Experimental and Computational Design of Nanostructured Materials for High Performance Supercapacitor Devices

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Experimental and Computational Design of Nanostructured Materials for High Performance Supercapacitor Devices

A Thesis in Nanotechnology
By Basant Ali El-Shoky

Submitted in Partial Fulfilment of The Requirements for The Degree of Doctor in Philosophy in Nanotechnology

Feb. 2021
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Both energy conversion and storage technologies need to be developed hand-to-hand simultaneously to overcome the energy crises. To this end, supercapacitors (SCs) have the potential to be the energy storage platform due to their fast charging capability and long cycling stability. However, their low energy is the bottleneck towards their wide implementation compared to batteries. Also, current research is based on guess and check methods to modify electrode materials with limited properties prediction. In this thesis, density functional theory (DFT) has been employed as a tool to identify potential SC electrode materials. Then, the gained knowledge was used to develop sustainable solutions for the synthesis of SC electrode materials. The results showed that the use of basic electrolytes should ensure the highest capacitance performance of functionalized carbon-based electrodes, while neutral electrolytes should enable the highest potential window. Moreover, CNTs were shown to deliver the highest capacitance in comparison to various carbon allotropes. A symmetric device of CNTs revealed an energy density of 23.2 Wh/Kg at a power density of 475 W/Kg. Also, the results showed ion intercalation to enhance the quantum capacitance and stabilize the 1T phase of MoS$_2$ and recommended the use of Cs$^+$ intercalation for concentrated electrolyte supercapacitors and K$^+$ intercalation for the diluted counterpart. Moreover, the 2H and 3R-MoS$_2$ phases should be used only as positive electrodes, while the 1T-MoS$_2$ can be employed as positive and negative electrodes. The 1T-MoS$_2$ symmetric device revealed an energy density of 4.19 Wh/Kg at a power density of 225 W/Kg. Further, multi-metal sulfides showed superior performance, where the hybrid Ni-Mn-Co-S//graphene hydrogel device delivered an energy density of 49.55 Wh/Kg at a power density of 800 W/Kg. Interestingly, Li-Ni-Mn-Co hydroxides recycled from spent batteries showed a specific capacitance of 951 F/g at 1 A/g. Finally, a silk in-vivo chemically-modified electrode exhibited 5 folds of capacitance increase compared to the unmodified silk. Therefore, quantum capacitance and other DFT predictions are useful in screening electrode materials. Also, sulfide electrodes can exhibit very high capacitance performance either through intercalation or redox processes if combined in hybrid supercapacitor devices.
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<td>B3LYP</td>
<td>Becke, Three-Parameter, Lee-Yang-Parr</td>
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<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
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<tr>
<td>BJH</td>
<td>Barrett–Joyner–Halenda</td>
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<tr>
<td>CB</td>
<td>Conduction Band</td>
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<tr>
<td>CC</td>
<td>Carbon Cloth</td>
</tr>
<tr>
<td>CCCD</td>
<td>Constant Current Charge/Discharge</td>
</tr>
<tr>
<td>cDFT</td>
<td>Classical Density Functional Theory</td>
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<tr>
<td>$C_{dl}$</td>
<td>Double Layer Capacitance</td>
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<td>CNTs</td>
<td>Carbon Nanotubes</td>
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<td>Cs</td>
<td>Specific Capacitance</td>
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<tr>
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<td>Density Functional Theory</td>
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<tr>
<td>DMF</td>
<td>Dimethyl Formamide</td>
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<tr>
<td>DOS</td>
<td>Density of States</td>
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<tr>
<td>DW</td>
<td>Distilled Water</td>
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<tr>
<td>EDCC</td>
<td>Electric Double-Cylinder Capacitor</td>
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<tr>
<td>EDL</td>
<td>Electrical Double Layer Capacitor</td>
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<tr>
<td>EDX/EDS</td>
<td>Energy-Dispersive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi Level</td>
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<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
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<tr>
<td>ESR</td>
<td>Equivalent Series Resistance</td>
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<td>EWCC</td>
<td>Electric Wire in Cylinder Capacitor</td>
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<tr>
<td>FT-IR</td>
<td>Fourier-Transform Infra-Red Spectroscopy</td>
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<tr>
<td>GCD</td>
<td>Galvanostatic Charge/Discharge</td>
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<td>GGA</td>
<td>Generalized Gradient Approximation</td>
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<tr>
<td>Gr</td>
<td>Graphite</td>
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<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>HRTEM</td>
<td>High-Resolution TEM</td>
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<tr>
<td>IL</td>
<td>Ionic Liquid</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>LCAO</td>
<td>Linear Combination Atomic Orbitals</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
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<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<td>MGHG</td>
<td>N-Doped Mesoporous Grapheme Hydrogel</td>
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<td>MOF</td>
<td>Metal-Organic Framework</td>
</tr>
<tr>
<td>NL-DFT</td>
<td>Non-Local Density Functional Theory</td>
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<td>OCV</td>
<td>Open Circuit Voltage</td>
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<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
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<tr>
<td>PVA</td>
<td>Poly Vinyl Acetate</td>
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<td>Polyvinylidene Difluoride</td>
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<td>PW</td>
<td>Perdew-Hung</td>
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<td>PZC</td>
<td>Potential of Zero Charge</td>
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<td>QS-DFT</td>
<td>Quenched Solid DFT</td>
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<tr>
<td>rGO</td>
<td>Reduced Graphene Oxide</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
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<tr>
<td>SCE</td>
<td>Standard Calomel Electrode</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
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<td>TGA</td>
<td>Thermogravimetric Analysis</td>
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<tr>
<td>VASP</td>
<td>Vienna Ab-Initio Simulation Package</td>
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<tr>
<td>VB</td>
<td>Valence Band</td>
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<td>VdW</td>
<td>Van der Waals</td>
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<tr>
<td>W</td>
<td>Warburg Resistance</td>
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<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
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<td>XRD</td>
<td>X-Ray Diffraction</td>
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ACKNOWLEDGEMENT

All praise is due to Allah. We praise Him, seek for His assistance and forgiveness and we seek refuge with Him from evils of our souls and our misdeeds. No one can mislead whosoever Allah guides and none can guide whosoever Allah causes to go astray. And as our Prophet (ﷺ) said: “He who does not thank people does not thank Allah” we shall abide and obey. This being said, I am utterly grateful and thankful to all who supported and guided me through the journey of the PhD degree. A special appreciation goes to my father who supported me all the way since teaching me how to speak until accompanying me in my interview in the EML, and also, I want to thank my mother who backed me heart and soul throughout my life in each and every single aspect of life with hearts full of unconditional love; they literally sacrificed everything to make me the way who I am now. Comes second to my parents is the support of my beloved Husband who brightened up my life from day one of our marriage. He was always there for me, helped me a lot in my research and paved the way for my graduation that would have been impossible without his support and encouragement. He was very helpful and understanding during writing my thesis, and his computational skills and academic background were very valuable to my research. Also, I want to thank my sisters for their support. For my son Al-Baraa, I would like to thank him for his endurance during my thesis writing period.

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DEDICATION

I dedicate this thesis to my parents, my beloved husband Ahmed Biby, my kind son Al-Baraa, and my sisters.
Chapter I: Introduction

1.1 Supercapacitors as a solution for energy storage

Our daily need for energy is increasing dramatically and fossil fuels-based sources will soon be consumed. Therefore, it is important to rely on renewable energy resources such as solar cells, wind, and other resources. Since most of the renewable sources are time limited and generate energy in the form of electricity, it is mandatory to find suitable electrical energy storage devices. The most commonly known electrical energy storage devices are batteries, fuel cells, and supercapacitors. As early as the 18th century, the idea of a capacitor was discovered in a Leyden Jar,\(^1\) while in 1920, the first electrochemical capacitor was developed.\(^1\) However, In 1957, the first EDL supercapacitor was presented by Becker.\(^2\) Moreover, the pseudocapacitive behavior was introduced for the first time by Conway using \(\text{RuO}_2\) electrode in 1980.\(^1\) Since then, supercapacitors have gained a great attention by the research community for their high power density. However, their limited energy density has restricted their practical use. Researchers are actively looking for new electrode materials that can provide both high energy density and high power density, with the research increasing year by year as illustrated in Figure I-1 (as indexed by Web of Science). Interestingly, the IDTechEx expect that by 2025 the supercapacitors’ market will attain up to $8.3 billion as illustrated in Figure I-2.\(^1\)

![Figure I-1 (A) The research articles, books, and other publications on supercapacitors by year.](image-url)
Figure I-2 Projected global supercapacitor market between 2014-2025.\(^1\)

The development of the supercapacitors’ electrodes is forked between different merits.

Figure I-3 illustrates the most important factors controlling the supercapacitor performance.\(^3\) However, one research track is not enough to reach the ultimate cell performance. On the other hand, materials science researchers are focusing on developing electrode materials that can cover most of the controlling factors to develop the best supercapacitor device.

Figure I-3 Development factors for supercapacitor cells.\(^3\)
1.2 Charge storage mechanisms in supercapacitor

1.2.1 Electrical Double layer capacitors

The first proposed supercapacitor device and the most commonly investigated type is the electrical double layer capacitor (EDL). To simplify the idea of the EDL capacitor, let us assume two carbon rods in an electrolyte with current applied. When current starts following, the charges accumulate at the electrode/electrolyte interface as illustrated in Figure I-4. The ions form the electrolyte accumulate on their counterpart charge electrode surfaces. Moreover, when the circuit is opened, the energy is stored, and the voltage is maintained. The formed two parallel regions of charges are named “inner Helmholtz double layer” and it is the driving source of the energy storage. The concentration and ionic size control the thickness of the EDL. When an electrode is in contact with electrolyte ions without having a net charge, there will be a potential of zero charge (PZC). At the PZC, the electrolyte ions do not have a preference of accumulation near the electrode and an applied voltage will be needed to form the aggregates of ions on the surface of the electrode (EDL). The electrode/electrolyte interface can be explained by the classical Helmholtz model where two parallel planes represent the electrode surface and the electrolyte ions spaced by a distance d. The two parallel plates are oppositely charged and the electrostatic potential between them drops linearly and is independent of the distance of the outer charges. However, the Helmholtz model is not accurate for some systems. On the other hand, another model “Gouy-Chapman model” is more accurate since it depends on the application of Maxwell-Boltzmann statistics to the electrolyte charges in which the countercharges are distributed along the diffuse layer and decrease with distance from the electrode so that the electrostatic potential decreases with increasing distance from the electrode. The Helmholtz model and the Gouy-Chapman model were combined in a new model “Stern model” in which the electrolyte ions form a parallel plane of countercharge to the electrode but do not completely neutralize the electrode charge instead a diffuse layer of the net countercharges exist beyond the ionic plane. In an EDL capacitor, no charge is transferred between the electrode and electrolyte. So, the electrolyte solution is constant during the
charge/discharge process and the fast adsorption/desorption causes a high power density. However, the EDL capacitor is limited by the surface area available for adsorption. It is noteworthy to mention that density functional theory was proved to be successful in screening a plethora of electrode materials based on their quantum capacitance, which estimates the EDL electronic contribution, hence its overall capacitance performance. However, the literature pertaining quantum capacitance screening so far has only been devoted to graphene and graphene-doped materials with no available data on other 2D materials such as transition metal dichalcogenides (TMD), necessitating the need to develop such data to build up materials library for potential applications in energy storage technologies.

![Electrical double layer models](image)

**Figure I-4** Electrical double layer models.

1.2.2 Pseudocapacitors

"Pseudo" is a Latin word meaning false, fake, or almost. In the electrochemical capacitor community, pseudocapacitor is a name for an electrode that exhibits an EDL behavior despite the existence of charge transfer process (Faradic). Therefore, pseudocapacitors are not pure EDL capacitors nor totally Faradic in nature, but lay in a middle ground between both, where a Faradic process occurs at the surface or near surface of the electrode such as the intercalation process as illustrated in **Figure I-5**. Hence, the reaction has fast kinetics that gives it an EDL-like characteristics. In case of monolayer proton adsorption of where a charge transfer can occur, the pseudocapacitive behavior can be observed and named the adsorption
pseudocapacitance. Furthermore, the intercalation process is usually occurring in an electrode material with an empty d-orbital and layered structure to allow fast adsorption/desorption. For the surface redox reactions, it is important to note that upon reducing the electrode materials size to the nanoscale, the surface area becomes very high and almost all the reactions on the surface results in a pseudocapacitive behavior even for redox and battery-like materials, as presented in Figure I-6. However, in bulk, the redox electrode material may maintain its pseudocapacitive behavior (intrinsic pseudocapacitive) or turn into a battery-like behavior (extrinsic pseudocapacitive). The pseudocapacitive behavior was first proposed when Conway observed the capacitive behavior of RuO$_2$ in acidic medium. Since pseudocapacitor is in the “gray” region between EDL capacitors and batteries, the pseudocapacitor concepts are changing all the time according to the developed materials, mechanisms, or theories as illustrated in Figure I-7. Note that, it is yet to generalize a pseudocapacitor definition.

Figure I-5 Pseudocapacitor charge storage mechanisms.

Figure I-6 Redox behavior in thin layer vs. bulk electrode materials.
1.2.3 Battery-Like supercapacitors

A battery-like electrode is the electrode exhibiting a bulk redox reaction with clear redox peaks. Usually, battery-like electrodes are not considered a “true” supercapacitor electrode unless it is used in a hybrid device against an EDL capacitor or pseudocapacitor. However, when using the battery-like electrodes in hybrid devices or in symmetric devices, the low rate measurements are considered misleading. Also, thin film of redox materials would lead to short cycling life and limited performance. Usually the performance of supercapacitor electrodes with a battery-like behavior is measured in terms of specific capacitance and capacity. To this end, battery-like electrodes are hot research area that need more investigation.
1.3 Designing electrode materials for ultimate capacitance performance

The research community has been focusing to identify the best electrode material for supercapacitor devices to allow high power and energy densities. To this end, a road map has been proposed to guide researchers reaching their goal as illustrated in Figure 1-8. However, it is still very expensive to try any materials experimentally. Therefore, this thesis shows the potential of the density functional theory (DFT) in screening many materials and identifying the potential candidates. Then synthesis of the potential materials using the best synthesis methods and testing their performance in both three-electrode and two-electrode systems. Finally, a note on the availability of using the potential material at the industrial scale is proposed. From Figure 1-9, it can be noticed that the research so far is focused on carbon-based electrodes with an increasing interest in hybrid supercapacitors. Besides, the sulfide and transition metal chalcogenides have not been fully investigated in the literature as the metal oxides in spite of their high capacitance performance. On another note, the recycling of spent batteries is poorly addressed in the literature, necessitating the importance of investing more time and efforts to address this topic. Moreover, the use of the density function theory (DFT) in the prediction of materials’ capacitance performance prior to the synthesis and testing is rarely addressed in the literature and was only limited to graphene and doped graphene materials.
Figure I-8 A roadmap for designing and testing electrode materials: From materials perspective to real device fabrication.

Figure I-9 The number of publications on different supercapacitor electrode materials in last 5 years.

To this end, designing a supercapacitor device that can be used commercially needs electrode materials with high density and power densities. Although carbon materials are heavily studied in the literature, the identification of the effect of electrolytes on the performance of carbon materials’ potential window is not intensively investigated. Moreover, Fullerenes, as electron rich carbon allotropes, are rarely addressed in the literature of supercapacitors. The previous shortages and limitations make the gap in the EDL supercapacitors’ research clear and open for investigation. Also, the effect of intercalation on
the transition metal dichalcogenides’ charge storage mechanism, and the effect of intercalants are gaining much interest as a new route for developing pseudocapacitors. Thus, innovation in intercalation and investigation of the quantum capacitance effect are highly desirable to be addressed in details. Furthermore, the used of battery-like electrodes and hybrid devices should ensure high capacitance and stability. However, the effect of multi-metal sulfides and the nature of the substrate on the battery-like behavior are still unexplored and need very intensive research. Finally, sustainable solutions to electrode fabrication are mandatory to provide environmentally-friendly supercapacitors.
1.4 Scope of the thesis

Designing high performance supercapacitor electrode materials with high energy density while retaining their high power density is urgently needed to satisfy our ever growing need for energy storage devices. To this end, the thesis presents a strategy to achieve such goals by applying computational and experimental approaches to identify the proper electrode materials, electrolytes, and charge storage mechanisms.

Chapter II presents information on scientific background needed to go through the thesis work.

Chapter III provides insights on the difference between supercapacitors and batteries. Also, it highlights the previous work on developing electrodes with different charge storage mechanisms such as EDL carbon electrodes, Faradic-based electrodes, and mixed EDL/Faradic electrodes. Moreover, the chapter highlights the importance of designing fabric electrodes for possibility of wearable electrodes, as well as recycling battery electrodes to fabricate supercapacitor devices. Finally, the chapter presents the importance of density functional theory (DFT) as an efficient tool in designing electrode materials.

Chapter III describes the scientific background of the electrochemical and computational parameters used in the study.

Chapter IV gives details on the experimental and computational techniques used through the thesis.

Chapters VI-VII constitutes the results and discussion section of the dissertation:

Chapter V discusses the development of carbon-based supercapacitor electrode materials. It starts with comparing the different carbon structures in different electrolytes and highlighting the effect of structure and ions on the positive and negative potential windows and the capacitance performance. The DFT calculations were used to give insights on the studied carbon materials and proved their excellence in terms of quantum capacitance calculations. Then, DFT was used to model the N-doped graphene that was synthesized and tested, showing superior electrochemical performance.
Chapter VI discusses the development in Faradic-based electrodes. The chapter starts with modeling single sulfide-based chalcogenide (MoS$_2$) intercalated with different alkali metals (Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$) and H$^+$ ions. Then, MoS$_2$ was synthesized and tested as a supercapacitor electrode in different electrolytes based on Li, Na, and K ions to confirm the results obtained from the DFT modeling. Afterwards, MoS$_2$ was mixed with the best carbon materials resulted in Chapter V and in the best acting electrolytes resulted in Chapter V. Further, the double sulfide electrode of Ni and Mn was electrodeposited and tested to give a superior supercapacitor performance that led to the electrodeposition and testing of the tertiary sulfide Ni-Mn-Co-S electrode. Moreover, to apply the results in wearable electronics, the sulfide electrodes were tested on both Ni-foam and carbon cloth to investigate the overestimation in capacitance when Ni-foam is used. Hence, the tertiary sulfide was assembled and tested as positive electrodes on carbon cloth substrate against the negative electrode synthesized and tested in Chapter V to reach the best device performance.

Chapter VII uses the gained experience to develop sustainable solutions for developing supercapacitor electrodes. First, recycling Li-ion batteries into supercapacitor materials with high performance depending on the gained knowledge on the electrodeposition technique. Second, the developed nanomaterials were used as feeding materials to silkworms and resulted in an in-vivo production of conductive silk that can be easily used to produce wearable supercapacitor electrodes.

Chapter VIII is the conclusion of the dissertation and suggestion for future plans.
Chapter II: Supercapacitor Background

2.1 Electrolyte

The electrolyte of the electrochemical cell and device consists mainly of solvent and supporting electrolyte. The criteria to choose a good solvent are as following:

1) It maintains its phase at the temperature of the experiment.
2) It can dissolve the electrolyte ions completely in the desired concentration.
3) It will not undergo a parasite reaction with the electrolyte ions or upon applying voltage.

It is usually preferable to use a high concentration of the electrolyte for the following reasons:

1) Increase conductivity. Since the electron transfer at the electrode surface will cause a migration for the electrolyte ions to balance the charge and complete the circuit, a high concentration is needed to maintain conductivity. The electrolyte will resist charge transfer if the charge balance was not maintained.
2) Minimization of the migration of ions between concentration gradients.

Noteworthy to mention that the electrolyte solution should be purged with inert gas such as N\textsubscript{2} to remove any traces of reactive gases such as O\textsubscript{2} that may interfere with the redox reaction and a Teflon cover is preferred to be used throughout the experiment to prevent the reinsertion of interfering gases.

Moreover, choosing an electrolyte compatible with the supercapacitor electrode is mandatory to provide the best supercapacitor performance as illustrated in Figure II-1. Electrolyte composition can affect the conductivity, potential window, charge storage mechanism, and capacitance value of the supercapacitor electrode.\textsuperscript{14} It also important to match the ionic size of the electrolyte with the pore size of the electrode material taking into consideration the pH of the electrolyte and its relation to pseudocapacitance and battery-like performance of the electrode material. To this end, before choosing an electrolyte for the supercapacitor device, the following points should be taken into consideration:
1) The interaction with the electrode material.
2) The solvent/electrolyte interaction.
3) The potential window of the electrolyte.
4) Ionic size.

**Figure II-1** Effect of electrolyte on the supercapacitor performance.\(^{14}\)

Electrolytes used in supercapacitor devices can be classified depending on its type and phase as expressed in **Figure II-2**.

