranging from 100 to 1000 mAh g$^{-1}$ depends on the nature of the graphene synthesis and the number of defects. The capacity obtained is based on the active material: 100% of GNRs, and it is the same for the entire electrode due to the nature of the free-standing film, where additives and binders are not needed. The lower capacity of the GNR anode in comparison to that of graphite does not cause a problem since the capacity is still higher than that of the CF-CNT cathode. Therefore, per g of the cathode, only 0.3 g of the anode is needed to match the capacities in both electrodes.
Figure 78 | Galvanostatic charge-discharge profile for the GNR anode at 0.1 A g⁻¹.

The redox reactions, or Faradaic processes, that occur in the GNR anode can also be confirmed in the GNR voltammogram. Figure 79 shows the CV curve with the presence of broad redox peaks and an asymmetric behavior in the charge and discharge cycles, which arise from the hysteresis of the Li⁺ ion intercalation/deintercalation. More voltammograms were obtained at different current densities (Figure 80a) and it can be seen that the cathodic and anodic peaks have a linear relationship to the square root of the different scan rates, indicating a reversible Li⁺ ion diffusion between the GNRs (Figure 80b).

Figure 79 | Current-voltage curve for the GNR anode at 1 mV s⁻¹.
The GNRs showed a specific capacity of about 200 mAh g⁻¹ over 100 cycles at 0.1 A g⁻¹ with Coulombic efficiencies slightly above 100% (Figure 81), which indicates that the discharge capacity was slightly higher than the charge capacity. The rate capability of the anode was also tested. Figure 82a shows the rate performance where the capacity was about 200 mAh g⁻¹ at 0.1 A g⁻¹ and decreased to 30 mAh g⁻¹ at 10 A g⁻¹, with Coulombic efficiencies close to 100% (Figure 82b).

Figure 80 | a) Current-voltage curves for the GNR anode at different scan rates, b) dependence of the current-voltage curves on the square root of the different scan rates.

Figure 81 | a) Cycling performance and b) Coulombic efficiency for the GNR anode at 0.1 A g⁻¹; the darker green corresponds to the discharge cycle and the lighter green to the charge cycle.
5.7 Fabrication and electrochemical characterization of the CF-CNT/ GNR LIC

For the fabrication of the full LIC, each electrode (the CF-CNT cathode and GNR anode) was electrochemically cycled five times in half-cell configurations at a current density of 0.1 A g\(^{-1}\) to form the SEI layer on each one and pre-lithiated the GNR anode. The CF-CNT cathode was cycled from 3.0 to 4.5 V and stopped in the charged state; the anode was cycled from 0.01 to 3.0 V and stopped in the discharged or lithiated state, which increased the weight of the GNR film by about 6%. The mass increment was attributed to the intercalated Li\(^+\) ions. Both electrodes were extracted from the half-cells and used to fabricate full Li-ion capacitors in pouch cell configurations (see section 2.14 of chapter 2).

From the studies of the cathode and anodes alone, it was shown that the mass ratio between these two electrodes should be 1:0.3. However, that will result in GNR films with densities of 0.3 mg cm\(^{-2}\), which are difficult to make and handle. The lowest density achieved with optimal properties for their use and handling was 0.8 mg cm\(^{-2}\). Therefore, the anode was used in excess in the full cells, more than twice that needed.
One of the advantages of LICs is the capability to operate at high voltages, such as 4 V. As previously reported by the Tour group, the all-carbon LICs based on CNT structures will function from 0.01 to 4.5 V.\textsuperscript{18} For this study the selected voltage window was limited to a range from 0.01 to 4.2 V.

The full electrochemical properties of the LIC combined the characteristics of the GNR anode and the CF-CNT cathode. Figure 83 shows the voltammmograms of the full device at different potential scan rates (from 10 to 200 mV s\textsuperscript{-1}). The shape of the curves is a deformed rectangle, typical of pseudocapacitors, where the redox peaks distort the perfect rectangular shape of ideal capacitors, which also corroborates the pseudocapacitance properties of the CF-CNT cathode.