1) Aqueous electrolytes are the ones widely used due to their low cost and easy preparation. However, they provide a low potential window due to the limitation of the water splitting occurring upon applying voltage. Moreover, the reduction in the potential window is increased due to the catalytic effect of the acidic and basic medium. Making the neutral aqueous electrolytes such as Na\(_2\)SO\(_4\), the best in terms of potential window enhancement.\(^{15}\) However, neutral aqueous electrolytes are usually not compatible with battery-like electrode materials.\(^{16,17}\) The usual concentration of the aqueous electrolytes are in the range of 0.5 M to 3 M and it can reach up to 6 M in some cases.\(^{14}\)
2) For non-aqueous electrolytes, they provide a high potential window that can be easily predicted using density functional theory methods. The non-aqueous electrolytes are either in the form of ionic liquid (IL) which is an organic salt in its liquid form at room temperature or organic salt dissolved in organic solvent. Although IL has a high thermal stability and high stability, it is expensive, and its large ionic size hinders its use. However, IL has a variety of combinations between the cations and anions opening the door for a large development. Another disadvantage of the IL is its high viscosity which reduces the capacitance at high scan rates besides, it is not helpful in case of pseudocapacitors or battery-like capacitors. For, the organic electrolytes, although it is cheaper than IL, it is flammable, volatile, and the lowest amount of impurities may poison the electrolyte reducing the specific capacitance and the self-discharge. In summary, non-aqueous electrolytes are good for commercial production due to their high operating voltage up to 3.5 V and the possibility of improvement in the composition of the electrolyte.

3) For the solid-state electrolytes, they present the upcoming target for researchers since they provide a leakage-free device that can be easily backed and used in wearable and flexible devices. Although inorganic solid electrolytes and dry polymer electrolytes were used in some literature, the widely used solid-state electrolyte is the gel electrolyte. The gel electrolyte provides a wide range of electrolyte types since it uses a polymer such as poly vinyl acetate (PVA) to turn aqueous electrolytes (hydrogels), ionic liquid (ionogel), and organic electrolytes (organogels) to solid-state electrolytes without losing their original properties. However, the ionic conductivity is usually lower in case of gel electrolytes and this can be overcome through increasing concentration.

4) For the reactive electrolytes, they are usually used to increase the capacitance value through using the electrolyte as a source of additional redox reaction rather than the electrode material only. This type of electrolytes can be found in the form of aqueous electrolytes, organic electrolytes, ionic liquids, or gel electrolytes. The specific
capacitance of a normal carbon electrode with KI reactive electrolyte can reach 1840 F/g and a supercapacitor device can reach 125 F/g at 50 A/g. However, reactive electrolytes usually work in a narrow potential window reducing the power density and limiting the specific capacitance in the device since it may have effect in positive or negative potential window only. Besides, the self-discharge is usually higher in case of using reactive electrolytes. To overcome the self-discharge problem, an ion-exchange membrane such as Nafions can be used as a separator, or using an electrolyte that could be reversibly converted into insoluble species during the charge/discharge process.\textsuperscript{14}

![Figure II-2 Supercapacitor electrolyte classification.\textsuperscript{14}](image)

Furthermore, it is mandatory to use a separator and electrode substrate that will not react or corrode upon using the electrolyte. Also, the electrolyte should not be hydrophobic towards the used binder and its ions should be easily preamable through the separator.

2.2 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) measures the current response upon applying voltage in a three-electrode system or two-electrode system and the resulted curve is usually referred to as a voltammogram. The CV curve can be found in literature in two forms, the IUPAC form and the US form depending on the starting potential to scan the reaction as illustrated in Figure II-
The potential applied in the CV technique should be in a defined speed (scan rate) and this scan rate affects the electrode/electrolyte interface reactions. As an example, the redox reaction in Figure II-4 presents the cathodic scan (reduction occur) from $E_1$ to $E_2$ and the anodic scan (oxidation occur) from $E_2$ to $E_1$. The peaks in the voltammogram can be attributed to two main effects. First, the current response with time as the concentration of ionic species change near the electrode. Second, the formation of reduced ionic species at specific applied potential as indicated by Nernst equation. Moreover, for a reversible redox reaction, the peak to peak separation (anodic to cathodic peak difference) is usually $\sim 57$ mV and the half max width of the peak $\sim 59/n$ mV as $n$ is the number of electron transfer. Besides, the anodic current/the cathodic current equals 1 and the potential energy does not depend on scan rate. However, for an irreversible redox reaction, the electron transfer barrier is high, and the reaction needs more (positive or negative) applied potential to perform the redox reaction and hence a wide peak to peak separation.

For a multi-step reaction, the CV curve will depend on the thermodynamic stability of every reaction. As an example, for a two-step reaction, if the second redox reaction is more favorable than the first redox reaction, the CV will have one redox peak with peak to peak separation of $28.5$ mV/s as if it was a two electron reaction. However, if the more favorable the first redox is than the second redox reaction, the more peak to peak separation will increase until it reaches a peak to peak separation of $140$ mV/s then the peak will be divided into two peaks each with a peak to peak separation of $57$ mV/s. It worth mentioning that the observation of a redox peak that have a one diminishing peak with time or one peak that turns to redox.
peaks with time means that the two-step reaction contains a one irreversible reaction either the second or the first reaction, respectively.

![Figure II-4 CV for the reduction of Fc+ to Fc reaction.](image)

2.2.1 Capacitance calculations

CV can be used to determine the specific capacitance ($C_s$) of supercapacitor electrode in a three-electrode cell or supercapacitor device in a two electrode cell. However, for the three-electrode system, eq. II-1 can be used,\(^1\) on the other hand, for the symmetric two-electrode system, the total capacitance ($C_T$) is calculated as illustrated in eq. II-2\(^1\)\(^2\) and the total specific capacitance for the symmetric device ($C_{sT}$) is illustrated in eq. II-3 indicating a reduction of the electrode capacitance by 25\%.\(^3\)

\[
C_s = \frac{C_E}{m} = \frac{\int I \, dV}{vm \Delta V} \quad \text{(II-1)}
\]

\[
\frac{1}{C_T} = \frac{1}{C_E} + \frac{1}{C_E} = \frac{2}{C_E} \quad \text{(II-2)}
\]

\[
C_{sT} = \frac{C_E}{4m} \quad \text{(II-3)}
\]

where \(m\) is the mass of the electrode (g) or the surface area (m\(^2\)), \(v\) is the scan rate (V/s), \(\Delta V\) is the potential window (V) and \(\int I \, dV\) is the integration of the CV curve. However, for an asymmetric device, the total capacitance should be divided by the combination of the masses of the two electrodes. Moreover, for the CV data to be reliable, the scan should be recorded after 20 cycles ad from zero to the desired voltage to avoid the unreliable increase in the current.
due to reverse polarity of the electrode.\textsuperscript{21} It worth noting that CV should be measured for different scan rates to indicate the real capacitance performance of the electrode and to indicate the charge storage mechanism.

2.2.2 Energy storage mechanism

The simplest method to define the charge storage mechanism is the shape of the CV as illustrated in \textbf{Figure II-5}.\textsuperscript{22} The intercalation, surface redox, or simple adsorption/desorption gives a rectangular shape CV. While the deviated CV shape presents the pseudocapacitive behavior and the full redox peaks represents a battery-like capacitor.

\textbf{Figure II-5} CV shapes for different charge storage mechanisms.\textsuperscript{22} 

One of the mainly used methods to define the charge storage mechanisms is the application of Randles–Sevcik equation (\textbf{eq. II-4} simplified as \textbf{eq. II-5}) as $b$ is the slope. When the relation between the $i_p$ vs. $v^{0.5}$ gives a linear line, the detected process is a reversable electron transfer. However, the deviation from linearity indicates either a quasi-reversable reaction (the peak to peak separation vary with scan rate) or surface adsorbed species (no peak to peak separation).\textsuperscript{18}

\begin{equation}
    i_p = 0.446nFAC \left( \frac{nFvD}{RT} \right)^{0.5}
\end{equation}

(II-4)
\[
\log (i_p) = \log (a) + b \log (\nu)
\]  

(II-5)

where \(i_p\) is the peak current (A), \(n\) is number of transfers electrons, \(\nu\) is the scan rate (V/s), \(F\) is Faraday’s constant, \(A\) is the electrode surface area (cm\(^2\)), \(C\) is the electrolyte concentration (mol/cm\(^3\)), \(D\) is the diffusion coefficient of the oxidized species (cm\(^2\)/s). However, the previous equation assumes that the concentration near the electrode surface is equal to that of the bulk which makes the results inaccurate if considered for the back scan or the second voltammetry scan. Moreover, Dunn et al. have modified the previous equation to give the percentage of the diffusion current and capacitive current in case the \(b\) value was between 1 and 0.5 as illustrated in Figure II-6 using eq. II-6.\(^{23}\) where the capacitive resulting current is \((k_1 \nu)\) and the diffusion-controlled mechanism resulting current is \((k_2 \nu^{1/2})\), where \(k_1\) and \(k_2\) are obtained from the slope and intercept of the \(\nu^{1/2} vs. \nu^{1/2}\) plot, respectively.

\[
\frac{i_{\nu}}{\nu^{1/2}} = k_1 \nu^{1/2} + k_2
\]

(II-6)

One of the drawbacks of the Dunn’s method is that the current should be measured at a fixed potential. However, for quasi-reversible redox reactions, the peak current position changes with scan rate and the Dunn’s method is no longer valid. It is worth mentioning that with increasing the scan rate, the electrode expresses more capacitive behavior than reality. Therefore, it is mandatory to choose the right scan rate range that gives a straight line to correctly indicate the charge storage mechanism.\(^{24}\) An alternative method to investigate the charge storage mechanism effect on the total capacitance, Trasatti’s method can be used.\(^{25}\) This method assumes that at scan rate of 0 mV/s, the charges are accessible to the surface and inner regions of the electrode, which corresponds to the total capacitance, while at scan rate of \(\infty\), the charges are only related to the outer surface and the related capacitance is due to EDL capacitance mechanism. Thus, when plotting specific capacitance \(versus\) the inverse of the square root of the scan rate (mV/s), one can get the EDL capacitance and when plotting the inverse of the
specific capacitance \textit{versus} the square root of the scan rate (mV/s), one can get the total capacitance.\textsuperscript{26,27}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{The b value in Randles–Sevcik equation.}
\end{figure}

\textbf{2.3 Galvanostatic charge/discharge (GCD)}

Galvanostatic charge/discharge (GCD) or constant current charge/discharge (CCCD) is widely used to give insights on the capacitance performance of the supercapacitor electrode and supercapacitor device. GCD deals with applying a constant current in a specific potential window to output the voltage response with time. The specific capacitance can be calculated from the GCD using \textbf{eq. II-7}. The GCD is usually measured at different current densities and the more stable the electrode at high current densities, the more stable the electrode will be and the more affective the electrode can be used in commercial applications.

\[ C_s = \frac{I \Delta t}{\Delta V} \]  \hspace{1cm} (II-7)

where I is the constant applied current density, \( \Delta t \) is the time of charge or discharge, and \( \Delta V \) is the potential window. The GCD can be used to estimate other properties than the specific capacitance as following:

1) \textit{Equivalent series resistance (ESR)}: an internal resistance (R) is always present in the circuit and causes a voltage drop (IR drop) as presented in Figure II-7. The IR drop usually increases with increasing current density. Furthermore, the increasing current
causes a decrease in the ionic diffusion which makes the process controlled by mass transport. Hence, the ionic resistance increases, and the total resistance will increase. To illuminate the IR drop in the C₅ calculation form the GCD, eq. II-8 should be used instead of eq. II-7.³ And the equivalent series resistance (ESR) in the circuit can be calculated from the value of the IR drop through plotting a linear relation between the Vᵢᵣ and the current density in which the slope is the ESR according to eq. II-9.²⁸

\[ C_s = \frac{l\Delta t}{\Delta V-Vᵢᵣ-dro p} \]  \hspace{1cm} (II-8)

\[ ESR = \frac{Vᵢᵣ}{I} \]  \hspace{1cm} (II-9)

Figure II-7 IR drop in GCD curves.²⁸

2) **Coulombic efficiency**: the percentage ratio between the charge time and discharge time represents the coulombic efficiency. The closer the coulombic efficiency to 100%, the better the reversibility of the electrode. The coulombic efficiency is usually lower than 100% for the first 20 cycles since the ions are usually not accessible to all the active sites in the electrode material. The reasons for a low/high coulombic efficiency can be attributed to parasite reactions.
3) **Rate capability:** The high rate capability represents a high stability of the electrodes at high power densities with the minimum voltage loss. GCD can be used to calculate the rate capability through the percentage ratio between the specific capacitance at high current density to the specific capacitance at low current density.

4) **Charge storage mechanism:** the GCD curve can give insights on the charge storage mechanism as illustrated in Figure II-8. It can be observed that a straight linear charge discharge represents an EDL charge storage mechanism. The more deviation in the linearity of the charge/discharge curve reflects a more pseudocapacitor behavior. Moreover, the presence of steps in the charge/discharge curve proves the presence of a redox reaction. It is noteworthy to mention that the number of steps in the GCD curve represents the number of redox reactions in the reaction medium. However, if the redox reactions occur at close voltage, the GCD curve may show one step only.

![Figure II-8 GCD curves for different charge storage mechanisms.](image)

5) **Stability:** moreover, GCD test is used to give insights on the stability of the electrode or device through cycling up to 100,000 cycles at a high current density. The stability (retention %) is calculated as the percentage ratio between the capacitance of the final cycle to the capacitance of the first cycle.
2.4 Electrochemical Impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is an important electrochemical technique used to give insights on the resistance components of the electrochemical cell and the capacitance value of the cell. Impedance refers to the resistance of current flow depending on frequency ($\omega$). EIS experiment starts with applying alternating current (AC) of a specific frequency in Hz. To this end, impedance ($Z$) can be assumed as illustrated in eq. II-10 where $E_{\omega}$ is frequency dependent potential and $I_{\omega}$ is frequency dependent current. At the limit of zero frequency, we can get the Ohm’s law $R = E/I$.

$$Z_{\omega} = \frac{E_{\omega}}{I_{\omega}} \quad \text{(II-10)}$$

An impedance spectroscopy test is simply applying a small sinusoidal preparation current or potential and detect the response at a fixed frequency, then repeating for a large number of frequencies and plot the results this is where the word (spectroscopy came from). Moreover, the EIS data can be expressed in two ways. The first, is using log frequency against both phase shift and log impedance (Bode plot). The other, is using real and imaginary impedance quantities (Nyquist plot). Both methods are presented in Figure II-9 where $Z$ is the impedance, $\Phi$ is the phase shift, $f$ is the amplitude of frequency, $Z''$ is the imaginary impedance part, and $Z'$ is the real impedance part. Although Nyquist plot is the one usually used to identify supercapacitor performance, frequency values and small impedance values are more identified in Bode plot. In Nyquist plot, impedance is represented by a vector of length $|Z|$ and a phase angle (angle between vector and X-axis) of $\phi$, where $Z = |Z|(\cos\phi + i\sin\phi)$. The electrochemical impedance is defined by eq. II-11 where $\psi_0$ is the amplitude of the oscillating potential at frequency $f$, $j_0$ is the amplitude of the oscillating current density, and $\phi(f)$ is frequency-dependent phase angle.

$$Z = \frac{\psi_0}{j_0} e^{i\phi(f)} = Z_{re} + Z_{im} \quad \text{(II-11)}$$
The impedance response for different circuit elements are as following: (where $i=\sqrt{-1}$ and $\omega=2\pi f$)

1) For resistor, $Z=R$ (Ohm) with zero phase shift.

2) For capacitor, $Z=-\frac{i}{\omega C}$ (Farad) with $-90^\circ$ phase shift.

3) For inductor, $Z=i\omega L$ (Henry) with $90^\circ$ phase shift.

4) Warburg, $Z=\text{mass transfer resistance}$ with $45^\circ$ phase shift.

5) Constant phase element (imperfect capacitor), $80^\circ$-$90^\circ$ phase shift.

The phase shift means a shift in the sinusoidal wave response as illustrated in Figure II-10.

For Bode plot, it is easier to identify the impedance response with frequency. From Figure II-11, it can be observed that Bode plot can give information on the resistance parameters and capacitance value through the equation $\log|Z| = -\log 2\pi f + \log \frac{1}{C}$. At the
highest log f, ohmic resistance \( (R_{\Omega}) \) dominates the impedance and log \( (R_{\Omega}) \) can be evaluated from the high log f horizontal plateau. At the lowest log f, charge transfer resistance \( (R_p) \) also can be evaluated from the lowest log f plateau. Moreover, the double layer capacitance \( (C_{dl}) \) can be evaluated from extrapolating the (log impedance vs. log f) line to log f=0. Also, electrical double layer capacitance \( (C_{dl}) \) can be calculated from the log f vs. \( \theta \) curve through eq. II-12.\[^{32}\]

\[
2\pi f(\theta_{max}) = \frac{1}{\sqrt{C_{dl} R_p (1 + \frac{R_p}{R_{\Omega}})}} \tag{II-12}
\]

**Figure II-11** Bode plot example.\[^{32}\]

Beside the clear relation of frequency to the resistance in Bode plot, it also can identify the multistep reactions and give insights on each step resistance components and distinguish the rate determining step which is not provided by Nyquist plot. However, Bode plot changes with changing the ohmic resistance giving misleading capacitance values.

2.4.1 Evaluation of capacitance from EIS:

The capacitance can be calculated from the EIS test through eq. II-13 and specific capacitance can be calculated through dividing capacitance by the mass, volume, or surface area.

\[
C = \frac{-1}{2\pi f Z''} \tag{II-13}
\]
where $f$ is the lowest applied frequency or the frequency at which the phase angle is $45^0$, $Z''$ is the imaginary part of impedance.\(^3\)

### 2.4.2 Charge storage mechanism evaluation from Nyquist plot:

The shape of Nyquist plot can give insights on the charge storage mechanism. Besides, the slope of the line in the low frequency region and the values of $x$-axis intercept can give insights on the resistance origin in the system. **Figure II-12** shows the different Nyquist plots for ideal charge storage mechanism in supercapacitor. Some EDL electrode materials such as graphite and graphene presented a semicircle in their Nyquist plot due to the redox occurring by the functional groups on their surface.\(^{13}\) Besides, pseudocapacitor electrodes usually express a small semicircle in the high frequency region due to fast Faradic reaction on surface followed by a straight line of a $90^0$ slope. However, real battery-like electrodes express a much larger semicircle followed by a straight line with a $45^0$ slope due to slow ion diffusion and charge transfer. The relaxation time for battery-like supercapacitor and the charge transfer time for pseudocapacitor can be calculated as $1/(2\pi f_m)$ where $f_m$ is the peak frequency.\(^{13}\)

![Nyquist plot for ideal EDL capacitor, Pseudocapacitor and battery-like capacitor.\(^{13}\)](image)

**Figure II-12** Nyquist plot for ideal EDL capacitor, Pseudocapacitor and battery-like capacitor.\(^{13}\)

### 2.4.3 Evaluation of ESR using simple Nyquist plot:

A supercapacitor cell can be modeled as a capacitor in series with a resistor, this resistor is referred to as the equivalent series resistance (ESR). To this end, a small ESR means a better
performing supercapacitor. The ESR can be extrapolated from the electrochemical impedance spectroscopy (EIS) technique through the Nyquist plot using either of two methods. The first through the real part of impedance at 1 kHz and the second through linear interpolation of Nyquist plot at the low frequency part to imaginary impedance of zero.

**Figure II-13** Simple evaluation of ESR using Nyquist plot.

### 2.4.4 Evaluation of ESR using Randles equivalent circuit:

The commonly used method to get the value of the ESR is fitting the Nyquist plot to its equivalent electrical circuit. However, for one Nyquist plot, several equivalent circuits are possible and choosing the correct circuit depends on the physical matching with the tested system. The circuit usually consists of common components such as:

1) The ohmic resistance of the electrolyte between the working electrode and the reference electrode ($R_\Omega$ or $R_s$).

2) Faradic resistance or charge transfer resistance ($R_F$ or $R_p$) which can give insights on the rate of reaction.

3) Warburg resistance ($W$).

4) Double layer capacitance ($C_{dl}$).

5) Faradic pseudocapacitance ($C_\phi$).
Here are some commonly studied circuits in supercapacitor and their equivalent circuits:\textsuperscript{11}

![Diagram of circuits](image)

**Figure II-14** Examples of Randles circuits for supercapacitors.\textsuperscript{11}

### 2.4.5 Evaluation of ESR using numerical method:

Circuit fitting does not account for the different concentration distribution of electrolyte ions and ion diffusion, also more than one circuits may account for the same Nyquist plot. So, Lion et al. have developed a numerical Nyquist plot fitting to provide information about the charge storage mechanism, and the resistance origin and values.\textsuperscript{33} As illustrated in **Figure II-15**, The EDL capacitor Nyquist plot can be modeled to give the value of electrode resistance, electrolyte resistance, and diffuse layer resistance. It worth mentioning that the slope of the line BC reflects the charge storage mechanism, the steeper the slope, the more reflected EDL
behavior. However, some electrodes give very low diffuse layer resistance and/or electrode resistance. Moreover, this ideal shape may vary dramatically since the model assume binary and symmetric electrolyte, no free charge in Stern layer, thickness of Stern layer is the same as the ionic radius, constant transport properties for the electrolyte, no redox or intercalation, ignored temperature effect, ignored self-discharge, and ignored contact resistance. Therefore, this model is very tricky and hard to be universal for all EDL systems.