![Figure 83](image)

**Figure 83** | Current-voltage curves for the GNR anode at different scan rates.

The specific capacities for the CF-CNT/GNR LIC were calculated based on the total mass of the CNT and GNR. Figure 84a shows the specific capacities at different current densities. Capacitors, in general, are known for their ability to receive and deliver energy at high rates, unlike Li-ion batteries. The average specific capacities for the LIC were 42.6, 28.6, 24.1, 20.3 and 18.6 mAh g\textsuperscript{-1} at 0.1, 0.5, 1, 2, and 3 A g\textsuperscript{-1} respectively; the capacity decreased 56% when the current density was 30 times larger. When the current
was back at 0.5 A g\(^{-1}\) the capacity obtained decreased by 9%, which indicates the stability of the LIC when it is stressed at high rates. Figure 84b shows the rest of the cycling performance at 0.5 A g\(^{-1}\) where the capacity loss is minimal after more than 400 cycles (8%), a characteristic typical of capacitors since energy storage mechanisms do not degrade the electrodes as fast as Li-ion batteries; thus, they have longer cycle lives. The Coulombic efficiencies for the rate present are shown in Figure 84c, where their values were close to 100%. Figure 84d shows the galvanostatic charge-discharge curves at the different scan rates; the discharge time at 0.1 A g\(^{-1}\) was about 25 min, and 27 s at 3 A g\(^{-1}\).

At higher currents the capacitive property of the Li-ion capacitor predominates more; thus, the profile resembles that of a triangle.

**Figure 84** | a) Rate performance, b) extended cycling at 0.5 A g\(^{-1}\) after the rate performance (gray area) in a, c) Coulombic efficiency for the rate performance, and d) galvanostatic charge-discharge profile for the different current rates of the full CF-CNT/GNR Li-ion capacitor. The darker blue in a and b represent the discharge cycle and the lighter blue the charge cycle.
Figure 85 shows the gravimetric energy and power density of the CF-CNT/GNR LIC for the scan rates from 0.1 to 3 A g\(^{-1}\). The gravimetric power density ranged from 137 to 4712 W kg\(^{-1}\), and the gravimetric energy density from 60 to 33 Wh kg\(^{-1}\), based on the total weight of the cathode and anode without the current collectors. These values are common in all-carbon Li-ion capacitors where energy densities ranged from 11 to 300 Wh kg\(^{-1}\) and power densities from 50 to 10000 W kg\(^{-1}\). In this case, the electrode is composed 100% by the active materials (CNT and GNR) while in other work the active material constitutes 60-80% of the electrode.\(^{18, 25, 30, 32, 36-38}\)

![Figure 85](image_url)

**Figure 85** | Gravimetric energy density and power density for the CF-CNT/GNR Li-ion capacitor at the current densities from 0.1 to 3.0 A g\(^{-1}\).

### 5.8 Effect of pressure on the CF-CNT/GNR LIC

As mentioned previously, the LIC was assembled in a pouch cell for the pressure tests, see sections 2.14, 2.15 and 2.16 of chapter 2. The pouch cells consisted of a separator sandwiched by the electrodes in a flat stack configuration, everything enclosed in a flexible aluminum laminated film and immersed in an electrolyte solution. A pouch cell was used because of their flexibility; when the cell is exposed to higher pressures the flexible aluminum laminated film transmits the pressure to the electrodes and electrolyte
evenly; conversely, in coin cell configurations the distribution is not even, causing inhomogeneous mechanical stress. In this study, the selected pressures were atmospheric pressure (15 psi), 500 psi, 1500 psi, 3000 psi, and 4000 psi.

Figure 86a shows the cycling performance of CF-CNT/GNR LICs at the different pressures. The current density used was 0.5 A g\(^{-1}\). As shown, at 15 psi the LIC has a typical behavior, the capacity decays in the first cycles and then stabilizes at about 20 mAh g\(^{-1}\). When the LICs where cycled at higher pressures, the cycling performance differed from the one at 15 psi. The first noticeable change was the increment in capacity between 46 to 240% of the original specific capacity. A study of the effect of pressure on capacitor electrodes showed that pressure of ~2000 psi improves the capacity of the electrodes, presumably because the pressure improved the connectivity between the different grains in the electrodes decreasing the internal resistance, which is inversely proportional to the capacity obtained by an electrode.\(^\text{16}\) This decrease in internal resistance can explain the increase in specific capacity when the LICs were cycled at higher pressures. The pressures of 500 and 1500 psi showed a more significant effect than 3000 and 4000 psi. The Coulombic efficiencies are shown in Figure 86b. At atmospheric pressure, the CF-CNT/GNR LIC has an average efficiency of 99.9%. At higher pressures, the efficiency slightly decreases and in the majority of the cycles, it remained ~99%. The cells exposed to 1500 and 3000 psi had the lowest efficiencies, and in the case of 1500 psi, after the cycle 300th cycle, there was a visible decrease, an indication of irreversible damage in the electrodes.

The second noticeable effect is the oscillation of capacities during the cycling. Typically, the capacity fades upon cycling; this fade is less for capacitors than for batteries, which is one of their advantages. However, upon being pressurized, the rate of capacity decay was slower at higher pressures than at 15 psi; then the capacity started increasing and decreasing. The contact improvement and the lower internal resistance could explain the capacity increment. The subsequent decrease in capacity could be ex-
plained by a possible collapse of the electrode structure and porosity. To the best of our knowledge, this work is the first to analyze the cycle performance of an energy device under high pressure. The mechanical stress to which the electrodes are exposed under high pressure could cause damage to their structure.

**Figure 86** | a) Cycle performance and b) Coulombic efficiency for CF-CNT/GNR LIC cycled at 15, 500, 1500, 3000 and 4000 psi at a current density of 0.5 A g\(^{-1}\).

To further understand the effect of pressure on the LICs, half-cells of the GNR anode and CF-CNT cathode were made in a pouch cell configuration and cycled 5 times at the different pressures. Figure 87 shows the galvanostatic charge-discharge profiles for the electrodes at the different pressures at 0.1 A g\(^{-1}\) and 0.5 A g\(^{-1}\). As shown, the voltage profile did not change upon cycling under pressure. In the case of the cathode, the capacity changed up to 14% of that obtained at 15 psi. For the anode, the difference in capacity was up to 53%. When the cathode and anode started being charged and discharged, there was a sudden decrease or decrease in the measured voltage; this difference in the jump of the voltage is proportional to the internal resistance in the cell. In Figure 87, it can be seen that at the beginning of the charge cycle, the voltage is lower at the high pressures, indicating a lower internal resistance. From these results, it is observed that the anode (battery-type electrode) was more affected than the cathode (capacitor-type electrode).
Figure 87 | Galvanostatic charge-discharge profiles for the CF-CNT cathode at a) 0.1 A g⁻¹ and b) 0.5 A g⁻¹; and for the GNR anode at c) 0.1 A g⁻¹ and d) 0.5 A g⁻¹.

Figure 88 shows the galvanostatic charge-discharge profiles at different points in the cycle performance of the LICs. The first cycle is different from the rest of the cycles; this profile is expected since decomposition of the electrolyte and formation of the SEI layer occurs in the first cycles. At 15 psi, the rest of the cycles are similar and overlap each other; they also have sloping profiles typical of capacitors. For the case of the profiles at 500, 1500, 3000 and 4000 psi, a different behavior can be distinguished. The sloping profile is not as pronounced and started resembling more that of a typical battery profile, dominated more by redox reactions such as Li⁺ ions intercalation and de-intercalation.
Figure 88 | Cycle performance of CF-CNT/GNR LICs at a) 15 psi, c) 500 psi, e) 1500 psi, g) 3000 psi.
psi, i) 4000 psi; and the selected Galvanostatic charge-discharge profiles at b) 15 psi, d) 500 psi, f) 1500 psi, h) 3000 psi, j) 4000 psi, the current density used was 0.5 A g⁻¹.