![Diagram](image)

**Figure II-15** A modeled Nyquist plot for EDL supercapacitor device.\(^{33}\)

Also, Pilon et al. have modeled the Faradic Nyquist plot numerically as illustrated in **Figure II-16 (A).**\(^{34}\) The ideal redox electrode consists of two semicircles representing electrolyte resistance, and charge transfer + mass transfer resistance in the high frequency, and low frequency regions, respectively. However, either of the semicircles may be too small to be observed. For intercalated pseudocapacitors as illustrated in **Figure II-16 (B).**\(^{34}\) The intercalated MoS\(_2\) expressed two overlapped semicircles in the high frequency region that was attributed to the simultaneous ionic transport (R\(_{\text{ct}}\)) and ionic intercalation processes (R\(_{\text{ct}}\) or R\(_{\text{m}}\)). Also, the nonvertical line following the two overlapped semicircles could be attributed to ionic transport limitation.\(^{34}\)
2.5 Device electrochemistry

A supercapacitor device consists of anode, cathode, electrolyte, and a separator. The separator is usually a membrane that allows the diffusion of ions while not conducting electricity. The usual used separators are the ones based on cellulose material.

2.5.1 Device classification

Since real performance of electrode materials is identified through two-electrode system fabrication, it is mandatory to illustrate the types of possible devices and their electrochemistry. Devices are generally classified into symmetric, asymmetric, and hybrid devices according to the charge storage mechanism and the type of both electrode materials.

1) **Symmetric device**: The simplest device form is the symmetrical device where the positive electrode and the negative electrode are both the same exact material either EDL, pseudocapacitive, or battery-like materials. It worth mentioning that the device in which both electrodes are from the same material but with different potential window or different behavior is identified as an asymmetric device not as symmetric device.

2) **Asymmetric device**: When the two electrodes are from the same material with different behavior or either of the two electrodes has a different material with the same behavior
or close behavior (such as EDL and pseudocapacitor), the device is classified as an asymmetric device. As illustrated in Figure II-25.9,29

3) **Hybrid device:** When the two electrodes are from different materials or behavior, one of them is a battery-like behavior as illustrated in Figure II-17.9,29,35 Although, hybrid devices provide a high energy density, the sluggish charging and phase transformation of the battery-like electrode reduce the stability and reversibility of the device.29

![Figure II-17 Supercapacitor device classification.](image)

2.5.2 Device capacitance performance

The capacitance performance of the device can be identified using the specific capacitance calculation from the CV, GCD, and EIS tests discussed earlier in this chapter. However, the device performance should also be tested for its power density (P in W/Kg) and energy density (E in Wh/Kg). Since energy density is simply the integration of the discharge curve, eq. II-14 can be used to calculate the energy density of the supercapacitor device. However, in case of symmetric and asymmetric devices, V₂ equals zero and the energy density
The equation is simplified (eq. II-15) as illustrated in Figure II-18. The power density can be calculated from the energy density as illustrated in eq. II-16.

\[
E_{\text{hybrid}} = \frac{C_s V_2^2}{2 \times 3.6} - \frac{C_s V_1^2}{2 \times 3.6} \quad \text{(II-15)}
\]

\[
E_{\text{symmetric}} = \frac{C_s V_2^2}{2 \times 3.6} \quad \text{(II-16)}
\]

\[
P = \frac{3600 \times E}{\Delta t} = \frac{1000 \times (V_2 - V_1)}{2} \quad \text{(II-17)}
\]

where \( E \) is the energy density (Wh/Kg), \( P \) is the power density (W/Kg), \( C_s \) is the specific capacitance (F/g), and \( \Delta t \) is the discharge time (s).

Figure II-18 Calculation of energy density for different supercapacitor devices.

2.5.3 Adjusting operating voltage

An overestimated potential window can affect the stability of the device, while an underestimation of potential window can affect the power density of the device. Therefore, it is mandatory to find the correct potential window for a perfect device performance.

\textit{CV and GCD}, The CV curve shape is the easiest method to primarily indicate the potential window. It is usually used through observing any deviation from the normal CV shape or an irreversible peak. The deviation upwards or downwards in the CV curve indicates the presence of other reactions such as water splitting as illustrated in Figure II-19 (A-B) and the
potential window should be reduced before the limits of the parasite reactions. Also, the presence of irreversible peaks as illustrated in Figure II-19 (C) indicates a parasite reaction and require the reduction of the potential window. However, since CV is used to indicate the potential window visually, it is not very accurate. However, the GCD test works as a more accurate indicator. As illustrated in Figure II-19 (E), if the GCD curve presented a plateau for a long time, this means the presence of parasite reactions and the potential window should be reduced. Moreover, the GCD may discharge normally as illustrated in Figure II-19 (D), but the coulombic efficiency is very low and increases with cycling, this may indicate that there is another reaction that must be avoided and usually reducing the potential window below the semi-plateau is enough to reach the true potential window.

![Figure II-19 Deviation in CV and GCD curves indicating a wrong potential window.](image)

**Charge balance,** To reach the ultimate potential window and keep the best capacitance performance, charge balance between the anode and cathode of the supercapacitor device should be maintained. Since charge of the electrode is related to mass and capacitance of the electrode, balancing the mass of both electrodes can balance the stored charge as illustrated in eq. II-18:

\[
\frac{m_+}{m_-} = \frac{C_+ \Delta V^+}{C_- \Delta V^-} 
\]  

(II-18)
where \( m \) is the mass, \( C_s \) is the specific capacitance, and \( \Delta V \) is the potential window.

**Potential of zero charge,** To identify the starting point of charging for an electrode, the potential of zero charge (PZC) should be identified to allow a true potential window for anode and cathode and provide a more accurate charge balance calculations. The PZC can be estimated from EIS through testing the electrode in a low concentration electrolyte in a three-electrode system. The EIS should be measured along the tested potential window (e.g. -1 to 1 for aqueous electrolytes) and the related capacitance should be plotted vs. the potential used, the minimum capacitance value indicates the PZC as illustrated in Figure II-20 where PZC was -0.2 V and 0.2 V for EDTA-Carbon and Bio-Carbon, respectively.\(^{37}\)

![Figure II-20 EIS estimation of PZC.\(^{37}\)](image)

**Stacking supercapacitor cells,** Some applications need a high operating voltage up to 60 V, this is why connecting cells in series is used to widen the potential window. For a stacking supercapacitor, the capacitance is calculated as illustrated in eq. II-19 and eq. II-20.\(^{38}\)

\[
\frac{1}{C_{\text{stack}}} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \ldots = \sum_i^n \frac{1}{C_i}
\]  

\text{(II-19)}

for symmetric devices \( C_{\text{stack}} = \frac{C_i}{n} \)  

\text{(II-20)}

where \( n \) is the number of stacking devices. The colligative voltage of the stacking device hence is as illustrated in eq. II-21 and eq. II-22.\(^{38}\)
\[ V_{stack} = V_1 + V_2 + V_3 + \cdots = \sum_i^n V_i \]  \hspace{1cm} (II-21)

for symmetric devices \( V_{stack} = nV_l \) \hspace{1cm} (II-22)

Moreover, the energy density of the stacked device is described by eq. II-23.\textsuperscript{38}

\[ E_{stack} = \frac{1}{2} C_{stack} (V_{stack})^2 \] \hspace{1cm} (II-23)

### 2.6 Density Functional Theory (DFT)

#### 2.6.1 Introduction to DFT

In 1998, Kohn won the Nobel Prize in chemistry for simplifying one of the most watchful chemistry problems; Schrödinger equation.\textsuperscript{39} Instead of solving the Schrödinger equation through the exact wave functions of electrons, Kohn and Sham showed that electrons can be treated implicitly and the wave function can be replaced by electronic density.\textsuperscript{40} By minimizing the electronic density energy, the equation can be simplified into a functional (function of function). The new functional is divided into two parts, the first treats the density through minimization through all the wave functions then the densities are minimized as well.\textsuperscript{41,42} Kohn and Hohenberg proved that the properties of a given electronic system can all be driven through the electronic density.\textsuperscript{39} However, the multi-electron systems showed inaccurate results. Kohn and Sham also provided another solution for this problem through the introduction of electrons in terms of non-interacting particles that have the same density of the interacting ones.\textsuperscript{40} The KS orbitals were presented by a wave function of a slater determinant of the product of all electrons of all spins. As the KS kinetic energy was also considered as the contribution of all electrons, the energy equation was simplified as \( E = T_s + U + V + E_x \), where \( T_s \) is the kinetic energy, \( U \) is the interelectron repulsion (Hartree energy), \( V \) is the one-body potential couple and the \( E_x \) is the exchange correlation term (energy).\textsuperscript{41} Since the DFT was depending on the approximation that electrons are not interacting, a term representing those interactions should be used to correct the result, which is named the
exchange correlation energy. The $E_x$ is also divided into two terms, the exchange energy and the correlation energy. While the exchange energy is the electron-electron repulsion minus Hartree energy, the correlation energy is the hard part to solve. This led researchers to come up with approximations for the exchange correlation function. One of the approximations is the local density approximation (LDA), where only the local density is used to approximate the exchange-correlation functional. Another approximation is the generalized gradient approximation (GGA) in which the functional is defined by both local electron density and gradient in the electron density. Although the physical terms used in GGA are more than those used in LDA, the way by which the gradient of electron density included in the functional is the key point to define its accuracy. One of the most commonly used approximated functionals is the Perdew-Burke-Ernzerhof (PBE). The functionals differ in accuracy according to the property, structure, and chemical formula of the studied systems. The strongly correlated systems, as in solid state materials, need some extra treatment such as hybrid functionals or Hubbard correction. Some functionals are hybrid, which combine exact correlation calculated from the Hartree-Fock with either GGA and/or LDA exchange correlation such as the Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional. In order to solve the wave function, the equation should be expressed in terms of basis sets. The basis sets can be either plane wave or atomic orbital basis set. Atomic orbital basis sets are more computationally cheap, but they are non-orthogonal that depend on the atomic positions and having superposition errors when atoms are close to each other. On the other hand, the plane waves function is orthogonal, does not depend on atomic position, and does not have a basis set superposition error. However, it needs many functions to be solved. Thus, the previous knowledge of the electronic structure and the needed properties will make it easier to decide which functional to use. Although the electronic DFT is considered computationally expensive, it has been used during the past decades to model molecules and solid-state materials for energy applications due to its high accuracy and cost efficiency compared to experimental methods.
The PBE method was introduced as an approximation to the GGA functional where all the parameters are constant fundamentally. The Perdew-Wang (PW) correlation functional and the Burk exchange contribution are the main component of this approximation.\textsuperscript{50} The PBE functional proved to be successful in modeling semiconductors since The PBE functional provides a smooth pseudopotential, fulfills the Lieb-Oxford bound, and allows the accurate linear response of the uniform electron gas under the correct uniform scaling.\textsuperscript{51} The enhancement in the PBE functional is in the form of \( F_{X}^{PBE} \).\textsuperscript{51,52}

\[
F_{X}^{PBE}(s) = 1 + k - \frac{k}{(1 + \frac{\mu s^2}{k^2})} \tag{II-24}
\]

where the \( k \) value is set to its maximum allowed value by the Lieb-Oxford bound and equals 0.804 on \( E_{XC} \). To correct the linear response of the uniform gas, the \( \mu \) is set to equal 0.21951 where the effective gradient coefficient of correlation and exchange are canceled.\textsuperscript{51,52} The correlation function of the PBE can be identified as following:

\[
H_{PBE} = H^{0} = g^3 \frac{\beta^2}{2\alpha} \ln \left[ 1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2t^4} \right] \tag{II-25}
\]

where \( \alpha \) equals 0.0716, \( g \) is the spin scaling factor, and \( t \) is a dimension-less density gradient.\textsuperscript{51,52}

2.6.1.2 Van der Waals (VdW) forces modeling

Since the carbon materials and chalcogenides can present a VdW forces between layers, it is mandatory to account for that effect in modeling those electrode materials. VdW forces results in an electrodynamic charge fluctuation on both sides of the atomic system. Thus, the VdW forced is a truly non-local correlation effect since it depends on charge effects at another region.\textsuperscript{53} Since both GGA and LDA depend on the local and semi-local density, they fail to account for the non-local VdW forces. One of the proposed approximations was the VdW-DF which underestimates the strength of the H-bonding and overestimates the equilibrium
separations. However, a more accurate method was presented by Langreth et al.\textsuperscript{53} The new modified VdW-DF2 functional uses the semi-local PW86 which is more accurate and uses a VdW kernel correction with more N-asymptote gradient. The new VdW-DF2 was proved to be more accurate in calculation of H-bonding strength, equilibrium separation, and VdW attractions. The VdW-DF2 functional can be represented by the following equation:\textsuperscript{53,54}

\[
E_{\text{XC}}^{\text{VdW-DF2}} = E_{\text{X}}^{\text{PW86}} + E_{\text{c}}^{\text{PW-LDA}} + E_{\text{c-\text{nl}}}^{\text{VdW-DF2}} \tag{II-26}
\]

\[
E_{\text{c-\text{nl}}}^{\text{VdW-DF2}} = \int d^{3}r \int d^{3}r' n(r) \phi(r,r') n(r') \tag{II-27}
\]

where \(E_{\text{X}}^{\text{PW86}}\) is the exchange functional of the refitted PW86 functional, \(E_{\text{c}}^{\text{PW-LDA}}\) is the local correlation part of the PW86 functional, and \(E_{\text{c-\text{nl}}}^{\text{VdW-DF2}}\) is a term added to the converged functional PW86 and the functionals (rPW86 and PWLDA) vary in the definition of the kernel \(\phi\)\textsuperscript{54} and represents the non-local part of the functional. This DFT-DF2 functional has proved to give accurate results for carbon materials with VdW forces that are used in this study.\textsuperscript{54–56} \(\phi\) is the kernel and is depends on \(Rf(r)\) and \(Rf(r')\) with \(f(r)\) is a function of \(n(r)\) and is proportional to the \(E_{\text{XC}}\), and \(R\) equals \(|r-r'|\).

2.6.2 DFT for modelling electrode materials

Josef MacDouall once said “Chemistry is a game that electrons play”.\textsuperscript{57} If one were able to know the roles, they could control the game and uncover the mysteries of materials, which are the backbone of our modern civilization. To this end, energy storage platforms are the bottle-neck hindering the efficient use of electronic devices. Although Li-ion batteries seem to provide an ultimate solution for the mobile phones and laptops, they are not sufficient for larger devices such as electrical cars and electrical factories. For electrical cars, they need to be charged and rework efficiently very fast, which is controlled by the power density of the energy storage device. In this regard, supercapacitor devices may provide a solution for the power density problem provided that the electrode materials can be tuned to provide such energy density values. For this to happen, both the operating potential window and the resulting maximum current
density need to be maximized.\textsuperscript{36} However, the reports so far are based on \textit{guess and check} selection of electrode materials and electrolytes, while the use of materials design and material-electrolyte interface design are not widely used.\textsuperscript{58} The limited use of computational prediction in designing materials for supercapacitor devices could be due to the wide variety of computational tools from molecular dynamics to density functional theory (DFT) and many others. Even DFT is divided into many versions. While classical DFT is usually used to predict the properties of porous carbon materials, the electronic DFT is usually used to predict the electronic properties of the materials. In this regard, the materials used in supercapacitors can be divided into capacitive materials and Faradic materials, each with their own charge storage mechanism and hence their own properties. The variation between the energy storage mechanisms, the electrolyte material, and the computational methods used in materials design made it hard for researchers to decide where to start and how to find the way in designing good materials for use as supercapacitor electrodes. To this end, eDFT is a good tool to predict the band gap energy, electronic properties, and quantum capacitance from the density of states (DOS) of the materials of interest.\textsuperscript{59} Therefore, the combination of eDFT and cDFT should be a perfect tool to predict the capacitance of a plethora of electrode materials.

Supercapacitors are electrochemical energy storage devices. Hence, it is important to predict and identify the factors controlling their electrochemical performance upon their use in such devices.

\textit{2.6.2.1 Resistance calculations}

Supercapacitor electrodes need to have fast electron transfer during the charge/discharge processes. However, if the material is not conductive enough or cannot perform a redox reaction within the applied potential window, the electrode will not function as needed. To this end, DFT can be a good tool to predict the band diagram of the electrode material and gives insights on its electrochemical performance.\textsuperscript{60} For EDL-based supercapacitors, the capacitance of the material can be estimated via the permittivity of the
material, which can be calculated from the dielectric constant of the material. Sharma et al.\textsuperscript{61} have performed a screening to the capacitive performance of 267 polymers using DFT with the Generalized Gradient approximation (GGA) and the band gap correction Heyd-Scuseria-Ernzerhof (HSE06) functional. They were able to calculate the dielectric constant, the band gap value, the dielectric loss, and the dielectric breakdown of the studied polymers. The results showed a good agreement with experimentally reported values, highlighting the reliability of DFT in predicting the electronic properties of polymers.\textsuperscript{61} As the band diagram and charge density distribution at the electrode material and/or the interface between two different materials are crucial to evaluate the performance supercapacitors\textsuperscript{62,63}, Xiong et al.\textsuperscript{62} performed DFT calculations to investigate the origin of the high capacitive performance of MnO\textsubscript{2}/graphite petals on carbon nanotubes substrate using GGA and the plane-wave self-consistent field (PWSCF). The charge/discharge process was simulated by applying stress pressure and calculating the relaxation/compression of MnO\textsubscript{2} crystal on the graphite surface. They were able to calculate the density of states (DOS), the electronic structure, and the charge density distribution of the MnO\textsubscript{2}/graphite interface, indicating that the charge transfer at the MnO\textsubscript{2}/graphite interface was facilitated by the oxygen atoms in the MnO\textsubscript{2} without which the resistance of the material would have made it impossible for supercapacitor applications.\textsuperscript{62} On the other hand, defect states and vacancy formation energy of the Co\textsubscript{3}O\textsubscript{4} showed a great enhancement in its conductivity and electrochemical performance over other metal oxides.\textsuperscript{64} Thus, DFT is a promising tool to estimate the resistance of electrode materials and their promising performance either as an EDL or diffusion-based supercapacitors.

\textit{2.6.2.2 Predicting the binding energy of ions at electrode surface}

The binding energy between the electrolyte ion and the surface of the electrode material affects the adsorption/desorption of ions during the charge/discharge process. In this regard, DFT can predict the binding energy and the effect of the adsorption of electrolyte ions on the capacitive performance and conductivity of the electrode material. For example, to simulate the adsorption of ions from KOH electrolyte, the DOS of the adsorption of K\textsuperscript{+} and OH\textsuperscript{-} ions on
reduced graphene oxide (rGO) was calculated using DFT (GGA). The DOS was found to vary with the type of ions and the adsorption position, giving insights on the origin of the capacitance performance of rGO in KOH. The binding energy between K⁺ ion and different configurations of nitrogen-doped graphene oxide (N-GO) was also calculated using DFT (GGA) according to eq. II-28:

\[ BE = E_{N-GO} + E_{K^+} - E_{N-GO-K^+} \]  

(II-28)

where, \( E_{N-GO} \) is the energy of the N-GO alone, the \( E_{K^+} \) is the energy of K⁺ ion, and \( E_{N-GO-K^+} \) is the energy of the K⁺ bound to the N-GO. The results revealed the nature and strength of the bonding between the electrolyte ions and the electrode material relative to the position of N atoms.

2.6.3 Quantum capacitance

While the EDL capacitance of a material is usually controlled by the surface area, the pore size, and pore structure, the quantum capacitance (C_Q) is controlled by the electronic structure of the electrode material. Quantum capacitance represents the contribution of the electrode material to the capacitance of the Helmholtz layer at the EDL interface resulting from the electronic response of the electrode. Both C_Q and EDL capacitances are important to result in an overall high capacitance. The total surface capacitance (C_T) can be calculated according to eq. II-29 without the inclusion of the battery-like or pseudocapacitance effect.

\[ \frac{1}{C_T} = \frac{1}{C_Q} + \frac{1}{C_{DL}} \]  

(II-29)

where \( C_{DL} \) is the double layer capacitance, which includes the Helmholtz layer and diffuse layer. The electronic structure of the electrode material in an EDL capacitor can be described using the DOS, following two proposed models, to estimate the C_Q. For materials with high DOS such as metals, the change in electrode chemical potential (\( \mu_e \)) and the electrode potential does not change greatly by adding or removing few electrons, where the total capacitance is a function of the EDL capacitance only (not taking the battery-like and pseudocapacitive behavior into account). However, for materials with
low DOS such as semiconductor materials, any addition or removal of electrons may affect greatly the electrode potential. \(^{58}\) Hence, the quantum capacitance has a special importance for non-metals such as graphene-based electrodes. The quantum capacitance can be calculated as the ratio between the variation of charge ($dQ$) and electrode potential ($dV$) known as the differential electrode potential. \(^{67-69}\) Eq. II-30 is the commonly used relation between $C_Q^{\text{diff}}$ and DOS assuming uncharged electrode. \(^{67,68,70,71}\)

\[
C_Q^{\text{diff}} = \frac{dQ}{dV} = e^2 \text{DOS}(-Ve) \tag{II-30}
\]

where $e$ is the elementary charge, DOS is the electronic density of states and (-Ve) represents the relative electronic density with respect to Fermi level. However, for 2D materials, $C_Q^{\text{diff}}$ can be calculated according to eqs. III-31 and II-32. \(^{69,72-75}\)

\[
C_Q^{\text{diff}} = \frac{dQ}{dV} = e^2 \int_{-\infty}^{+\infty} \text{DOS} \text{F}_T(E - \mu) dE \tag{II-31}
\]

\[
\text{F}_T(E) = (4k_BT)^{-1} \text{Sech}^2\left(\frac{E}{2k_BT}\right) \tag{II-32}
\]

where $\text{F}_T(E)$ is the thermal broadening function, $E$ is the relative energy with respect to Fermi level, and $\mu$ is the electrochemical potential. For pristine graphene while ignoring temperature, $C_Q^{\text{diff}}$ can be calculated using eq. III-33. \(^{67,69}\)

\[
C_Q^{\text{diff}} = \frac{dQ}{dV} = e^2 \frac{g_sg_v}{2\pi(\hbar V_F)^2}|\mu| \tag{II-33}
\]

where $g_s$ is the spin degeneration (=2), $g_v$ is the valley degeneration (=2), and $V_F$ is the Fermi velocity of carriers ($\sim 108$ cm/s). One the other hand, the most important parameter for supercapacitor applications is the total energy storage capacity, which represents the effective storage capacity per unit of applied potential. The energy storage capacity relies on the integrated quantum capacitance ($C_Q^{\text{int}}$) instead of the differential quantum capacitance ($C_Q^{\text{diff}}$), which is the differential quantum capacitance integrated over the charge/discharge cycle using eq. III-34, assuming equilibrium at slow charge/discharge process. \(^{67,68,73}\) Calculations of the quantum capacitance are considered with respect to the Fermi level of the working electrode material instead of a reference
electrode, which can be considered as the potential at the potential of zero charge (PZC).