The LIC pouch cells were opened after cycle performance; Figure 89 shows the SEM images of the GNR anode and Figure 90 shows the SEM images of the CF-CNT cathode after 600 cycles at the different pressures. The SEI layer was visible coating the CNT bundles and GNRs. From these images, it was found that the CNT and GNR mats compact when the pressure is above 1500 psi, which results in a thicker SEI layer. It was also found that these pressures were not high enough to cause deformation in the CNTs, which have been shown to deform and change their electrical resistivity drastically above 200,000 psi.³⁹

Figure 89 | SEM images of the GNR anodes used in the cycle performance of Figure 86 at different pressures of 15, 500, 1500, 3000 and 4000 psi.
Figure 90 | SEM images of the CF-CNT cathodes used in the cycle performance of Figure 86 at different pressures of 15, 500, 1500, 3000 and 4000 psi.
A critical aspect of batteries and capacitors is how much energy is available per unit of mass or volume and how quickly that energy can be delivered. Therefore, in this study we explored the rate performance of the all-carbon LICs at different pressures; Figure 91a shows the performance from the current densities ranging from 0.1 to 2.0 A g\(^{-1}\). The device testing started at 15 psi; after the completion of all the current densities the pressure was increased to 500, 1500, 3000, and finally to 4000 psi. The result agreed with what was seen in the cycle performance; the capacity increased as the pressure increased, in this case with the higher values between 500 to 1500 psi. Figure 91b shows the Ragone Plots for the different pressures. The gravimetric energy densities at the tested current densities ranged from 15-59 Wh kg\(^{-1}\) at 15 psi, 49-99 Wh kg\(^{-1}\) at 500 psi, 41-111 Wh kg\(^{-1}\) at 1500 psi, 23-121 Wh kg\(^{-1}\) at 3000 psi, and 12-88 Wh kg\(^{-1}\) at 4000 psi. The gravimetric power densities ranged from 158-2535 W kg\(^{-1}\) at 15 psi, 178-3677 W kg\(^{-1}\) at 500 psi, 227-3599 W kg\(^{-1}\) at 1500 psi, 229-3136 W kg\(^{-1}\) at 3000 psi, and 229-2620 W kg\(^{-1}\) at 4000 psi. These results suggest that the stored energy and power capabilities are improved when the LIC is under pressure, reaching an optimal performance between 500 to 1500 psi. The performance at 3000 and 4000 psi is still better than at 15 psi, but it also suggests damage to the electrodes at pressures above 1500 psi, thus showing lower values in energy density and power density.

An additional experiment was performed to determine if the LIC functions after being exposed to high pressures. Therefore, the CF-CNT/GNR LIC was cycled 100 times at 15 psi; then the pressure was increased to 4000 psi, cycled again; finally, the pressure was returned to 15 psi, and cycled for 100 more times. Figure 92a shows the cycle performance where the LIC showed an increase in capacity under pressure. When the pressure was removed, the capacity decreased and remained about 70% of the capacity displayed at the 100th cycle. Figure 92b shows the Coulombic efficiency values during the entire process with average values above 99% (99.7% at 15 psi, 99.2 at 4000 psi, and 99.9% at 15 psi). This performance agrees with past observations where the capacity
improved the electrochemical performance.

Figure 91 | a) Rate performance and b) Ragone plots of the CF-CNT/GNR LICs tested at different pressures (15, 500, 1500, 3000, and 4000 psi).

Figure 92 | a) Cycling performance and b) Coulombic efficiency of the CF-CNT/GNR LIC cycled at 2 different pressures at a current density of 0.1 A g\(^{-1}\).

The electrochemical performance of the CF-CNT/GNR LIC showed that the LIC could function while they are being exposed to different pressures, allowing their possible applications in subsea conditions where the LIC can be used to provide power during the acceleration or breaking of the underwater vehicles. The use of capacitors for these applications is predicted in combination with a battery where the capacitor will extend the life of the battery by moderating the current drawn from it. Thus, as a proof of concept, the CF-CNT/GNR LIC was connected to a Li-ion battery in a circuit.
Figure 93 shows the circuit between the LIC and a Li-ion battery made of a lithium cobalt oxide cathode and a graphite anode, developed by the Ardebili group. The Li-ion battery was used to trickle-charge the LIC under the different pressures (Figure 94). Since the working voltage of the Li-ion battery was 3.8 V, the voltage window for the LIC was limited from 1 to 3 V. The setup described in section 2.16 of chapter 2 was used for these tests. Both the battery and the LIC were inside the high-pressure vessel and connected in the circuit through a protoboard circuit card with a toggle switch and a charging resistor to avoid current drain in the battery when the voltage on the LIC was smaller. The current the battery supplied to the LIC was ~0.1 mA, which corresponds to a current density of ~0.2 mA g\(^{-1}\). Both devices worked at all the measured pressures. The voltage of the battery dropped when current was supplied to the LIC. When the LIC reached 3.0 V, the circuit was closed, and the voltage of the battery increased closer to the initial value. As the pressure increased, the voltage dropped to lower voltage values. In batteries, the voltage drops during discharging are associated with the internal resistance of the cell. After the initial voltage drop, the voltage will decrease at a slower rate, which will depend on the amount of the current that is being drawn. This result suggested an increase in the internal resistance of the battery as the pressure increased. The LIC showed the typical galvanostatic charge-discharge profile obtained in previous experiments, where the discharge rate was 2.5 faster than the charge rate. The LIC appeared to withstand more pressure than the battery, suggesting that a combination of a capacitor with a battery will help prolong its lifetime by decreasing the stress at which it can be exposed in subsea conditions.
**Figure 93** | Scheme of the circuit for the Li-ion battery and the CF-CNT/GNR LIC. The LIC was trickle charged by the battery while both devices were under pressure.

**Figure 94** | Voltage profile of the Li-ion battery and the CF-CNT/GNR LIC while the battery trick-
le charged the capacitor at a) 15 psi, b) 500 psi, c) 1500 psi, d) 3000 psi, and e) 4000 psi. The LIC was charged at a current of density $\sim 0.2 \text{ A g}^{-1}$ from the battery, and discharge at a current density of $\sim 0.5 \text{ A g}^{-1}$.

5.9 Conclusions

In this study, it is shown the fabrication and characterization of an all-carbon Li-ion capacitor capable of performing under high pressure. The cathode was formed by a free-standing electrode made of CNT bundles growth over a carbon fiber paper. The anode was also a free-standing electrode formed by a GNRs. The cathode stores energy based on surface-redox limited reactions and double-layer capacitance, whereas the anode uses redox reactions (Li$^+$ ion intercalation and de-intercalation).

The performance of the Li-ion capacitor was tested at atmospheric pressure (15 psi), 500 psi, 1500 psi, 3000 psi, and 4000 psi. The pressure enhanced the capacitor’s specific capacity and the power capability, especially at pressures between 500 and 1500 psi, which can be attributed to the improvement in connectivity and decrease of the internal resistance. However, there is a balance between the enhancement of performance by pressure and the possible collapsing of the electrode structure, which deteriorates the electrodes. It was also observed that pressure has a substantial effect on redox reactions or Faradaic processes, as the anode showed a stronger dependence than the cathode on the pressure. The performance of the all-carbon Li-ion capacitor under pressure opens the possibility of its application in subsea operations, which will likely be supporting a battery. Therefore, a proof of concept was carried out, where the capacitor was trickle charged by a Li-ion battery at the different pressures. It was shown that both devices performed under extreme conditions.

Some of the future applications for energy storage devices require their use under extreme environments. Future work is required to explore the effect of different electrolyte concentrations and cell configurations in the electrochemical performance
of capacitors and batteries under pressure. A better understanding will provide tools for the design of devices for extreme conditions.

5.10 Bibliography


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Chapter 6

Conclusions

"I think and think for months and years. Ninety-nine times, the conclusion is false. The hundredth time I am right."