The total charge storage capacity of an electrode at a given charging potential can be calculated as the $C_Q^{\text{int}}$ multiplied by that given potential.\(^6\)

$$
C_Q^{\text{int}} = \frac{q}{V} = \frac{1}{V e} \int_{0}^{V} C_Q(V') dV'
$$

(II-34)
Chapter III : Literature Review

3.1 Electrode materials for supercapacitor applications

To develop high performance supercapacitor devices, researchers have been working to identify non-Faradic and Faradic materials and investigate their advantages and limitations.

3.1.1 Development of non-Faradic electrodes

Non-Faradic electrodes are the materials exhibiting only adsorption/desorption behavior with EDL as the energy storage mechanism. Usually, electrodes used in this type are carbon-based materials. To this end, developments in this type are centered around increasing the surface area of the carbon material and/or its conductivity through doping. Cheng et al. boosted the performance of carbon electrodes through mixing carbon black, activated carbon, and carbon nanomaterials to achieve a rate capability of 77.5 % between 5 A/g and 80 A/g. The electrode also exhibited a stability of 91% after 30,000 cycles with a capacitance of 66 F/cm³, energy density of 29.6 Wh/L, and power density of 101.7 KW/L.76 Doped carbon was used to modify the morphology of the porous carbon and to give a higher surface area and a better capacitance performance. The carbon material was synthesized form carbonization of Ginger, then doped through re-carbonization in the presence of thiourea. The resulted product showed a surface area of 720 m²/g and was used in a three-electrode system with Na₂SO₄ as the electrolyte to provide a specific capacitance of 456 F/g at 0.3 A/g. Also, the symmetric device showed an energy density of 48.3 Wh/Kg and a power density of 400 W/Kg in the potential window of 1.4 V with a cycling stability of 95% after 10,000 cycles.77 Moreover, Shang et al. doped porous carbon with nitrogen to obtain flower-like shape with a high micro and meso pores and a surface area of 2090 m²/g. Houttuynia was used as the source for carbon, which was freeze dried, then carbonized in N₂ atmosphere, and finally activated in the presence of melamine and KOH. The resulted material showed a specific capacitance of 473 F/g at 1 A/g and maintained half of its capacitance at 20 A/g. Its symmetric device showed an energy density of 15.99 Wh/Kg of at a power density of 500 W/Kg with a retention of 95.7% after 10,000 cycles.
cycles.\textsuperscript{78} Also, agriculture waste was used as a source of carbonaceous electrodes by Bahat et al. The fabricated symmetric device exhibited a specific capacitance of 119 F/g and energy density of 32.6 Wh/Kg with a stability of 93% after 10,000 cycles.\textsuperscript{79} Therefore, the effect of structure and doping can vary the capacitance outcomes greatly. Moreover, carbon allotropes were used as supporting materials along with pseudocapacitive materials and battery-like materials. Tian et al. studied MoS$_2$/MoO$_2$ nanoparticles grown on the surface of CNTs, which showed a capacitance of 228.4 F/g at 0.5 A/g, an energy density of 11.88 Wh/kg, and a power density of 2 kW/Kg with high cycling stability in KOH electrolyte at 0.55 V.\textsuperscript{80} Samuel et al. used Zn$_2$SnO$_4$/SnO$_2$/CNTs nanocomposite as a supercapacitor electrode that exhibited a capacitance of 260 F/g at 10 A/g in 6 M KOH and a potential window of 1 V.\textsuperscript{81} The Ni-MOF (metal-organic framework) on graphene reported by Xiao et al. showed a capacitance of 987 F/g at 0.5 A/g with a stability of 85% after 3000 cycles in KOH electrolyte and 0.45 V potential window.\textsuperscript{82} A composite of graphene and MnO$_2$ nanorods was tested in Na$_2$SO$_4$ electrolyte and resulted in a capacitance of 759 F/g at 2 A/g.\textsuperscript{83} Also, a hybrid graphite nanosheet-supported CoMoS$_4$ was tested as a supercapacitor electrode, which showed a capacitance of 774 F/g at 1 A/g with 95% stability after 6000 cycles in 3 M KOH at 0.55 V.\textsuperscript{84} To this end, the effect of the electrolyte properties on the performance of reduced graphene oxide (rGO) has been briefly investigated.\textsuperscript{85,86} To this end, the most intensively investigated carbon allotrope is graphene due to its high mechanical elasticity, high chemical stability, light weight, high surface area, and perfect electrical conductivity. However, the strong interaction between graphene layers usually causes them to restack and lose their unique properties. Therefore, the reported capacitance of graphene-based supercapacitors so far is way below the theoretical capacitance (550 F/g), leaving room for improvement.\textsuperscript{87,88} To this end, porous 3D graphene materials, such as sponges, aerogels, and foams, have been engineered as alternatives to graphene, due to their high electrical conductivity, continuously interconnected porous structure, large surface area, and low mass density that help to facilitate charge transfer dynamics, create better contact with the electrolyte interface, and prevent the restacking of graphene sheets.\textsuperscript{89} Also, fullerenes, another electronic rich carbon allotropes, have been used
to enhance the performance of Li-ion batteries and supercapacitor devices. Specifically, $C_{60}$ was incorporated in Li-ion batteries to enhance their performance and stability.\textsuperscript{90-94} The addition of $C_{60}$ to graphene sheets provided extra acceptor states that enhanced the charge transfer in the electrodes.\textsuperscript{95} Fileti \textit{et al.} reported that $C_{60}$ was able to enhance the supercapacitor performance by up to 150%.\textsuperscript{96} On the other hand, Kim \textit{et al.} reported the usefulness of using $C_{60}$ along with Ni-Fe layered double hydroxide to form a mesoporous stacking structure with enhanced capacitance.\textsuperscript{97} Moreover, computational tools have been used to predict the effect of fullerenes on the performance of supercapacitor electrode materials.\textsuperscript{7} Zhan \textit{et al.} predicted that the addition of $C_{60}$ to graphene could enhance both quantum capacitance and EDL capacitance.\textsuperscript{98} Although some electrodes were tested in different electrolyte media as illustrated in 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Dependence of potential window on electrolyte.\textsuperscript{29}}
\end{figure}

\textit{Figure III-1} Dependence of potential window on electrolyte.\textsuperscript{29}
3.1.2 Development of Faradic electrode materials (sulfide-based electrodes)

Faradic electrodes are made of materials in which the charge is stored through a process including charge transfer either through intercalation process or redox reaction. One of the famous class of electrode materials used in supercapacitors is sulfide-based electrodes. 2D sulfide-based electrodes, such as dichalcogenides, can undergo pseudocapacitance charge storage mechanism through alkali metal intercalation. 3D sulfide electrodes, such as Ni, Mn, or Co sulfides can undergo reversible redox reactions in alkaline media. As illustrate in Figure III-2, the pseudocapacitive and battery-like behaviors can reach higher charge transfer (capacitance values), while they have limited kinetics. Consequently, sulfide-based supercapacitor electrodes have extensively been investigated to combine the Faradic behavior into the supercapacitor devices.

![Electrochemical Energy Storage Mechanisms](image)

**Figure III-2** Electrochemical energy storage classification.\(^\text{10}\)

The polymorph MoS\(_2\) (which is the prototypical transition metal dichalcogenide) has three main phases; the stable hexagonal 2H phase, the metastable rhombohedral 3R phase, and the metastable octahedral 1T phase, of which only the 1T phase has metallic character.\(^\text{101-103}\) However, the 1T phase is unstable over large retention cycles in different electrolytes.\(^\text{102,104}\) Therefore, many attempts were done to enhance the performance of MoS\(_2\) by mixing with
carbon materials,\textsuperscript{48} synthesis of different morphologies\textsuperscript{108-111} or tuning the phase of MoS\textsubscript{2}.\textsuperscript{102-104} Xuyen \textit{et al.}\textsuperscript{102} studied the effect of the percentage of the 1T phase on the performance of MoS\textsubscript{2}, reaching a specific capacitance of 259 F/g in KCl electrolyte. Despite this high performance, higher capacitance is needed to achieve high energy density.\textsuperscript{102} Moreover, the 1T/2H polymorph MoS\textsubscript{2} was also studied in KOH electrolyte, resulting in a specific capacitance of 338.8 F/g at a sweep rate of 20 mV/s on Ni-sheet substrate with very good cycling stability.\textsuperscript{104} However, the used Ni substrate may interfere with the KOH, increasing the Faradic behavior of the electrode.\textsuperscript{112,113} Acerce \textit{et al.}\textsuperscript{103} studied the 1T MoS\textsubscript{2} capacitance performance in different electrolytes reaching a capacitance of 300 F/cm\textsuperscript{3} without shedding the light on the charge storage mechanism or device performance. The charge storage mechanism in a monolayer of 1T and 2H MoS\textsubscript{2} was studied computationally using first principles.\textsuperscript{114} However, charge storage mechanism of the 3R phase was not studied. Besides, the monolayer MoS\textsubscript{2} is not a real practical example. Furthermore, hydrothermally synthesized 2H-MoS\textsubscript{2} with flower-like structure showed a specific capacitance of 382 F/g with its solid state symmetric device delivering an energy density of 16.4 Wh/Kg at a current density of 0.2 A/g with a stability of 97.5 for 4,000 cycles. The reported high performance was attributed to the oxygen functional groups existing at the edges of the MoS\textsubscript{2} flowers.\textsuperscript{115} Also, Gupta \textit{et al.} have investigated the capacitance performance of MoS\textsubscript{2} synthesized via a one-step hydrothermal process, which showed a specific capacitance of 255 F/g and an energy density of 35.5 Wh/Kg.\textsuperscript{116} To this end, ion intercalation has been one of the leading charge storage mechanisms in energy storage materials, especially alkali metal-ion batteries. Despite their high energy density, the intercalation in batteries does not meet the present-day demand for high power density. Consequently, recent studies have been targeting supercapacitors as an alternative platform for energy storage.\textsuperscript{117} However, to accommodate alkali-metal ions, the host active material's lattice must have large interlayer space to accommodate such ions with relatively larger ionic radii. Layered-2D materials, such as transition metal dichalcogenides (TMDs), have been investigated due to their high interlayer spacing that facilitates the insertion of such larger ions. In literature, the intercalation process of Na\textsuperscript{+} ions in the layered 2H and 1T-MoS\textsubscript{2} was
investigated and the study gave insights on the phase transformation and the favorable adsorption sites. Also, Zhang et al. have studied the intercalation process of the Li$^+$ ions on the surface of single layer 2H and 1T-MoS$_2$. The study unveiled the pseudocapacitance performance of the polymorph MoS$_2$. Besides, the possibility of K$^+$ intercalation was reported by Kang et al. However, the effect of the intercalation process on the quantum response upon applying voltage was not discussed. Furthermore, although TMDs are greatly affected by the Van der Waals forces, it was only studied in terms of mechanical behavior without highlighting its effect on the electronic response of the electrode material. To this end, Li-ion batteries rely on the pseudocapacitive intercalation process as the main storage process. Whereas in case of supercapacitors, the electrical double layer (EDL) behavior presents high power density and high cycling stability. However, the origin of the capacitive behavior (EDL and surface intercalation) in the different phases of MoS$_2$ and the intercalated MoS$_2$ is yet to be revealed. Noteworthy, although co-intercalation of different cations may lead to synergistic effects, it was not addressed in literature. Li et al. reported the use of bulk MoS$_2$ in Li-ion batteries with a capacity -after 100 cycles- of 1189 mA h/g (200 mA/g). Being more abundant than Li, Na-ion batteries have recently emerged as alternatives to Li-ion batteries. Barik et al. investigated the impact of defects on the properties of MoS$_2$ in Li- and Na-ion batteries using first-principles calculations. Also, Mortazavi et al. studied the binding sites and stability upon Na-ion intercalation in MoS$_2$, revealing a maximum capacity of 146 mAh/g with an average electrode potential of 0.75-1.25 V. This was much lower than that obtained experimentally for MoS$_2$-based Na-ion battery, which exhibited a capacity of 220 mA h/g at 2 A/g. As it has the highest transference number among all alkali metals, K ion intercalation has recently been extensively investigated. Comparing Na, Li, and K-ion intercalation for MoS$_2$ supercapacitor electrodes, the 1T-MoS$_2$ electrode exhibited 590 F/g at a scan rate of 5 mV/s in K$_2$SO$_4$ electrolyte, while the symmetric device gave a power density of 225 W/kg and an energy density of 4.19 Wh/kg. Additionally, K-ion intercalated MoS$_2$-based batteries have been investigated by Du et al. proving their superior performance.
The charge storage mechanism in disulfide-based electrodes was thought to go via redox reactions. Wu et al. have grown flowers of Zn and Co on Ni-foam using the hydrothermal method to fabricate binder-free Zn_{0.76}Co_{0.24}S electrode. The three-electrode system investigation revealed a diffusion controlled process in KOH electrolyte, resulting in a specific capacitance of 1906 F/g at 1 A/g and the sulfide electrode was used in an asymmetric device and showed 75.7 Wh/Kg energy density at a power density of 700 W/Kg with a retention of 86.7% after 8,000 cycles. Li et al. also studied the Zn-Co binary sulfide that was synthesized via a hydrothermal process followed by a sulfurization process. The resulted nanoparticles had a diameter of 15 nm, which resulted in a specific capacitance of 1269 F/g at 0.5 A/g, with its asymmetric device showing an energy density of 45.5 Wh/Kg at a power density of 805 W/Kg. The high performance of the binary sulfide was attributed to the low charge transfer resistance in contrast to their oxide counterparts. Further studies on binary sulfides were performed by Zhang et al. who synthesized Mn-Co binary sulfide nanoparticles using hydrothermal method, 50 nm in diameter with a surface area of 63 m²/g. The tested three-electrode system gave a specific capacitance of 1150 F/g at 1 A/g with a cycling stability of 88.2% after 5,000 cycles. The binary Mn-Ni sulfide nanosheets was also synthesized using hydrothermal method. The resulted material was tested as an asymmetric supercapacitor electrode and showed an energy density of 76.6 Wh/Kg. Furthermore, the tertiary Ni-Mn-Co sulfide was investigated in a core-shell structure @Co(OH)_2. The electrode was used in an asymmetric device, exhibiting an energy density of 51.5 Wh/Kg at a power density of 751.5 W/Kg with a stability of 93.3% after 10,000 cycles. In this regard, Evariste et al. have studied the electrodeposition of MoNiCoS on Ni-foam that exhibited a capacitance of 1472 F/g at 0.5 A/g. Further, substrate modification was performed by the same group, as they used reduced graphene oxide/Ni-foam as a substrate for electrodeposition of MnNiCoS to reveal a capacitance of 1302 F/g at 0.5 A/g. In this aspect, Zhang et al. have used the Carbon Cloth (CC) to electrodeposit NiCoS with a capacitance of 1454 F/g at 1 A/g. Evarist et al. synthesized hierarchical mesoporous Zn–Ni–Co–S that delivered a capacitance of 627 F/g at 0.25 A/g. While Huang et al. synthesized Ni–Zn–Co–S nanosword arrays that exhibited an
energy density of 91.7 Wh/kg. On the other hand, Ni-Mn-Co-Son carbon nanotubes fiber (MNCS/CNTF) was studied by Wang et. al to give an areal capacitance of 2554 F/cm³ at 1 mA/cm². The ternary sulfide was compared to their oxide counterparts as illustrated in Figure III-3 (A and C) to present the superior performance of sulfide electrodes. Moreover, Figure III-3 (B) shows the clear redox peaks that reflects the battery-like nature of the electrode material. The mesoporous Ni-Co-Mn-S exhibited a capacitance of 1360 F/g at 1 A/g, and the Ni-Co-Mn-S nanosheet showed 2717 F/g at 1 A/g. However, the Ni-foam was the leading substrate in most of the studies, which limit the flexibility of the electrode. On the other hand, flexible electrodes such as carbon nanotube fibers substrate electrodes of Ni-Co-Mn-S showed a relatively low capacitance in comparison to those on the Ni-foam substrate and the synthesis method was tedious multistep hydrothermal process.

![Figure III-3 Capacitance performance of MNCS/CNTF (A) comparative GCD curves, (B) CVs at different scan rates, (C) comparative rate capability, and (D) stability of MNCS/CNTF.](image-url)

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In summary, it can be observed that pseudocapacitance behavior of transition metal dichalcogenides intercalation (e.g., MoS$_2$) can give higher specific capacitance than carbon materials, with acceptable cycling stability. However, the effect of intercalation on the charge storage mechanism has not been intensively investigated. On the other hand, battery-like materials such as binary and tertiary sulfides can result in extraordinary capacitance values, however, their cycling stability is much lower than that of the carbon EDL material. Therefore, it is important to use hybrid electrodes and/or devices to overcome the shortage in the single charge storage mechanism type.

### 3.1.3 Development of Hybrid Electrodes

As presented in Figure III-4, the Ragone’s plot shows the importance of finding a “gray” region that mixes the advantages of battery-electrodes and supercapacitor electrodes, here comes the “hybrid electrodes and devices”. One of the hybrid systems for supercapacitor applications is the composite electrode between an EDL material (Carbon) and a Faradic material (either pseudocapacitive or battery-like). Sangabathula et al. synthesized a composite of MoS$_2$ and carbon derived from candle soot. The composite was used in a three-electrode system in KOH electrolyte, resulting in a specific capacitance of 453 F/g at 1 A/g and a retention of 94% after 10,000 cycles. Moreover, the composite was used in an asymmetric device, showing an energy density of 40 Wh/Kg and a power density of 200 W/Kg with a retention of 100% after 10,000 cycles. Also, Sangeetha et al. have recycled plastic bottles to activated carbon and used it in a composite with carbon doped MoS$_2$, resulting in a capacitance of 288 F/g, 36 Wh/Kg energy density, and 469 W/Kg power density. Moreover, a carbon nanosheet-MnO$_2$ composite was used in a supercapacitor asymmetric device to give a specific capacitance of 87 F/g at 0.5 A/g and an energy density of 31 Wh/Kg at a power density of 193 W/Kg.
3.2 Fabric electrodes

Wearable devices are the next generation of electronics development to allow easy and fast reach to electronic devices for daily use. Therefore, the development of energy storage wearable devices is one of the main goals when identifying electrode materials. Barakzehi et al. have developed conductive textile for manufacturing all-solid-state supercapacitor devices.\textsuperscript{141} Their work used a polyethylene terephthalate fabric as the base material that was treated by reduced graphene oxide (rGO) and polypyrrole nanoparticles. The developed device showed a specific capacitance of 0.23 F/cm\textsuperscript{2} at 1 mV/s, an energy density of 11 μWh/cm\textsuperscript{2}, and a power density of 0.03 mW/cm\textsuperscript{2} with a cycling stability of 76% after 6,000 cycles with perfect bending stability.\textsuperscript{141} Moreover, the superconductive fabric based on carbon black/graphene was synthesized by Jia et al. using microfluidic fabrication. The developed fabric had a conductivity of 22316 S/m and a surface area of 296 m\textsuperscript{2}/g.\textsuperscript{142} The manufactured supercapacitor device provided a specific capacitance of 176 F/cm\textsuperscript{3}, energy density of 5.6 mWh/cm\textsuperscript{3}, and retention of 92% after 10,000 cycles.\textsuperscript{142} Furthermore, conductive fabric such as carbon cloth (CC) was used as a substrate for supercapacitor applications. Liu et al; investigated the deposition of cobalt metal-organic framework (MOF) on carbon cloth, then the ion exchange process was used to
turn the MOF into Ni-Co hydroxide that was sulfurized and used as a supercapacitor electrode.\textsuperscript{143} The fabricated flexible electrode provided a specific capacitance of 1,653 F/g at 1 A/g and a retention of 84\% after 3,000 cycles. A device of the fabricated Ni-Co-S electrode on CC against activated carbon was tested and showed a specific capacitance of 128 F/g at 0.5 A/g, energy density of 40 Wh/Kg, and power density of 379 W/Kg.\textsuperscript{143}

Since Silk is a cheap economic-friendly material, researchers devoted their efforts to create conductive silk. \textit{Bombyx mori} silkworms feed quite exclusively on mulberry leaves. It is fairly well-known in the silk industry that particular dyes can be directly fed to silkworms so as to color the silk in-vivo.\textsuperscript{144–149} Many studies have evaluated this technique’s efficiency and lethality for a number of dyes, including some florescent dyes for biomedical applications.\textsuperscript{144–146,148–154} The interest in this technique lies in its more environmentally friendly approach to utilizing potentially harmful chemicals to dope silk. In relatively recent developments, studies have proven that silkworms can tolerate a surprisingly wide range of chemicals beyond just dyes (from metal nanoparticles to carbon nanotubes and graphene) the end result being to produce doped silk fiber.\textsuperscript{147,155–158} Histograms and amino acid analysis of the cells in the silk glands showed that the worms remained largely healthy under the altered feeding regimes.\textsuperscript{159} Most studies aimed at improving the mechanical strength of silk using various metal-based nanoparticle regimens.\textsuperscript{151,155–157,160,161} Other studies investigated the possibility of making the silk conductive by feeding the worms nanosilver, carbon nanotubes, and graphene.\textsuperscript{156,162} Interestingly, nanosilver enhanced the cocoons conductivity and the cocoon device was able to light up a blue Light Emitting Diode (LED).\textsuperscript{162} Besides, the carbon nanotubes fed to silkworms produced super-tough silk fibers through enhancement of their mechanical properties. In another unique study, Zheng \textit{et al.} fed silkworms with Yb\textsuperscript{3+} and Er\textsuperscript{3+} compounds, which are upconverting phosphors in order to create florescent silk for particular biomedical applications.\textsuperscript{163} The possibilities of in-vivo modified silk are indeed vast and are open to far more investigation and research. In particular, nearly all the studies published on feeding silkworms on nanomaterials have been mostly proof-of-concept. Questions with regards to
toxicity, economic viability, and feeding efficacy have been well-studied for dyes, however, remain largely unanswered for nanomaterials and inorganic materials. For this field to develop further, these issues must be addressed in order to determine the merit of the in-vivo modified silk by nanomaterials. As can be seen in Figure III-3, the in-vivo modified silk can be used as electrode materials with different routes of post-modification and the field of development is widely opened.