- Albert Einstein
6.1 Sulfur cathodes based on hybrid carbon structures

6.1.1 Seamless three-dimensional graphene/carbon nanotubes structure as a host material for sulfur cathodes

GCNT was used as a host material for sulfur cathodes. The GCNT consisted of CNTs grown from a graphene layer. An important advantage of the GCNT is that there is no need for conductive additives or binders, which weights decrease the energy density of the battery. Sulfur was infiltrated via a melt-diffusion method into the 3D conductive network; the results suggested the sulfur coated homogenously the surface of GCNT structure.

The use of conductive carbon materials as host for sulfur is essential for high-performance cathodes. However, the lithium polysulfide diffusion needs to be considered in the design of the cathode. The main findings using GCNT as a host material were:

1. The GCNT exhibits a high surface area of about \(>2,000 \text{ m}^2 \text{ g}^{-1}\), which makes possible high sulfur loadings. The S-GCNT cathode can have sulfur loadings of 60% or above (considering only the mass of sulfur and carbon). The percent can be tuned by additional heating periods at 250 \(^{\circ}\)C in an inert atmosphere.

2. The seamless junction between the current collector (Ni), graphene, and carbon nanotubes proportionate excellent electrical conductivity for sulfur utilization and outstanding rate performances. The S-GCNT cathodes exhibited initial capacities above the 900 mAh g\(^{-1}\). The good rate capability was demonstrated where the capacity changed less than 40% when the current was 20 times higher, from 0.1 to 2.0 C.

Nevertheless, since the infiltration of S occurs on the surface of the GCNT structure, there is a limited ability to prevent the diffusion of lithium polysulfides. Therefore,
the S-GCNT exhibited capacity retentions between 50 to 67% after 200 charge-discharge cycles.

6.1.2 Use of carbon interlayers to improve the cycle stability of S-GCNT cathodes

The capacity retention of the S-GCNT cathodes was further improved by placing carbon-based interlayers between the cathode and the separator. One interlayer was a compact GNR film coating the battery separator. The other interlayer used consisted in a coating of the cathode with an aligned carbon nanotube film.

1.- Both approaches increased the capacity retention between 60 to 87% after 200 cycles.

2.- Both approaches acted as blocking layers for lithium polysulfides. The electrical conductivity of GNRs and CNTs allowed the utilization of the trapped polysulfides by proportioning electron pathways; therefore, they decreased the capacity loss upon cycling.

3.- The aligned CNT film performed better than the GNR-coated separator. It also had additional advantages, it is eight times lighter, which means it adds less additional weight that decreased the energy density of the whole electrode. The superior performance can be attributed to the direct contact between the CNT and the S-GCNT electrode.
6.1.3 Sulfurized PAN composites for long-cycle life sulfur cathodes

Another type of sulfur cathode was synthesized by the reaction between sulfur and PAN with the addition of GNRs to increase the electrical conductivity. Sulfur is believed to be covalently bonded to the PAN chain and to be trapped in the form of small sulfur. The resulting cathode presented excellent cycle stability, after 700 cycles the capacity retention was 96.3%, with specific capacities of ~800 mAh g⁻¹. The structure of this cathode proved that the bonding and the effective trapping of sulfur make possible the fabrication of stable cathodes capable of competing with commercial Li-ion batteries. However, the sulfur content of the final cathode is limited since there is only a specific amount that can react with PAN. The typical sulfur loadings were ~50%.

6.1.4 Future work

The GCNT structure is attractive due to its conductivity and high sulfur loadings. However, it also showed that new cell configurations are needed for stable Li-S batteries, which currently use the typical configuration of Li-ion batteries. The wrapping of the sulfur cathode by conductive materials resulted in an effective approach to solve the lithium polysulfide diffusion. Future work should explore different materials and wrapping methods; this concept can also be translated to standard cathodes (composite on aluminum foil), where layered cathodes can result in a better approach. For example, a configuration can be the aluminum current collector, a layer of the sulfur composite, and an external layer of a material that will prevent the diffusion of polysulfides, such as carbon materials or metal oxides. The weight of the external layer should also be optimized.

In the case of S-PAN cathodes, for commercially competitive cathodes, the final sulfur content needs to be increased to sulfur loadings above 60%. Since there is a limited amount of sulfur that can be bonded and trapped to the polymer backbone, it would
be interesting to explore the performance of mixtures of elemental sulfur with the sulfurized polyacrylonitrile. Although, there should have a careful design able to prevent the diffusion of polysulfides to maintain excellent capacity retention. The optimal concentration of the electrolyte should also be studied since S-PAN cathodes work better with high-concentrated electrolytes and elemental sulfur cathodes with low-concentrated electrolytes.

### 6.2 Stable lithium metal anodes by controlling Li-ion flux through a lithium diffusion interface

A MWCNT film was used as a Li\(^+\) ion diffusion interface to suppress the growth of Li dendrites. The MWCNT film coated the Li metal surface, the proximity and the addition of concentrated electrolytes promoted the full lithiation of the MWCNT film (Li-MWCNT). The Li-MWCNT interface acted as a reservoir for Li\(^+\) ions; during stripping, the Li\(^+\) ions are ejected from the Li-MWCNT interface and refilled from the Li metal. During plating, the Li\(^+\) ions stored in the Li-MWCNT interface are reduced at the Li metal surface, while the Li\(^+\) ions from the electrolyte filled the MWCNT. The main findings were:

1. The lithiation of MWCNT is a key element in the protection of Li metal anodes since they form a Li\(^+\) ion conductive layer, which resembles an artificial SEI layer.

2. The Li-MWCNT interface can also act as a blocking layer for parasitic reaction in the Li metal surface.

3. A new test to characterize the effectiveness of protective layers in Li metal anodes was developed. Lithium polysulfides were added into the electrolyte of a symmetrical cell to simulate the environment in a Li-S battery.
4. The weight contribution of the MWCNT film can allow high capacity Li metal anodes, and the whole anode had specific capacities up to 2200 mAh g\(^{-1}\) (considering the mass of Li metal and the MWCNT film), which corresponds to 57% the theoretical specific capacity for Li metal. Commercial graphite anodes have capacities of \(~300\ mAh\ g\(^{-1}\).}

5. The Li metal anodes protected with Li-MWCNT could perform in full Li-S cells.

6. The Li-S cells showed excellent rate capabilities.

6.2.1 Future work

The used of Li\(^+\) ion conductive interfaces results in effective protection for Li metal anodes. It would be promising to explore the performance of other lithiated carbon materials, the effect of the layer thickness and the concentration of the electrolyte. An additional concept, it is to explore the performance of 1D versus 2D structures, which can modify the Li\(^+\) flux.

6.3 All-carbon Li-ion capacitor for subsea and high-pressure applications

An all-carbon LIC was fabricated using a free-standing GNR film as the anode, and a hybrid carbon fiber-CNT structure as the cathode. The LIC showed capacities above 20 mAh g\(^{-1}\) and excellent rate capabilities. The main findings were:

1. The LICs were able to perform at high pressures.

2. The pressure increased the specific capacities of the LIC cells.
3. The energy density and power density improved with the pressure. The best performances were at 500 and 1500 psi.

4. The pressure seemed did not change the morphology of the cathode and the anode.

5. The effect of pressure showed that the capacity increased by possible promoting the surface redox reactions, due to the decrease in internal resistance.

7. The pressure had a more significant effect on the battery-type electrode (based on redox reactions) that in the capacitor-type electrode (based on double layer capacitance).

8. The LIC could be trickle charged from a Li-ion battery at high pressures.

6.3.1 Future work

Further research is needed to explore higher pressures and the balance between the improvement in energy density and the collapsing of the electrode structure upon pressure application. Also, the effect that pressure can have on the Gibbs free energy of redox reactions can be further analyzed for the design of batteries that produce better electrochemical performances at high pressures.