![Figure III-5 A map of the different modification possibilities of silk.](image)

### 3.3 Recycling of energy storage devices

Charge storage devices such as batteries contain a lot of valuable metallic resources that can be recycled and reused instead of polluting the environment with charge storage wastes. To this end, Ali et al. recycled Zn-C battery cathode powder using heat treatment to obtain Mn$_3$O$_4$ that was deposited on Ni-foam and electro-converted into MnO$_2$ that was used as a supercapacitor electrode. The recycled electrode showed a specific capacitance of 309 F/g at 0.1 A/g and a retention of 93% after 1650 cycles.\textsuperscript{164} Also, Farzana et al. have recycled Zn-C battery to prepare Mn$_3$O$_4$ and used as a supercapacitor electrode without any further treatment. Their electrode exhibited a specific capacitance of 125 F/g at 5 mV/s and a retention of 80% after 2100 cycles.\textsuperscript{165} Li-ion spent battery was also recycled by Garcia et al. to electrodeposit the
cobalt metal from the spent battery electrolyte onto a Pt electrode to be used as a supercapacitor electrode. The recycled electrode showed a capacitance of 625 F/g. Further recycling was performed by Mao et al. by using the leaching solution of the spent battery as a source of cobalt. The solution was used to synthesize hollow microspheres of Co₃O₄ through a solvothermal process. The recycled electrode showed a capacitance of 50.8 F/g at 1 mV/s with a retention of 89% after 1000 cycles. However, researchers are still working on developing methods for recycling spent batteries and making use of all of their components. Provali et al. reported the recovery of Li, Fe, and Mn from cathodes of spent batteries using HCl and H₂O₂. Others recycled lithium ion batteries (LIBs) via mechanical processing to separate metals based on their density. Georgi-Maschler et al. developed a process to recycle LIBs by combining mechanical pretreatment with hydro- and pyro-metallurgical processes followed by the use of electric arc furnace to refine the extracted metals. This process managed to recover cobalt and lithium as well as cobalt alloy. Chang-Heum et al. used a combination of hydrometallurgical and physical processes, based on the solubility variation of different metals in several solvents, to recycle lithium and cobalt compounds with high purity. On the other hand, Tran et al. were able to extract cobalt and lithium by deep eutectic solvents with efficiency more than 90%. Despite such success in recycling spent LIBs, the utility of the recycled metals was rarely reported. Aboelazm et al. reported on the recovery of cobalt oxide (Co₃O₄) from spent Li-ion battery and tested its performance as a supercapacitor material in 3-electrode cell. Although the recovered Co₃O₄ showed a specific capacitance of 1273 F/g, the recovery process suffers from the high cost due to the multi-steps used to selectively deposit Co₃O₄ under magnetic field. Rochaab et al. were able to recover CuFe₂O₄ ferrites from spent Li-ion battery, which showed a specific capacitance of 2.4 F/g with high charge efficiency and reversibility upon use in supercapacitor cell. Aravindan et al. reported the reuse of recovered graphite from spent LIBs as negative electrode, However, the material suffered from large irreversibility in the system compared to freshly used graphite. Therefore, it is essential to develop methods to better recover the active components from LIBS and improve their performance upon reuse in technological applications.
3.4 Quantum capacitance calculations ($C_Q$)

Quantum capacitance calculations are widely used to guide researchers to enhance the performance of graphene-based electrodes.\textsuperscript{67,69,75} Wood \textit{et al.}\textsuperscript{67} used the PBE method with ultrasoft pseudopotential to investigate the $C_Q$ of pristine graphene along with doped graphene and strained graphene.\textsuperscript{67} For the study of doped graphene, point defect and substitution were performed in a unit cell of 54 atoms. However, for the stress effect, rippled graphene sheet of 32 atoms was used. The rippling of graphene sheets was applied such as the in-plane lattice parameter was decreased convoluting the out of plane lattice parameter with a sinusoidal variation. The results revealed that when comparing the $C_Q$ of the defected graphene (Stone-Wales, divacancies and monovacancies), the divacancy resulted in a large DOS around the $E_F$ and hence a high $C_Q$. On the other hand, the Stone-Wales and the monovacancy slightly enhanced the $C_Q$. Furthermore, by adding H, N, and O to the monovacancy, the DOS along with the $C_Q$ changed dramatically around the PZC and gave a much higher $C_Q$ values. Moreover, the doping of graphene with N and B increased the $C_Q$ values. However, the effect of dopants also affected the position of enhancement of the $C_Q$ values according to the potential window. It was found that N-doping enhanced the $C_Q$ of graphene in the negative potential window, while boron doping enhanced the $C_Q$ of graphene in the positive potential window as illustrated in Figure III-6 (A). This was attributed to the increase in the DOS of the related electronic structures relative to the $E_F$. Upon folding the graphene sheet, the PDOS of the carbon atoms along the folded edge was changed. This impacted the resulted $C_Q$ and caused an enhancement in the total capacitance performance of graphene.\textsuperscript{67} The quantum capacitance of graphene oxide that has epoxy and hydroxyl groups on its basal plane was studied by Song \textit{et al.}\textsuperscript{68} to show the possible enhancement in graphene capacitance. The study showed that the oxygen-containing groups shifted the fermi level, affected the DOS, and improved the quantum capacitance. Quantum capacitance calculations showed that graphene oxide with epoxy groups performs symmetrically in positive and negative applied potential windows, while graphene oxide with hydroxyl groups showed asymmetric behavior with better performance in the positive potential.
The improvement in the DOS and quantum capacitance of graphene can also be enhanced via N-doping, vacancy defects, and adsorption of transition metal atoms as discussed by Yang et al. As presented in Figure III-6 (D-F), the increase in defects concentration, increased the defect states and enhanced the quantum capacitance of graphene. The Si, S and P-doped graphene along with the Si-N, S-N, P-N co-doped graphene were also investigated using the DFT to estimate their quantum capacitance. In Figure III-6 (G and H), other dopants such as Si, S, and P were compared to the N-dopant in their effect on $C_Q$ of graphene. P-doping increased the $C_Q$ around the PZC dramatically in comparison to other dopants, while Si and S did not show a great impact on the $C_Q$ of graphene. On the other hand, when combining different N-doping positions with the other dopants the effect changed. It was also observed that S doping with graphitic N-doping increased the $C_Q$ greatly in the negative potential window, while the Si doping with graphitic N-doping increased the $C_Q$ around the PZC. However, the combination between the pyrrolic N-doping and the pyridinic N-doping with P, Si, and S doping did not have a great impact on the enhancement of the $C_Q$ in comparison to bare N-doping. $C_Q$ has also been used to calculate the capacitance performance of hybrid electrodes. Mohsin et al. studied the $C_Q$ of hybrid graphene/Cu sheets. The study included the modelling of three layers of Cu $<$111$>$ plane with graphene monolayer. It was observed that the $C_Q$ of pristine graphene increased greatly, which was attributed to the weakening of the e-e interaction and Fermi velocity modulation. In summary, DFT can provide a great insight on the proper electrode material to be used in supercapacitor electrodes. However, more screening of materials is required to provide a library of $C_Q$ values of the desired carbon materials that will allow a fast-cheap method to choose the right electrode material for the perfect supercapacitor performance. For 2D materials such as MoS$_2$, any change in the electronic cloud will directly affect the resulting capacitive behavior, substantiating the significance of the $C_Q$ calculations. Moreover, the new trend of hybrid supercapacitor electrodes that combines MoS$_2$ with carbon materials requires unveiling the effect of the Van der Waals forces (VdW) on $C_Q$. 


Figure III-6 (A) $C_Q$ of graphene and defected graphene,\textsuperscript{67} (B-C) $C_Q$ and stored charges of graphene (Gr), epoxy functionalized graphene (-O-) and hydroxyl functionalized graphene (-OH),\textsuperscript{68} (D) DOS and $C_Q$ of graphene with different single-vacancy concentrations: (a) 1.4%, cell (6 × 6), (b) 3.1%, cell (4 × 4), (c) 5.6%, cell (3 × 3), and (d) 12.5%, cell(2 × 2),\textsuperscript{69} (F) Trend chart of the maximum of $C_Q$ for different vacancy concentrations,\textsuperscript{68} (G) $C_Q$ for doped graphene,\textsuperscript{71} and (H) $C_Q$ for N-co-doped graphene.\textsuperscript{73}
4.1 Materials synthesis

4.1.1 Preparation of N-doped mesoporous graphene hydrogel (MGHG)

Graphene oxide (GO) was prepared via the improved Hummers’ method as previously reported.\textsuperscript{178-180} Then, the N-doped mesoporous graphene hydrogel (MGHG) was prepared via a hydrothermal technique. Briefly, 60 ml of GO solution was sonicated for 4 h, during their sonication ammonia solution was added till the pH reached 13.8. The mixed solution was transferred to a Teflon sealed autoclave (180°C for 10 h) and the resulting black rod was washed and dried at 60°C. The GHG slurry was prepared by mixing MGHG (90 wt.%) and Polyvinylidene Difluoride (PVDF) (10 wt.%) in dimethyl formamide (DMF), and stirred overnight till a homogenous slurry was obtained, which was then drop-casted onto graphite sheet, followed by drying at 60°C for 12 h as shown in Figure IV-1.

![Figure IV-1](image)

Figure IV-1 Stepwise Synthesis of N-doped mesoporous graphene hydrogel.

4.1.2 Synthesis of different MoS\(_2\) phases

For the synthesis of MoS\(_2\) nanomaterials, ammonium molybdate and thiourea were used as precursors for molybdenum and sulfur, respectively. The formation of MoS\(_2\) goes through a four-stage growth process:\textsuperscript{181}
CS (NH₂)₂ + 2H₂O → H₂S (g) + 2NH₃ (g) + CO₂ (g)

(NH₄)₆Mo₇O₂₄ → 7MoO₃ + 6NH₃ + 3H₂O

MoO₃ + 3H₂S + H₂O → MoO₂ + SO₄²⁻ + 2H⁺

MoO₂ + 2H₂S → MoS₂ + 2H₂O

Note that thiourea was used as a precursor for sulfur as well as a reducing agent, which can precisely and effectively reduce MoO₃ to MoS₂. Ammonia in the reaction could effectively diffuse beneath the parallel planes of the MoS₂ nanosheets, leading to expansion of the lattice and generation of more active unsaturated sulfur atoms in more disordered structure (i.e. 1T/2H phase). Water serves as a solvent and is adsorbed onto the surface of MoS₂ to form a molecular layer that controls layer stacking. As more thiourea is used (in case of 3R phase), MoO₃ becomes insufficient due to the following two reasons. One is simply due to the fact that higher thiourea concentration consumes more MoO₃. Secondly, with a higher thiourea concentration, the pH value will be higher, leading to the conversion of MoO₃ to MoO₄. This counter effect reduces the amount of MoO₃ and therefore the formation of 1T MoS₂ phase. In addition, as the sulfur concentration increases, the probability of having lattice mismatch during layer stacking increases, leading to the partial formation of 3R phase. Phase transformation upon thermal treatment of either 1T/2H and/or 3R/2H materials into stable and pure 2H phase was previously reported for MoS₂ prepared either via hydrothermal or CVD routes. The structure of the three MoS₂ phases is as presented in Figure IV-2.

Figure IV-2 MoS₂ different phases structure.
4.1.3 Preparation of MoS$_2$/carbon composites

The synthesized MoS$_2$ was mixed with carbon nanotubes (CNTs, Sigma) in the ratios of 1:1, 1:3 and 3:1 wt%, then sonicated in 100 ml of deionized water (DI) for 30 min, and finally dried overnight at 80°C. The resulting composites are named as: MCNT 1:1, MCNT 1:3 and MCNT 3:1, respectively. The MoS$_2$ was also mixed with graphene nanoflakes (GNFs, Sigma) in the ratios 1:1, 1:3 and 3:1 wt%, then sonicated in 100 ml DI for 30 min, and finally dried overnight at 80°C. The resulting composites are labeled MGNF 1:1, MGNF 1:3 and MGNF 3:1, respectively. Finally, the MoS$_2$ was mixed with CNTs and GNFs in the ratio 1:1:1 wt%, then sonicated in 100 ml DI and dried overnight at 80°C. The resulting composite is labeled MCG.

4.1.3 Electrodeposition of sulfides 3D interconnected sheets

The Mn-Ni-S 3D interconnected sheets were electrochemically co-deposited onto the flexible Ni-foam using a biologic SP 300 potentiostat/galvanostat. The electrodeposition solution consists of 0.01M Ni(NO$_3$)$_2$.6H$_2$O, 0.01M MnCl$_2$.4H$_2$O, 0.01M KCl, and 0.1 M Thiourea (CS(NH$_2$)$_2$). Before preparing the working electrode, the Ni-foam substrate was cleaned by concentrated HCl solution with sonication for 15 min to remove the native NiO layer, then it was rinsed with DI water and ethanol. The deposition was carried out in a three-electrode cell in an electrochemical glass cell using cleaned Ni-foam as the working electrode, platinum sheet as the counter electrode, and saturated calomel electrode as the reference electrode using cyclic voltammetry at a scan rate of 5 mV/s for 5 cycles in the potential range of -1.2–0.2 V. The prepared electrodes were washed several times by DI water followed by drying at 60°C for 12 h. The mass of the deposited film on the Ni-foam was determined by subtracting the mass of the Ni-foam before and after electrodeposition using a microbalance. The typical mass loading of the positive Mn-Ni-S electrode was about 0.6 mg/cm$^2$. For Mono-sulfides, the biologic SP 300 potentiostate was used to deposit the triple sulfide on 1 cm$^2$ Ni-foam and on 1 cm$^2$ CC. The substrates were cleaned in concentrated hydrochloric acid in ultrasonication bath for 15 minutes followed by rinsing with deionized water and ethanol.
solution used in electrodeposition process consists of 0.1 M thiourea (CS(NH$_2$)$_2$), and of 0.01 M KCl with 0.01 M Ni(NO$_3$)$_2$·6H$_2$O, 0.01 M Co(NO$_3$)$_2$·6H$_2$O, 0.01 M MnCl$_2$·4H$_2$O for NiS, CoS, and MnS respectively. The electrodeposition process was performed in three-electrode cell with the Ni-foam or CC as the working electrode. The tertiary sulfide Mn-Ni-Co-S was deposited on CC using the same electrodeposition technique.

![Figure IV-3](image-url)

**Figure IV-3** Stepwise synthesis of the Ni-Co-Mn-S nanostructures.

### 4.1.4 Synthesis of magnetite–graphene (Fe$_3$O$_4$-GR) composites

Graphene oxide was synthesized via the improved Hummers’ method as previously reported.$^{179,180}$ The Fe$_3$O$_4$-GR was prepared via hydrothermal method. A specific amount of graphene oxide was first dispersed in 50ml DI water, then 5 mg FeCl$_3$·6H$_2$O and 2 mg FeCl$_2$·4H$_2$O were added to the GO solution. The mixed solution was stirred overnight at 70°C. Then, 30% ammonia solution was added to the solution to form a solution of pH =11, then the mixture was transferred to a Teflon sealed autoclave and set at 150°C for 2 hours, followed by filtration, washing, and drying. The Fe$_3$O$_4$-GR slurry was prepared by mixing 80 wt.% active material, 10 wt.% carbon and 10 wt.% in DMF as a solvent to produce a slurry, which was then drop-casted onto Ni-foam. Then, dried at 60°C for 12 h.

### 4.1.5 Fabrication of Mn-Ni-S // Fe$_3$O$_4$-GR asymmetric supercapacitor.

The fabrication of the Mn-Ni-S // Fe$_3$O$_4$-GR asymmetric supercapacitor was conducted by using the Mn-Ni-S and Fe$_3$O$_4$-GR as the positive and negative electrodes, respectively and a filter paper as the separator. A 1.0 M KOH solution was used as the electrolyte and a piece of
a filter paper as the separator. The masses were balanced for two electrodes. The typical mass loading of an asymmetric supercapacitor is about 5.2 mg/cm².

4.1.6 Spent battery recycling process

A spent laptop Li-ion battery (NCM 18650 E-200) was used as the starting point for recycling. The battery plastic shell was stripped, and one cell was taken from this battery. However, discharge and dismantling are very important steps prior to dealing with the battery cell. For the discharging process, platinum (Pt) wires were connected to the battery poles and submerged into 1 M NaCl as an electrolyte solution for about 24 h or until a complete discharge of the cell. For the manual dismantling, liquid nitrogen was used to deactivate harmful substances. At this point, the cell was dismantled and separated into cathode, anode, steel and separators. The anode and cathode electrodes were dried at 80°C for 24 h, then washed with distilled water at 40°C for 1 h under agitation to eliminate organic solvents (Propylene Carbonate (PC) and Ethylene Carbonate (EC)) and to facilitate the detachment of the active material from cathode and anode. This active material was filtered and washed with distilled water at 40°C to remove possible lithium salts such as LiPF₆ and LiClO₄. Then, the filtered material was dried in air for 24 h. The whole active material was dissolved in a solution containing HCl (3.0 M) and H₂O₂ (35%), where each 9.17 g of the electrodes used 470 ml of HCl and 30 ml of H₂O₂. The system was maintained under constant magnetic agitation at 80°C for 2 h. After that, the solution was filtered using a syringe filter and the pH was adjusted in the 6-7 range, see Figure IV-4.

4.1.5 Electrodeposition of Li-Ni-Mn-Co-Based Nanostructured Materials

The Li-Ni-Mn-Co-hydroxide nanomaterials were co-deposited onto Ni-foam electrochemically using potentiostat/galvanostat (Biologic SP 300), Ni-foam (working electrode), platinum sheet (counter electrode), and SCE (reference electrode) via cyclic voltammetry at a scan rate of 5 mV/s in the potential window from -1.2 to 0.2 V for 5 cycles. The prepared electrodes have been washed using distilled water followed by drying at 50°C for
10 h. The mass of the deposited material was taken as the difference between the weight of the Ni-foam before and after deposition using microbalance (see Figure IV-4)

Figure IV-4 Stepwise synthesis of Li-Ni-Mn-Co-based nanostructures from spent Li-ion batteries.

4.1.6 Silkworm feeding process and silk electrodes preparation

The B. mori larvae were divided into 5 groups and each group has 10 larvae and were kept in a transparent dry box with good ventilation. The first group was only feeding on diet of blank mulberry leaves (S/B). While the rest 4 groups were feeding on diet of mulberry leaves previously wetted with suspensions of 0.5 wt% graphite (S/G), 0.5 wt% TiO2 (S/TiO2), 0.5 wt% MoS2 (S/MoS2) and 0.5 wt% KMnO4/MnCl2 (S/Mn), respectively. The modified diet started at the worms’ 5th instar and ended by starting the spinning process. The produced cocoons were partially degummed before the characterization and the electrochemical measurements. The degumming process included drying the cocoons at 80°C for 2 hours then the cocoons were immersed in a solution of 0.5 wt% of Na2CO3 at 100°C for 30 minutes and this process were repeated 3 times then the cocoons were washed with distilled water for 2 minutes and repeated 3 times.
4.2 Materials characterization

The materials synthesized in the thesis work was characterized using characterization techniques as following:

1) The crystal structure and composition were investigated using x-ray powder diffractometer (Panalytical X’pert PRO MPD X-Diffractometer) with Cu Ka radiation ($\lambda = 0.15418 \text{ nm, 40 kV, 30 mA}$)

2) The phase and coordination of the elements in the synthesized materials were investigated using the X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo-Scientific).

3) Fourier transform infrared spectroscopy (FT-IR) via Perkin Elmer Spectrum One spectrophotometer using KBr pellets.

4) High-resolution transmission electron microscope (HR-TEM, JOEL JEM-2100) was used for imaging and selected area diffraction analysis.

5) The morphology and nanostructure of the studied samples were investigated using the field emission scanning electron microscopy (FEDEM, Zeiss SEM Ultra 60, 5 kV). For the Silk fibers, the fibers were sputtered with gold at 15 A for 5 minutes before the SEM imaging.

6) The accelerated surface area and porosimetry were used for measuring the adsorption/desorption of nitrogen isotherm at -196°C, the Brunauer-Emmett-Teller (BET) plot with nitrogen adsorption isotherm was used to indicate the specific surface area. The data were also analyzed using the NLDFT (cylindrical pore) model using the NOVATouch LX2 instrument and software.

7) The composition of the fibroin was detected using the energy dispersive X-ray analysis (EDX) (JED 2300).

8) Thermogravimetric analysis (TGA) was conducted on the natural silk using the device (TGA NETZSCH STA 409 C/CD) at a heating rate of 10° C/min and a nitrogen flaw rate of 20 ml/min.
9) Raman spectroscopy was performed using a dispersive Raman microscope (Pro Raman-L Analyzer) with an excitation wavelength of 512 nm and laser power of 1 mW.

4.3 Electrochemical specifications

The studied electrodes were electrochemically investigated using the BioLogic SP-300 potentiostat to in terms of two and three-electrode systems with specifications as following:

- *For the CNTS, GNF, Gr and C$_{25}$*

  The three-electrode cell was used with the Pt coil as the counter electrode, a calomel electrode as the reference electrode, and the materials on the graphite sheet as the working electrodes. Different electrolytes were used in the system (0.5 M H$_2$SO$_4$, 0.5 M Na$_2$SO$_4$, and 0.5 M KOH) to measure cyclic voltammograms (CV) at different scan rates (from 1 to 150 mV/s). The galvanostatic charge/discharge (GCD) experiments were performed at different current densities (0.7, 1, 2, 3, 4, 5, 7, and 10 A/g). The electrochemical impedance spectroscopy (EIS) measurements were conducted to measure the resistance of the CNTs electrode in the device in the frequency range of 100 kHz to 100 mHz.

- *For the MGHG*

  The three-electrode cell was used with the Pt coil as the counter electrode, a calomel electrode as the reference electrode, and the materials on the graphite sheet as the working electrodes. Different electrolytes were used in the system (1 M K$_2$SO$_4$) to measure cyclic voltammograms (CV) at different scan rates (from 5, 10, 20, 30, 40, 50, and 100 mV/s). The galvanostatic charge/discharge (GCD) experiments were performed at different current densities (1, 1.5, 2.5, 3.5, 5, 7.5, and 10 A/g). The electrochemical impedance spectroscopy (EIS) measurements were conducted to measure the resistance of the electrode in the frequency range of 100 kHz to 50 mHz.
• **For the MoS$_2$**

For the 3-electrode cell, a calomel electrode was used as the reference electrode, a Pt coil was used as the counter electrode, and different electrolytes were used in the system (0.5 M Li$_2$SO$_4$, 0.5 M Na$_2$SO$_4$, and 0.5 M K$_2$SO$_4$). Cyclic voltammetry (CV) measurements were carried out at scan rates from 5 to 300 mV/s in the potential window (−0.4 to 0.5 V). The galvanostatic charge/discharge (GCD) tests were carried out at current densities (0.5, 0.7, 1, 2, 3, 4, 5, 7 and 10 mA/g). The EIS measurements were carried out in the frequency range of 10 kHz to 100 mHz. The materials were tested for 2000 cycles and the EIS was re-measured after the 2000 cycles.

• **For the Di-sulfides and Tri-sulfides**

The supercapacitive properties of the fabricated electrodes were examined in a three-electrode cell with a platinum wire counter electrode, and a saturated calomel electrode (SCE) as a reference electrode in a 1 M KOH solution. The CV measurements were performed in the potential window of 0 - 0.45 V at different scan rates from 5 to 50 mV/s. The GCD measurements were also conducted at different current densities from 1 to 20 A/g in the potential window of 0 - 0.4 V. The EIS measurements were performed over the frequency range of 0.01 Hz to 100 kHz at the open circuit potential with a sinusoidal perturbation of 10 mV amplitude.

• **For the Li-Ni-Mn-Co hydroxide**

The electrochemical behavior of the fabricated electrodes has been investigated in 1 M KOH solution using a 3-electrode cell. The cyclic voltammetry (CV) measurements were performed in the potential range of 0–0.45 V at different scan rates ranged from 5 to 50 mV/s. The constant current charge/discharge (CCCDs) measurements were carried out in the potential range of -0.1– 0.45 V at different current densities (1–5 A/g). The electrochemical impedance spectroscopy (EIS)
measurements were performed in the frequency range from 10 mHz to 100 kHz (at open circuit potential).

- **For silk electrodes**

  The capacitive performance of the resulted silk was tested using three-electrode system in which 6 M KOH was used as the electrolyte, coiled Pt as the counter electrode, calomel electrode as the reference electrode and the silk as the working electrode. The silk working electrode was fabricated in two separate methods. To be able to test the performance of the fiber itself, the degummed inner layer of the cocoons was cut into a square of 2*1 cm² and a drop of Ag paste was used as a current collector on the point of attachment to the crocodile of the potentiostat. Half the piece of fiber was immersed in the electrolyte and half the weight of the fiber was taken as the weight of the active material in the electrode. Since the electrolyte upwards in the fiber besides the fiber piece was not homogeneous so another method was used to assure the results. The strands of fiber were weighted and coiled over a length of 1 cm of a glassy carbon (GC) rod. The part covered with the fiber was immersed completely in the electrolyte and used as the working electrode. The CV was measured in potential windows (0.0 to 0.4) and (-0.4 to 0.0) in order to identify the performance of the active materials as positive and negative electrodes, respectively. The cyclic voltammetry was measured at different scan rates (10, 50, 100 and 500 mV/s). The galvanostatic charge/discharge measurement (GCD) was performed at different applied currents (0.1 to 0.5 A/g). The stability of the silk fibers was measured up to 1000 cycle at applied current of 0.1 A/g. The electrochemical impedance spectroscopy (EIS) of the system was measured at frequency range between 1 MHz to 100 mHz. The measurements were repeated twice on two different samples from each type of fibroin.
4.4 DFT Calculations

- **For the CNTs, GNF, and Gr**

  In our study, VASP\textsuperscript{39} (Vienna Ab-initio Simulation Package) software was utilized for the DFT calculations\textsuperscript{191}. For the exchange-correlation scheme, the PBE-GGA (Perdew Burke-Ernzerh of Generalized Gradient Approximation)\textsuperscript{192} was chosen to model the electron-electron interaction. The PAW pseudopotentials\textsuperscript{193,194} (Projector augmented-wave) were adopted to account for the electron-ion interaction. In the framework of plane-wave basis set, the Kohn-sham wave functions were expanded with a kinetic energy cut-off of 800 eV for both geometry optimizations and total energy calculations. The Monkhorst-pack method was used to treat the sampling of k-points in the Brillouin zone and the generation of Density of States (DOS) profile. The Monkhorst-pack grids were set to 31x31x9, 31x31x1, and 1x1x16 for graphite, graphene, and CNT, respectively. For generation of DOS, Methfessel-Paxton smearing scheme was applied with a broadening factor of 0.2 eV. For graphite, the VdW-DF2 non-local correlation functional\textsuperscript{53} was implemented to account for the dispersion interactions result from Van Der Waals forces between the graphitic layers. For CNT, the chirality of the was (11,0). A 25x25 Å vacuum slab was introduced for the CNT in the X and Y directions while a 20 Å vacuum slab was constructed in the Z-direction to avoid the periodic image interactions. The resulted curves of the quantum capacitance were smoothed using the Adjacent-Averaging method.

- **For MGHG**

  VASP\textsuperscript{39} (Vienna Ab-initio Simulation Package) code was implemented for the DFT calculations\textsuperscript{191}. For the exchange-correlation scheme, the PBE-GGA (Perdew-Burke-Ernzerhof of Generalized Gradient Approximation)\textsuperscript{192} was used to treat the electron-electron interaction. The PAW pseudopotentials\textsuperscript{193,194} were utilized...
to account for the electron-ion interaction. Within the framework of plane-wave basis set, the Kohn-sham wave functions were expanded with a kinetic energy cut-off of 600 eV for both geometry optimizations and total energy calculations. A (5x5x1) graphene supercell was established to encompass the three different combined types of N-defects with a reasonable doping ratio that reflects the experimental part of this study. The Monkhorst-pack method was adopted to sample the k-points in the Brillouin zone and the generation of Density of States (DOS) profile. The Monkhorst-pack grids were set to 31x31x1, and 15x15x1 for graphene, and MGHG, respectively. For generation of DOS, gaussian smearing was applied with a broadening factor of 0.05 eV. A 20 Å vacuum slab was constructed in the Z-direction for both materials to avoid the periodic image interactions.

- **For C_{76}**
  
  The density functional theory (DFT) was used to optimize the commercially available fullerenes to calculate their bandgaps and electronic properties. The DFT calculations were performed using the Gaussian 16 software with the method B3LYP and the basis set 6-31G(d,p). The GaussSum software was used to generate the density of states of the fullerene under study.

- **For MoS_{2}**
  
  The density functional theory (DFT)\textsuperscript{39} was employed for total energy computations using Vienna Ab Initio Simulation Package (VASP)\textsuperscript{191}. For the exchange-correlation, the PBE-GGA\textsuperscript{192} was implemented to treat the electron-electron interaction instead of the HSE06 hybrid functionals as Gao et al.\textsuperscript{195} reported that PBE gave better results for MoS_{2} in agreement with the experimental data. To account for the electron-ion interaction, the PAW pseudopotentials\textsuperscript{193,194} were exploited. In this regard, PAW Rb_{sv} pseudopotential, where 4s^{2}4p^{6}5s^{1} electrons are treated as valence electrons, was used for accurate Rb intercalation calculations and PAW Cs_{sv}
pseudopotential, where 5s^25p^66s^1 electrons are treated as valence electrons, was used for accurate Cs intercalation calculations. For the expansion of Kohn-Sham wave functions, the kinetic energy cut-off was set to 600 eV within the plane-wave basis set framework. The three-layered-structures were adopted for the modelling of 1T, 2H, and 3R phase of MoS2. A (2x2x1) supercell was constructed to accommodate for the octahedral binding site for the intercalated ions. To avoid the periodic image interactions, a 30 Å vacuum slab was introduced in the z-direction for the intercalated structures (Ion-MoS2). The Monkhorst-pack scheme was utilized to sample the k-points in the Brillouin zone and for the generation of the density of states (DOS) profile. The Monkhorst-pack meshes 25x25x1, 6x6x1, and 8x8x2 were constructed for the pristine bulk MoS2, Ion-MoS2 (2x2x1) supercell with a vacuum slab, and the DOS profiling of the intercalated structures, respectively. To remedy the under estimation of the non-local dispersion interactions, vDW-DF2 non-local correlation functional was employed to describe the Van der Waals forces between the MoS2 layers. Concerning the smearing, Methfessel-Paxton scheme, with a broadening factor of 0.2 eV was applied in case of 1T-MoS2 structures. While, Gaussian scheme, with a broadening factor of 0.05 eV was applied in case of 2H-MoS2, and 3R-MoS2 structures. With respect to the co-intercalation study, A (4x2x1) supercell was established to model the three possible co-intercalation configurations of Li and Na in 2H-MoS2, which are horizontally-aligned similar ions (HASI), diagonally-aligned similar ions (DASI), and vertically-aligned similar ions (VASI). The Monkhorst-pack meshes 4x6x1, and 6x8x2 were used for (4x2x1) supercell, and the DOS profiling of the co-intercalation configurations, respectively. It is worth mentioning that this study has high conservative computational parameters in terms of the energy cut-off, the vacuum slab, the k-points mesh, and the VdW corrections. The PDOS was generated using the Pydef code and the charge density difference was generated using VESTA software.
The intercalated polymorph MoS$_2$ was studied with the formula of X$_{0.17}$MoS$_2$ where (X: H$,^+$, Li$,^+$, Na$,^+$, K$,^+$, Rb$,^+$, and Cs$^+$.)$^{122}$ The binding energy ($E_b$) between the intercalated ion and the MoS$_2$ can give an indication about the favored adsorbed ions according to eq. IV-1.$^{7,118,122}$

$$E_b = (E_{X-MoS_2} - E_{MoS_2} - nE_X)/n$$ (IV-1)

where $E_{X-MoS_2}$ is the total energy of the intercalated MoS$_2$, $E_{MoS_2}$ is the total energy of the pristine MoS$_2$, $n$ is the number of intercalated ions, $E_X$ is the energy of the intercalated atom in the BCC crystal (for hydrogen: an isolated H$_2$ molecule was used). For our intercalated systems, the formation energy $E_f$ of an intercalated MoS$_2$ can be calculated according to eq. IV-2.$^{122}$

$$E_f = (E_{X-MoS_2} - E_{MoS_2} - nE_X)/R$$ (IV-2)

where $R$ is the number of formula units of MoS$_2$ in the structure. For indicating the charge accumulation and charge transfer between the MoS$_2$ and the adsorbed ions, the isosurfaces of the charge density of adsorption ($\rho_{ad}$) were calculated according to eq. IV-3.$^{122}$

$$\rho_{ad} = \rho_{X-MoS_2} - \rho_{MoS_2} - n\rho_X$$ (IV-3)

where $\rho_{X-MoS_2}$ is the charge density of the intercalated MoS$_2$, $\rho_{MoS_2}$ is the charge density of the pare MoS$_2$, $n$ is the number of intercalated ions, $\rho_X$ is the charge density of the intercalated atom in the BCC crystal (for hydrogen: an isolated H$_2$ molecule was used).
Chapter V: Development of Carbon-Based Electrodes

5.1 A Roadmap Towards the Proper Selection of Carbon Electrodes for Energy Storage Applications: Experimental and Theoretical Insights

Although Faradic materials enjoy higher energy density than the EDL counterparts, they usually suffer from the lower power density and cycling instability due to the decomposition and/or corrosion of the electrode materials in high potential windows. In this regard, hybrid electrodes that contain both carbon materials and faradic materials have been proposed. However, the pseudo and battery-like materials are electrolyte-dependent as they are only electrochemically active in specific electrolytes. Therefore, choosing the right carbon material to be combined with the Faradic/pseudo material should take the electrolyte characteristics into account. Herein, I aimed at the development of a roadmap to better guide the choice of the proper carbon material in the suitable electrolyte and operating potential window. Specifically, the electrochemical performance of carbon nanotubes (CNTs), graphene nanoplates (GNPs), and graphite (Gr) was systematically investigated in the most commonly used aqueous electrolytes; the acidic H\textsubscript{2}SO\textsubscript{4}, the basic KOH, and the neutral Na\textsubscript{2}SO\textsubscript{4}. The materials were deposited on graphite sheet to avoid any contribution from the current collector. The materials were tested in 3-electrode system as well as in assembled two-electrode devices. The charge storage mechanism in each of the tested materials was further investigated using computational tools. The density functional theory (DFT) was used to elucidate the quantum capacitance of the three carbon materials under applied potential to identify the EDL performance in different potential windows and to correlate with the charge storage mechanism obtained experimentally. The applicability of the DFT for the 3D materials such as graphite was also investigated in comparison to the experimental results.
5.1.1 Structure and hybridization

**Figure V-1 (A)** shows the XRD pattern of the tested carbon materials, where the (002) graphitic carbon plane is notable at 26.5° for all samples. However, it is very intense and sharp in both Gr and GNPs, revealing their good crystallinity. On contrary, the (002) peak of the CNTs is very broad and almost disappeared, revealing the low content of graphitic carbon and the high porosity of the carbon allotrope.\(^{201-203}\) Moreover, both Gr and GNPs showed another sharp small peak at 55°, corresponding to the (100) plane that can be ascribed to the diffraction from the 2D layers of the aromatic structure of the carbon materials.\(^{204}\) The surface functional groups on the investigated carbon materials were characterized using FT-IR as depicted in **Figure V-1 (B)**. All studied materials showed a clear O-H vibration broad peak at 3408 cm\(^{-1}\). Note that the transmittance of the O-H peak in CNTs and GNP was ~95% while that of the Gr was ~91%, revealing a relatively lower OH content in the Gr sample. Also, the GNP spectra showed the sharpest O-H peak due to the absence of H-bonding. Moreover, the C=O and the C=C stretching vibration peaks at 1647 and 1566 cm\(^{-1}\), respectively are significant in all samples. The existence of functional groups on the surface, such as the O-H stretching of the COOH group, is evident via the peak appeared at 2318 cm\(^{-1}\) and the C-O bonding vibration of the COOH group at 1375 cm\(^{-1}\) in all tested samples.\(^{85,201,205,206}\) The disorder in the graphitic carbon hexagons in the studied materials was characterized using Raman spectroscopy as shown in **Figure V-1 (C)**, where two bands (G and D) were observed for all samples. While the G-band at 1580.7 cm\(^{-1}\) represents the E\(_{2g}\) symmetry in-plane bond stretching of the sp\(^2\) C-C bonds, the D-band at ~ 1335 cm\(^{-1}\) represents the breathing mode of the A\(_{1g}\) symmetry caused by the disorder in the perfect graphitic hexagons.\(^{207}\) The calculated intensity ratio (I\(_D\)/I\(_G\)) was found to be 1.07, 0.21, and 0.19 for the CNTs, GNP, and Gr, respectively, revealing more ordered graphitic structure in the Gr and GNP samples than that in the CNTs. The disorder in the graphitic hexagons in the CNTs may be attributed to the surface functional groups and the cylindrical shape that affects the bond stretching and the breathing mode of the A\(_{1g}\)
symmetry. The surface area and the porous structure of the carbon materials were studied using the N₂ adsorption/desorption isotherm at 77 K. The resulted isotherms for the three carbon materials were of the H₃ type, indicating the presence of both meso and micropores. The isotherm was fitted using both non-local density functional theory (NLDFT) with the cylindrical-shaped pores model and the Brunauer–Emmett–Teller (BET). The BET fitting showed surface areas of 423.5, 125.9, and 74.6 m²/g for CNTs, GNP, and Gr, respectively. The NLDFT fitting surface areas were 426.8, 128.3, and 70.7 m²/g, respectively, which are very close to those obtained from the BET fitting. The pore width distribution is presented in Figure V-1 (D). It can be observed that both GNP and Gr have a microporous structure with a large peak around 2-3 nm, the micropore surface area calculated from V-t method was 19.4% and 6.1% of the total surface areas of GNP and Gr, respectively. While, for the CNTs, it showed two main peaks around 3 and 8 nm with the total surface area attributed to the mesoporous structure.

Figure V-1 Structural characterization of the tested carbon materials: (A) XRD, (B) FT-IR, (C) Raman spectra, and (D) NLDFT pore width histogram.
The nature of hybridization in the studied carbon materials was investigated using XPS, Figure V-2 (A-C). For all samples, the deconvoluted C 1s XPS spectra showed three peaks for the sp² C-C at ~284.4 eV, sp³ C-C at ~285 eV, and C-O at ~289 eV. The peak analysis revealed that the CNTs consists of 46.7% sp² and 27% sp³ hybridization. The GNP showed 46.7% sp² and 34.2% sp³ hybridization, and the Gr has 49.5% sp² and 29% sp³ hybridization. Note that CNTs have the highest C-O content, reflecting the high content of OH groups on the surface, which is in agreement with the FT-IR results.

![Figure V-2 C 1s XPS spectra of the studied materials: (A) CNTs, (B) GNP, and (C) Gr.](image)

5.1.2 Electrochemical performance

The electrochemical performance of the three carbon materials was tested in three different aqueous electrolytes: the acidic H₂SO₄, the neutral Na₂SO₄, and the basic KOH. The performance was tested using cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS).

5.1.2.1 Three-electrode system

A three-electrode system consisting of Pt as the counter electrode, standard calomel electrode (SCE) as the reference electrode, and the active material as the working electrode was used to test the performance of each material. Note that graphite sheet was used as the current collector to avoid any contribution from the current collector and to provide more accurate results on the real performance of the carbon materials. The investigation of the electrochemical performance was done in both positive and negative potential windows.

Figure V-3 shows the electrochemical behavior in the positive potential window. All carbon materials showed clear redox peaks in H₂SO₄ electrolyte, Figure V-3 (A), which can be
ascribed to the reversible keto-enol tautomerism that occurs at 0.699 V_{SHE} (0.45 V_{SCE}).\textsuperscript{208}

The H\textsubscript{2}SO\textsubscript{4} electrolyte allowed a wide positive potential window of 1 V. Note that the redox peaks for Gr are more shallow than those for CNTs and GNP, which may be attributed to the low content of adsorbed OH groups on Gr surface. On contrary, the tested CNTs have a content of 15% OH functional groups and the GNP has dangling bonds that may accommodate adsorbed oxygen from air. Figure V-3 (B) shows the GCD of the carbon materials in H\textsubscript{2}SO\textsubscript{4}, indicating battery-like behaviour.\textsuperscript{22} On the other hand, the rate capability at different scan rates is presented in Figure V-3 (C). At 150 mV/s, the CNTs still retain very high capacitance of 130 F/g. In the Na\textsubscript{2}SO\textsubscript{4} electrolyte, the materials show an EDL-like capacitance behavior due to the adsorption/desorption process, Figure V-3 (D-E). The obtained rate capability in Na\textsubscript{2}SO\textsubscript{4} electrolyte is almost the same as that in H\textsubscript{2}SO\textsubscript{4} electrolyte. However, since the starting capacitance is lower than that obtained in H\textsubscript{2}SO\textsubscript{4}, the final capacitance is also lower than that in H\textsubscript{2}SO\textsubscript{4}. In KOH electrolyte, the potential window decreased dramatically to 0.55 V for Gr, 0.5 V for Na\textsubscript{2}SO\textsubscript{4}, and 0.45 V for CNTs. This may be attributed to the catalytic effect of KOH on the water splitting process that provides extra OH\textsuperscript{-} groups in the medium of the reaction. However, the materials in KOH electrolyte exhibited an EDL-like behavior as shown in Figure V-3 (G-H). Note that the rate capability, Figure V-3 (I), was slightly higher than that in both H\textsubscript{2}SO\textsubscript{4} and Na\textsubscript{2}SO\textsubscript{4} electrolytes.
In contrary to the behavior in the positive potential window, the tested carbon material in the negative potential window exhibited EDL-like behavior in all electrolytes. However, the potential window differed between the three electrolytes. For example, the potential window in H$_2$SO$_4$ was decreased to 0.3 V, due to the catalytic effect on the water splitting process, **Figure V-4 (A-B)**. However, the variation in the rate capability, **Figure V-4 (C)**, showed that CNTs can retain up to 30% of its capacitance at 150 mV/s. In the Na$_2$SO$_4$, the potential window was 1 V (**Figure V-4 (D-E)**) and the variation in the rate capability shows that CNTs can retain a capacitance of 80 F/g at 150 mV/s, **Figure V-4 (F)**. However, for the KOH electrolyte, the potential window was 0.65 V (**Figure V-4 (G-H)**) and the rate capability was 33% for CNTs at 150 mV/s, **Figure V-4 (I)**.
Table V-1 summarizes the outcomes of the electrochemical analysis of the carbon materials. Note that irrespective of the electrolyte type and the potential window, the capacitance decreases in the order CNTs > GNP > Gr. For the potential window, H₂SO₄ provided the highest positive potential window (1 V) while Na₂SO₄ provided the highest negative potential window (1 V). For the capacitance values, the capacitance decreased in the electrolytes in the order H₂SO₄ > Na₂SO₄ > KOH in the positive potential window and in the order Na₂SO₄ > KOH > H₂SO₄ in the negative potential window. This may be attributed to the width of the potential window provided by each electrolyte. Therefore, while the best capacitance behavior as a positive electrode is for CNTs in the acidic H₂SO₄, for a negative electrode, it is better to use CNTs in Na₂SO₄ electrolyte.
Table V-1 Comparative specific capacitance values for the studied carbon materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolyte</th>
<th>Positive potential window (V)</th>
<th>Negative potential window (V)</th>
<th>Cs at 5 mV/s (+Ve) (F/g)</th>
<th>Cs at 5 mV/s (-Ve) (F/g)</th>
<th>Cs at 0.7 A/g (+Ve) (F/g)</th>
<th>Cs at 0.7 A/g (-Ve) (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>H₂SO₄</td>
<td>0 to 1</td>
<td>0 to -0.3</td>
<td>453.60</td>
<td>176.75</td>
<td>441.90</td>
<td>236.80</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄</td>
<td>0 to 0.9</td>
<td>0 to -1</td>
<td>270.89</td>
<td>256.41</td>
<td>194.67</td>
<td>259.50</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td>0 to 0.45</td>
<td>0 to -0.65</td>
<td>218.28</td>
<td>212.49</td>
<td>77.14</td>
<td>87.70</td>
</tr>
<tr>
<td>GNP</td>
<td>H₂SO₄</td>
<td>0 to 1</td>
<td>0 to -0.3</td>
<td>242.98</td>
<td>100.34</td>
<td>441.90</td>
<td>236.80</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄</td>
<td>0 to 0.9</td>
<td>0 to -1</td>
<td>190.70</td>
<td>173.46</td>
<td>190.70</td>
<td>145.00</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td>0 to 0.50</td>
<td>0 to -0.65</td>
<td>135.78</td>
<td>139.28</td>
<td>78.45</td>
<td>98.43</td>
</tr>
<tr>
<td>Gr</td>
<td>H₂SO₄</td>
<td>0 to 1</td>
<td>0 to -0.3</td>
<td>174.36</td>
<td>65.34</td>
<td>131.32</td>
<td>23.77</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄</td>
<td>0 to 0.9</td>
<td>0 to -1</td>
<td>90.25</td>
<td>83.35</td>
<td>28.31</td>
<td>37.80</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td>0 to 0.55</td>
<td>0 to -0.65</td>
<td>88.48</td>
<td>74.97</td>
<td>48.36</td>
<td>53.95</td>
</tr>
</tbody>
</table>

The results showed that the proper choice of the material and electrolyte can result in the highest performance. For example, the studied materials showed much higher capacitance than those reported in literature, mainly due to the proper choice of the electrolyte and operating potential window. It can be observed from Table V-2 that CNTs were able to achieve a capacitance of 442 F/g in H₂SO₄ as a positive electrode and 281 F/g in Na₂SO₄ as a negative electrode with wide potential window of 1 V in low concentration electrolytes.

Table V-2 Comparative capacitance performance of similar studied materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Substrate</th>
<th>Potential window (V)</th>
<th>Electrolyte</th>
<th>Specific capacitance (F/g)</th>
<th>Conditions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC/CNTs/rGO</td>
<td>Aluminum Foil</td>
<td>0 to 3</td>
<td>1 M LiClO₄ in ethylene carbonate (EC) and diethyl carbonate (DEC)</td>
<td>101</td>
<td>0.2 A/g</td>
<td>205</td>
</tr>
<tr>
<td>CNTs/rGO composites</td>
<td>Carbon Cloth</td>
<td>0 to 0.8</td>
<td>H₂SO₄–polyvinyl alcohol (PVA) gel-electrolyte</td>
<td>93.1</td>
<td>2 mV/s</td>
<td>209</td>
</tr>
<tr>
<td>N, S doped porous carbon nanosheets</td>
<td>Ni-foam</td>
<td>0 to -1</td>
<td>6 M KOH</td>
<td>280</td>
<td>1 A/g</td>
<td>210</td>
</tr>
<tr>
<td>N-containing porous Carbon</td>
<td>Ni-foam</td>
<td>0 to -1</td>
<td>6 M KOH</td>
<td>278</td>
<td>1 A/g</td>
<td>211</td>
</tr>
<tr>
<td>Fibrous CNTs-aerogel</td>
<td>---</td>
<td>0 to -1</td>
<td>1 M H₂SO₄</td>
<td>160.8</td>
<td>0.5 A/g</td>
<td>212</td>
</tr>
<tr>
<td>Reduced graphene oxide/CNTs</td>
<td>---</td>
<td>0 to 1.2</td>
<td>6 M KOH</td>
<td>250</td>
<td>1 A/g</td>
<td>213</td>
</tr>
<tr>
<td>CNTs</td>
<td>Graphite Sheet</td>
<td>0 to 1</td>
<td>0.5 M H₂SO₄</td>
<td>281.33</td>
<td>0.7 A/g</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 to -1</td>
<td>0.5 M Na₂SO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To investigate the charge storage mechanism in the three carbon materials in different electrolytes, the Randles–Sevcik’s simplified equation \((i = v^n)\) was used, where the
value of $b$ can be used an indication whether the resulting current is due to Faradic or capacitive behavior. **Figure V-5 (A-F)** shows the obtained Randles–Sevcik’s slope of the three carbon materials tested in different electrolytes in the positive and negative potential windows. While in the positive potential window the carbon materials tend to acquire Faradic behavior, they tend to exhibit capacitive behavior in the negative potential window. To further investigate the nature of the charge storage mechanism, the Trasatti’s method was used, **Figure V-5 (G-I)**.\textsuperscript{19,25} Note that in all tested electrolytes and in both positive and negative potential windows, there is a diffusion-controlled capacitance contribution. However, the diffusion-controlled capacitance contribution is much higher in the positive potential window than in the negative potential window. For $\text{H}_2\text{SO}_4$ electrolyte, the diffusion-controlled capacitance in the positive potential window is higher for both CNTs and GNP than that for Gr, which is in agreement with the sharpness of the redox (keto-enol tautomerism) peaks in the CVs of the CNTs and GNP due to the OH$^-$ groups on the CNTs surface and the adsorbed oxygen on the dangling bonds of GNP as confirmed via the FT-IR and XPS analyses. However, in the negative potential window, the CNTs in $\text{H}_2\text{SO}_4$ showed almost complete capacitive behavior, while the diffusion-controlled capacitance was dramatically reduced for both GNP and Gr. This may be attributed to the easy adsorption/desorption of the H$^+$ ions on the surface of the carbon materials. Although there are no redox peaks in the CVs of the carbon materials in $\text{Na}_2\text{SO}_4$ and KOH electrolytes in the positive potential window, they showed even higher diffusion-controlled capacitance than in the $\text{H}_2\text{SO}_4$ electrolyte. This may be attributed to the diffusion of $\text{SO}_4^{2-}$ and OH$^-$ groups in the porous structure of the carbon materials as well as the strong binding of the negative ions to their surface. On the other hand, in the negative potential window, the GNP showed a moderate capacitive behavior in both $\text{Na}_2\text{SO}_4$ and KOH electrolytes with the Gr showing a slightly higher capacitive behavior. A more in-depth investigation of the origin of the capacitive behavior is presented below based on the density functional theory calculations.
Figure V-5 Charge storage mechanism: (A-C) Randles–Sevcik’s plot of the carbon materials in the positive potential window in different electrolytes, (D-F) Randles–Sevcik’s plot of the carbon materials in negative potential window in different electrolytes, and (G-I) Origin of capacitance using complex Randles–Sevcik’s equation at 1 mV/s.

5.1.2.2 Computational insights into the capacitance performance

Computational studies have been proven to be adequate in exploring the properties of energy materials. However, using the density functional theory (DFT) tools in exploring the capacitance performance of electrode materials is not common in literature. DFT can be used to explore different aspects of the electrode materials. One of the main important properties that DFT can reveal is the quantum capacitance. The quantum capacitance \( C_Q \) can be used as an indication for the electronic contribution of the electrode materials to the Helmholtz layer at the EDL interface. For 2D semiconductors, the \( C_Q \) is of great importance as adding or removing electrons would greatly affect the overall capacitance. For materials such as graphene and CNTs, the \( C_Q \) can reveal a representative
picture of their capacitance performance. On the other hand, for graphite (a 3D material), \( C_Q \) may be misleading due to the fact that not all the electrons of the bulk can travel to the surface and contribute to the EDL capacitance.\(^7\,214\) Note that the double layer capacitance is electrolyte-dependent. In this regard, I have investigated the \( C_Q \) as a primary tool to elucidate the overall qualitative insights on the origin of the EDL capacitance of the studied materials. In the calculations of \( C_Q \) from the DOS, the Fermi level can be taking as the point of zero charge, which may help identifying the proper potential window for the working electrode.\(^67\,215\) As shown in Figure V-6 (A), the DOS of CNTs, GNP, and Gr are centered around zero with the DOS of CNT>GR~GNP. The gravimetric quantum capacitance is presented in Figure V-6 (B) in the potential window between -1 to 1V, which is the maximum attained potential window experimentally. While CNTs showed the highest \( C_Q \) in both positive and negative potential windows, both GNP and Gr showed almost the same \( C_Q \). The high quantum capacitance of graphite was expected as DFT assumed that all the bulk material will contribute to the quantum capacitance. However, assuming that only the surface layers of graphite will contribute to the quantum capacitance, it can be estimated that the \( C_Q \) of graphene is higher than that of graphite. Note that both graphene and graphite exhibit V-shaped curves around the point of zero charge, in agreement with the literature.\(^67\,73\) However, CNTs showed a semi V-shape due to the unsymmetrical DOS around the Fermi-level.\(^214\) The V-shaped curve gives insights on the reason behind the increased capacitance with increasing the potential window range. However, CNTs showed a maximum capacitance of 1377 F/g in the positive potential window and 477 F/g in the negative potential window. Although the quantum capacitance of CNTs in the positive potential window is relatively high, the contribution of the EDL capacitance was very low. This can be attributed to the presence of adsorbed OH groups that contributed to the pseudocapacitance instead and lowered the overall capacitance than the expected pure EDL capacitance. On the other hand, in the negative potential window, the EDL was the leading charge storage mechanism, which made use of the quantum capacitance. However, the lower experimental capacitance can be attributed to the internal resistance and the presence
of the adsorbed functional groups. The calculated $C_Q$ explains the experimentally obtained higher capacitance of CNTs in the positive potential window than in the negative potential window and the higher capacitance than both of GNP and Gr. For the GNP and Gr, the symmetrical V-shaped $C_Q$ curve explains the almost equal capacitance values as positive and negative electrodes.

![Figure V-6](image)

**Figure V-6** Computational investigation of the carbon tested materials: (A) DOS of the studied carbon materials (inset: enlargement of the DOS of the GNP and Gr), and (B) the calculated quantum capacitance of the studied carbon materials.

5.1.2.3 Two-electrode system

To test the performance of the materials in real devices, the CNTs were assembled in a symmetric device and tested in $\text{Na}_2\text{SO}_4$ electrolyte. The $\text{Na}_2\text{SO}_4$ electrolyte is specifically chosen because it showed the largest potential window with high capacitance in the 3-electrode measurements. The CVs of the symmetric device were performed at various scan rates between 5 and 150 mV/s, **Figure V-7** (A). The device showed a capacitance of 54 F/g at 5 mV/s and maintained its behavior at higher scan rates. Note also that the CVs are not perfectly rectangular in shape, which may be attributed to the contribution of the diffusion-controlled process as was the case in the three-electrode system. **Figure V-7** (B) shows the GCDs of the device at various current densities between 0.5 and 10 A/g. Note that the GCDs exhibit a stable shape over the entire current range. The capacitance of the device at 0.5 A/g was 47 F/g. For further electrochemical insights, the EIS was performed to investigate the device internal resistance and to identify the dominant charge storage mechanism as depicted in **Figure V-7** (C). The model proposed by Mei *et al.* was adopted
to interpret the Nyquist plot. The total internal resistance was found to be 3.78 Ω, which is composed of two components 3.54 Ω and 0.24 Ω representing the electrode resistance ($R_e$) and the electrolyte resistance ($R_\infty$), respectively. As for the charge storage mechanism, the slope of the linear part in the low frequency region is 1.9 (>1), which implies that the EDL is the dominant mechanism in this case. Therefore, the EIS findings concerning the charge storage mechanism are perfectly matching the three-electrode system results and the theoretical quantum capacitance obtained from the DFT calculations, as the device covers the whole range of the potential window resulting in a higher EDL capacitance performance.

**Figure V-7 (D)** depicts the rate capability of the device, which was able to retain up to 35% of its capacitance at 150 mV/s, proving the stability of the device over a wide range of applied scan rates. Ragone plot, **Figure V-7 (E)**, presents the relation between the power density and energy density of the device. The device showed an energy density of 23.3 Wh/Kg at a power density of 475 W/Kg. The device showed an excellent stability with a capacitance retention of 97.8% after 2500 cycles and up to 5000 cycles, which is higher than those reported in literature.205,212,213

5.1.2 Conclusions

Carbon materials are essential additives to improve the performance of supercapacitor electrodes. However, a systematic study of the effect of the nature of electrolytes on various carbon materials in positive and negative potential windows is yet to be reported. Herein, I investigated experimentally and theoretically the capacitance performance of three commercially available carbon allotropes; carbon nanotubes (CNTs), graphene nanoplates (GNP), and graphite (Gr) in the commonly used electrolytes namely, the acidic H$_2$SO$_4$, the neutral Na$_2$SO$_4$, and the basic KOH. The electrochemical performance showed that CNTs exhibit higher capacitance than GNPs and Gr. However, CNTs performance varied according to the applied potential and according to the electrolyte medium. CNTs showed a higher capacitance in the positive potential window than the negative potential window. The highest capacitance (441.90 F/g at 0.7 A/g) was obtained in
H₂SO₄ at a potential window of 1 V. The electrochemistry investigation of the charge storage mechanism revealed that CNTs along with GNP and Gr can accommodate a high contribution of diffusion-controlled process that increases with applying positive potentials, which was ascribed to the adsorbed functional groups on the surface of the carbon allotropes. The EDL behavior of the pristine carbon materials were investigated using density functional theory (DFT) calculations that provided insights on the quantum capacitance (C₀). The calculated C₀ revealed the reasons behind the obtained higher capacitance of CNTs over the GNPs and the Gr and gave insights on the origin of the higher positive potential window capacitance of CNTs. GNPs and Gr exhibited almost equal experimental capacitance in the positive and negative potential windows due to the symmetrical V-shaped C₀ curves. The symmetric device made of CNTs as the active material was tested in Na₂SO₄ electrolyte, revealing a stable performance over 5000 cycles with an energy density of 23.2 Wh/Kg and power density of 475 W/Kg. Therefore, it can be concluded that the proper choice of the carbon material with the complementary electrolyte and potential window can help to design efficient electrode materials for energy storage.
Figure V-7 Electrochemical performance of the symmetric device: (A) CVs at different scan rates, (B) GCDs at different current densities, (C) Impedance spectroscopy, (D) Rate capability, (E) Ragone plot, and (F) Retention up to 5000 cycles.
5.2 Boosting the cyclic stability and supercapacitive performance of graphene hydrogels via excessive nitrogen doping: Experimental and DFT insights

Graphene hydrogel (GHG) has a soft 3D porous network structure functionalized with oxygen, carboxyl, and hydroxyl groups, which lead to improved wettability, conductivity, and operating potential window.\textsuperscript{216,217} Due to its high electronegativity, comparable atomic size to carbon, and its ability to create strong valence bonds with carbon, N-doped GHG should be a promising candidate for use in supercapacitor applications to increase the capacitance and cycling stability of the GHG.\textsuperscript{218} However, the fabrication of such electrode materials with high specific capacitance and high cycling stability is still an open challenge. Herein, I report on the successful fabrication of i) nitrogen-doped mesoporous graphene hydrogel electrodes via a facile hydrothermal route with a superior capacitance 595 F/g at 0.5 A/g in 1 M potassium sulfate, which is very close to the theoretical capacitance of graphene, ii) symmetric devices with high cell voltage (2.2 V), power density, and energy density, and iii) quantum capacitance performance of the three different combined types of N-defects in graphene (graphitic, pyrrolic, and pyridinic).

5.2.1 Morphological characterization

Figure V-8 (A,B) shows FESEM images of the fabricated MGHG, revealing a three-dimensional interconnected porous structure with randomly oriented structure and highly wrinkled sheets. This structure prevents the restacking of graphene sheets during the reduction process and should enable high specific surface area, which facilitates fast diffusion of ions\textsuperscript{219}. Note that the formed graphene sheets have a thickness $\approx$6-8 nm. The energy dispersive X-ray (EDX) spectra shown in Figure V-8 (C), reveal the existence of C, N, and O only without any traces of impurities, indicating the high purity of the fabricated MGHG. This was further confirmed via the EDX mapping, Figure V-8 (D-F), showing a homogeneous distribution of the corresponding C, N and O elements. Furthermore, the effect of nitrogen doping on the wettability of graphene hydrogel was investigated via water contact angle measurements,
**Figure V-8 (G)**. MGHG exhibits a contact angle of 58.9°, indicating the good hydrophilicity of the fabricated material.

**Figure V-8 (A,B)** FESEM images, (C) EDX spectra, (D-F) EDX mapping for C, N, and O respectively, and (G) contact angle analysis of the fabricated MGHG.

**Figure V-10 (A)** shows the X-ray powder diffraction (XRD) patterns of the fabricated GO and MGHG. The XRD pattern of GO showed a peak at 2θ = 11.04° with a d-spacing of 0.8 nm, which can be attributed to the (002) crystalline plane of graphene oxide (GO). Upon the hydrothermal reduction of GO in the presence of ammonia solution, the peak at 11.04° was nearly disappeared and two broad peaks centered at 24.63° and 43.44° were emerged for the MGHG with a d-spacing of 0.369 and 0.208, respectively, which can be assigned to (002) and (100) planes, respectively and confirm the reduction of graphene oxide. The Raman spectra of GO and MGMH are shown in **Figure V-9**, revealing the characteristic D and G bands. GO exhibited a D band at 1347.43 cm\(^{-1}\) (corresponding to the ring breathing modes of sp\(^2\) carbon atoms that are adjacent to a defect or an edge) and a G band at 1592.73 cm\(^{-1}\) (corresponding to sp\(^2\) carbon atoms in a planar and conjugated structure). Note that after the conversion of GO into MGHG, the D and G bands were shifted to 1345.16 and 1591.73 cm\(^{-1}\), respectively.\textsuperscript{219,221}
Also, the $I_D/I_G$ intensity ratio increases from 0.796 to 1.06, suggesting a decrease in the average size of the sp$^2$ domains, which reveal that more defects were generated during the reduction and N-doping. The surface area of the fabricated MGHG was investigated via the nitrogen adsorption/desorption technique, Figure V-10 (B). The loops indicate type III isotherm. The observed hysteresis loop type (H3) infers that the material has a mesoporous structure, with the mesoporous cavities assembled during graphene hydrogel formation. The specific surface area analysis shows that MGHG possesses high surface area of 318.226 m$^2$/g. Moreover, based on the Barrett–Joyner–Halenda (BJH) model, the calculated pore size distribution was found to be $\approx$3.7 nm as shown in the inset of Figure V-10 (C). To investigate the chemical composition and surface states of the elements, XPS was employed to analyze the types and valence of the elements in the fabricated MGHG. Figure V-10 (D) depicted the C 1s spectrum, where four fitted peaks at around 288.41 eV, 286.42 eV, 285.08 eV, and 284.8 eV were observed that can be ascribed to C=O, C-O, C-N, and C=C/ C=C, respectively. Figure V-10 (E) shows the high resolution N1s spectra, which were well-deconvoluted into 3 peaks located at 398.47 (pyridinic-N), 399.9 (pyrrolic-N), and 401.2 eV (graphitic-N). Note that the presence of pyridinic-N is expected to increase the electronic conductivity of neighboring carbon atoms. Figure V-10 (F) shows the high resolution O1s spectrum that can be deconvoluted into 3 peaks with binding energies of 533.74, 532.62, and 531.02 eV, representing C-OH , C=O, and quinone, respectively. It is worth noting that the presence of N and O elements will not only improve the graphene surface affinity to electrolyte, but also may contribute additional pseudocapacitance behavior to the total capacitance of the material.

![Figure V-9 Raman spectra of GO and MGHG.](image)
Figure V-10 (A) XRD spectra, (B) adsorption/desorption isotherm, (C) BJH bore diameter distribution, (D) HR-XPS of the C 1s, (E) HR-XPS of the N 1s, and (F) HR-XPS of the O 1s of the fabricated materials.

5.2.2 Three-electrode system

The electrochemical properties of N-doped graphene were characterized using cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) techniques in a 3-electrode system containing 1 M K$_2$SO$_4$. Figure V-11 (A) shows a typical CV curve of the fabricated MGHG within a positive potential value ranging from zero to 1.1 V, which is higher than the reported potential window of graphene. The CV plots show symmetrical CV curves with a quasi-rectangular shape, with no redox/oxidative peaks even at high scan rates. The linear variation of the potential with time indicates electric double layer capacitance (EDLCs) denoting fast reversible reactions. However, at different scan
rates, there are slight deviation in the CV shape, indicating a mixed charge storage mechanism of EDL and pseudocapacitive behavior related to the nitrogen doping. The specific current was enhanced, and the CV curves did not change with increasing the scan rates, revealing the good rate capability of the material. Variation of the calculated capacitance with scan rate for the N-doped graphene hydrogel shows a perfect specific capacitance of 376.7 F/g at 5 mV/s. Note that the specific capacitance decreases to 303.7 F/g at 10 mV/s, indicating that the electrode reaction occurs only at the external surface.

The charge–discharge curves at different applied current densities (Figure V-11 (C)) were nearly triangular with quasi-symmetric shape and long discharge time, indicating superior capacitive behavior. Moreover, a small IR drop was observed indicating that the electrodes possessed typical EDLC and pseudocapacitive behavior, in agreement with the CV results. Based on the GCD results, the specific capacitance (Cs) can be calculated from each discharging.

Figure V-11 (B) shows the variation of the specific capacitance with current density. The calculated Csp values obtained from each discharging curve are 595, 347, 271, 195, 158, 126, 102, and 88 F/g at 0.5, 1, 1.5, 2.5, 3.5, 5, 7.5, and 10 A/g, respectively. The specific capacitance gradually decreased with increasing the applied current densities from 595.7 F/g at 0.5 A/g to 347.18 at 1 A/g, proving that the ion diffusion process occurs only at the outer surface of the electrode. Note that the obtained electrochemical performance of N-doped graphene hydrogel is higher than that reported for N-doped carbon materials, as listed in Table V-3. It seems that nitrogen doping offers new active sites and helps in the formation of interconnected porous structure, which enhanced the Faradic reaction and electron transfer, leading to the observed increase in the capacitance. Also, the behavior of MGHG as a negative electrode is similar to its behavior as a positive electrode and the capacitance is in the same range as shown in Figure V-12.
Figure V-11 (A) CVs at various applied scan rates, (B) rate capability, (C) GCDs at various applied current densities, and (D) Nyquist plot (inset: fitting circuit) of the fabricated MGHG electrodes.

Figure V-12 Electrochemical behavior of MGHG as a negative electrode material (A) CVs of MGHG at various scan rates, (B) charge/discharge curves at various current densities, and (C) variation of the specific capacitance with current density.

The EIS was performed to provide further insights into the electrochemical behavior, capacitive property, and conductivity of the fabricated N-doped graphene hydrogel electrodes. The EIS measurements were carried out in the frequency range of 50 mHz–100 kHz at the open circuit voltage (OCV), providing strong evidence for the capacitive behavior. Figure V-11 (D) shows a small arc at higher frequencies and straight lines at lower frequencies. In the high frequency region, the x-intercept of the Nyquist plot represents the equivalent series resistance
(ESR), indicating very small ESR. The semicircle on the Nyquist plot film represents the charge transfer resistance ($R_2$), which was as low as 0.166 4 Ω, indicating high capacitive performance of the material. The low resistances of the material may indicate its high electrical conductivity as ascribed to nitrogen doping and the porous linked structure.

**Table V-3** Comparison of the specific capacitance, potential window, and experimental conditions of the reported supercapacitor electrodes made of N-doped graphene materials measured in 3-electrode system to our work.

<table>
<thead>
<tr>
<th>Material</th>
<th>Synthesis</th>
<th>Substrate</th>
<th>Electrolyte</th>
<th>Capacitance (F/g)</th>
<th>Condition</th>
<th>Potential window (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D graphene hydrogel</td>
<td>Hydrothermal</td>
<td>Ni-foam</td>
<td>1 M H$_2$SO$_4$</td>
<td>316.8</td>
<td>0.5 A/g</td>
<td>0 to -1</td>
<td>226</td>
</tr>
<tr>
<td>N-doped graphene sheets (NGs)</td>
<td>Hydrothermal</td>
<td>Stainless steel mesh</td>
<td>1 M H$_2$SO$_4$</td>
<td>242.0</td>
<td>1 A/g</td>
<td>0 to 1</td>
<td>227</td>
</tr>
<tr>
<td>N-doped graphene hydrogels</td>
<td>Solvothermal method</td>
<td>Pt foil</td>
<td>25% KOH</td>
<td>205.0</td>
<td>5 mV/s</td>
<td>0.5 to -0.5</td>
<td>228</td>
</tr>
<tr>
<td>N-doped graphene aerogels</td>
<td>Hydrothermal</td>
<td>Ni-foam</td>
<td>6 M KOH</td>
<td>175.0</td>
<td>0.5 A/g</td>
<td>0 to -1</td>
<td>229</td>
</tr>
<tr>
<td>Functionalized graphene</td>
<td>Solvothermal method</td>
<td>Glassy carbon</td>
<td>1 M H$_2$SO$_4$</td>
<td>276.0</td>
<td>0.1 A/g</td>
<td>0 to -0.8</td>
<td>229</td>
</tr>
<tr>
<td>Reduced graphene oxide</td>
<td>Thermal</td>
<td>Cu mesh</td>
<td>6 M KOH</td>
<td>260.5</td>
<td>0.4 A/g</td>
<td>0 to -1</td>
<td>230</td>
</tr>
<tr>
<td>N-doped reduced graphene oxide</td>
<td>Hydrothermal</td>
<td>Au foil</td>
<td>1 M H$_2$SO$_4$</td>
<td>519.8</td>
<td>1 mV/s</td>
<td>0 to -0.8</td>
<td>231</td>
</tr>
<tr>
<td>N-doped graphene</td>
<td>Solid microwave method</td>
<td>Ni-foam</td>
<td>6 M KOH</td>
<td>197.0</td>
<td>0.5 A/g</td>
<td>0 to -0.9</td>
<td>232</td>
</tr>
<tr>
<td>Nitrogen-doped carbon</td>
<td>Carbonization and KOH activation</td>
<td>Ni-foam</td>
<td>1 M H$_2$SO$_4$</td>
<td>278.0</td>
<td>0.1 A/g</td>
<td>0.9 to -0.1</td>
<td>233</td>
</tr>
<tr>
<td>N/S co-doped carbon</td>
<td>Self-assembly process</td>
<td>Zn substrate</td>
<td>6 M KOH</td>
<td>251.0</td>
<td>0.5 A/g</td>
<td>0 to 1</td>
<td>234</td>
</tr>
<tr>
<td>N-doped MGHG</td>
<td>Solvothermal</td>
<td>Graphite sheet</td>
<td>1 M K$_2$SO$_4$</td>
<td>595.7</td>
<td>0.5 A/g</td>
<td>0 to 1.1</td>
<td>This Work</td>
</tr>
</tbody>
</table>

Further investigation was performed to get full insights on the charge storage mechanism in the fabricated MGHG electrodes. The simple form of Randles−Sevcik’s equation ($i = av^b$) gives a preliminary indication of the charge storage mechanism. By plotting $log i$ versus $log v$ (scan rate), the slope (b) value can help identifying the charge storage mechanism.\textsuperscript{124,177}

From Figure V-13 (A), the estimated $b$ value is 0.71, indicating a mixed charge storage
mechanism of the surface EDL and the diffusion-controlled process. Moreover, the complex Randles–Sevcik \((i=K_1v+K_2v^{1/2})\) relation was used to get insights on the percentage of the EDL current and diffusion-controlled current via plotting \(i/v^{1/2}\) versus \(v^{1/2}\).\(^{24,235}\) The results reveal that the charge storage mechanism in the MGHG is mainly a diffusion-controlled process. The percentage of diffusion current was 77% at 5 mVs\(^{-1}\) and decreased to 41.66% at 100 mVs\(^{-1}\), which caused the capacitance to retain around 36% of its value at such extreme scan rate. To confirm the results, the Trasatti’s method was used to estimate the EDL capacitance contribution to the total capacitance.\(^{19,25}\) Figure V-13 (B,C). Note that the lines in the Trasatti’s relation are perfectly linear, indicating the stability of the material over a wide range of scan rates for charge storage. The Trasatti’s fittings resulted in 80% diffusion-controlled capacitance and 20% EDL capacitance as presented in Figure V-13 (D). The high diffusion controlled process may be attributed to the presence of the N atoms in the graphene hydrogel, which can provide defect states and electron-rich environment in the graphene electronic cloud, thus increase the electronic exchange instead of the usual adsorption/desorption process.\(^{236}\)

![Figure V-13](image)

**Figure V-13** Charge storage mechanism in the MGHG electrodes: (A) Randles–Sevcik’s plot, (B) Trasatti’s EDL capacitance estimation plot, (C) Trasatti’s total capacitance estimation plot, and (D) The percentage of the diffusion-controlled capacitance.
5.2.3 Two-electrode system

In order to demonstrate the practical potential of the fabricated MGHG electrodes, a symmetric (AC) device was assembled. The CV and GCD curves of the AC device are shown in Figure V-14 (A). Note that the CV curves exhibited a semi-rectangular shape and the GCD curves exhibited semi-symmetrical triangular shape, revealing typical pseudo and electric double-layer capacitance characteristics with a characteristic potential window of 1.1 V in the positive and negative regions (Figure V-13 (A)). The highest potential window of the symmetric device can reach 2.2 V, while still retaining the CV shape. To assess the performance of the symmetric device, the CV and GCD curves were recorded at various scan rates and current densities under the potential window of 0-2.2 V (Figure V-14 (B,C)). The shapes of the CV curves were almost similar, confirming the good reversibility and relatively high rate capability of the assembled AC. According to the discharge time of MGHG//MGHG in the GCD profiles, the specific capacitance of the device of was 64 F/g at 0.5 A/g.

The obtained device values show an energy density of 30 Wh/kg at a power density of 1000 W/kg, which retains 12 Wh/kg at high power density of 7000 W/kg. These values are higher than those of previously reported for carbon-based symmetric supercapacitors, such as porous activated carbon (8.2 Wh/kg at 100 W/kg),\textsuperscript{237} GMOF/RGO (30.3 Wh/kg at 137 W/kg), (10.6 Wh/kg \textsuperscript{1} at 11900 W/kg),\textsuperscript{238} cotton-based AC (13.75 Wh/kg at 225 W/kg),\textsuperscript{239} and 3D HPCs (21 Wh/kg at 875 W/kg).\textsuperscript{240} Moreover, our device showed an excellent cycling stability with a capacitance retention reaching ~88% even after 8500 cycles with Columbic efficiency reaching 100%. Further, two charged supercapacitors in series can illuminate a white LED as an indicator for high-performance of the assembled supercapacitor.
Figure V-14 Electrochemical behavior of the symmetric supercapacitor device: (A) CV curves at 20 mV/s, (B) CV curves at various applied scan rates ranging from 5 to 100 mV/s (C) GCD curves at different applied current densities ranging from 0.5 to 10 A/g, (D) specific capacitance at different current densities, (E) Ragone plot of the fabricated device with the inset showing the glowing of white LED using two in series connected devices, and (F) capacitance retention and Coulombic efficiency after 8500 cycles at 5 A/g.

5.2.4 Quantum capacitance performance

To further investigate the secret behind the high performance of the MGHG, a unit cell with N-doped graphene was simulated using DFT. The cell included graphitic nitrogen, pyridinic nitrogen, and pyrrolic nitrogen. The type of doping was chosen as resulted in the XPS data revealed. The results were compared to the pristine graphene. The bond distance between the N-Pyrrolic and the adjacent bonded carbon was 1.43 Å, while the bond distance between the N-Pyrrolic and the adjacent non-bonded carbon was 2.26 Å. For the N-Graphitic-C bond distance, it was ~1.39 Å, while It was 1.44 Å for the N-Pyridinic with the adjacent non-bonded carbon. The total density of states (TDOS) of the simulated MGHG was calculated as presented.
in Figure V-15 (A), the TDOS was compared to that of the pristine graphene (G). It can be observed that the TDOS of the MGHG was much higher than that of the G and that the bandgap was reduced dramatically from 0.44 eV for G to 0.09 eV for the MGHG. This may be attributed to the effect of the free electrons on the nitrogen atoms. Although it was reported that the N-doping increases the quantum capacitance ($C_Q$) of the graphene, a mixture of different nitrogen defects types was not yet reported. The $C_Q$ for the simulated MGHG in comparison to G was calculated in the desired potential window (0-1.2 V).

The $C_Q$ presented in Figure V-15 (B), shows that the mixed N-doping increased the $C_Q$ dramatically. The highest graphene $C_Q$ calculated was 792 F/g for G while it was 2440 F/g for MGHG. The experimental values usually are lower than the reported $C_Q$ due to the resistance from the electrolyte and from the other circuit parameters. Besides the electrode/electrolyte interaction directed by the diffusion-controlled process can lead to reduction in the total capacitance. However, the $C_Q$ can give a great insight on the origin of the total high capacitance resulted and the trend of increment of capacitance. To this end, I can conclude that the N-doping with mixed graphitic, pyrrolic and pyridinic can give a high impact on the capacitance performance of the electrode material.

![Figure V-15](image.png)

**Figure V-15** Calculated electronic properties: (A) DOS of graphene and MGHG, and (B) Quantum capacitance of graphene and MGHG.
5.2.5 Conclusions

I demonstrated the successful synthesis of N-doped mesoporous graphene hydrogel (MGHG) via a facile green hydrothermal technique as revealed by the FESEM, XRD, Raman, and XPS analyses. The as-prepared MGHG exhibits high wettability (contact angle = 58.9°) and large surface area (318.226 m²/g) with a 2.95% N-content. Upon its use as a supercapacitor electrode material in 1 M K₂SO₄ aqueous electrolyte, the MGHG exhibited a maximum specific capacitance of 595.7 F/g with a low equivalent series resistance (0.1664 Ω), which is ascribed to the high surface area, nitrogen redox active sites, and high porosity of MGHG. The assembled symmetric supercapacitor device using MGHM as negative and positive electrodes exhibited a specific energy of 30Wh/kg at a specific power of 1000 W/kg and retained 12Wh/kg at a specific power of 7000W/kg. These superior results demonstrated the utility of the fabricated MGHG as a functional material for supercapacitor devices. The DFT investigation shed the light on the quantum capacitance enhancement resulted upon doping graphene with graphitic, pyrrolic, and pyridinic nitrogen together. More importantly, the approach presented in this study highlights the potential of the N-doped graphene hydrogel as an exceptional candidate for energy storage systems.
5.3 Fullerene C\textsubscript{76}: An Unexplored Superior Electrode Material with Wide Operating Potential Window for High-Performance Supercapacitors

One of the interesting carbon sets is the Fullerenes. Fullerenes are balls of carbon with hexagon and pentagon carbon rings with small bandgaps that allow fast charge transfer due to their high conductivity\textsuperscript{241,242}. Besides, fullerenes can provide very high surface area and cage-like structure that may help in increasing the diffusion of ions in and out of the buckybells. The electronic cloud of fullerenes can provide extra credit to the charging/discharging process and binding of electrolytes on their surface. On the other hand, unlike carbon nanotubes, fullerenes are defect-free carbon materials\textsuperscript{243}. Herein, I investigated the bandgap of some of the commercially-available fullerenes using density functional theory (DFT) calculations. I found that C\textsubscript{76} has a superior band gap and quantum capacitance. However, it has rarely been investigated as a supercapacitor electrode material despite its facile ionization, which can support redox reactions and undergo battery-like capacitance performance\textsuperscript{99,244}. From symmetry point of view, C\textsubscript{76} has two structures; D\textsubscript{2} (can be easily synthesized) and T\textsubscript{d} (very hard to be synthesized)\textsuperscript{245}. In addition to the electrochemical unique properties of fullerenes, they behave as n-type semiconductors, which open the opportunity for being used as electrode materials in solar-based supercapacitors\textsuperscript{246}. To this end, I have studied, for the first time, the potential of C\textsubscript{76} as a supercapacitor electrode material in different aqueous electrolytes. C\textsubscript{76} showed superior performance over a wide pH range in commonly used electrolytes without any additives.

5.3.1 DFT insights into fullerenes performance

Some of fullerenes are commercially available such as C\textsubscript{60}-Ih, the C\textsubscript{70}-D\textsubscript{5h}, C\textsubscript{76}-D\textsubscript{2}, and C\textsubscript{84}-D\textsubscript{2d}. I have investigated the bandgap of the previous commercially available fullerenes using the density functional theory (DFT) as presented in Figure V-16 (A). Note that C\textsubscript{76}-D\textsubscript{2} has the lowest bandgap energy among the commercially-available fullerenes. Consequently, I focused our study on the C\textsubscript{76}-D\textsubscript{2} fullerene material. The capacitance performance of C\textsubscript{76} was investigated using DFT methods. The conductivity of C\textsubscript{76} was
calculated using B3LYP/6-31G (d,p) as implemented in Gaussian-16 to determine the highest unoccupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy positions. The C\textsubscript{76} was optimized in its two general symmetries (D\textsubscript{2} and T\textsubscript{d}), then the molecular orbital distribution and the bandgap were calculated using the single-point calculations. The binding energy of the C\textsubscript{76} with the ions on both anode and cathode were calculated where the ions tested were SO\textsubscript{4}\textsuperscript{2-}, OH\textsuperscript{-}, K\textsuperscript{+}, Na\textsuperscript{+}, and H\textsuperscript{+}.

The electronic properties of pristine D\textsubscript{2}-C\textsubscript{76} and C\textsubscript{76} with adsorbed ions on its surface were investigated using DFT calculations. The calculations showed that the bandgap of bare C\textsubscript{76} is 1.98 eV, in agreement with the literature.\textsuperscript{99,244} However, as presented in Table V-4, all adsorbed ions reduced the bandgap of C\textsubscript{76}, which should increase the conductivity of the electrode and enhance its capacitance. The bandgaps of C\textsubscript{76}-H\textsuperscript{+} and C\textsubscript{76}-SO\textsubscript{4}\textsuperscript{2-} were the lowest. On the other hand, the adsorption energy was calculated and listed in Table V-4. It was found that the binding energy of C\textsubscript{76}-H\textsuperscript{+} is very high followed by that of C\textsubscript{76}-OH\textsuperscript{-} and C\textsubscript{76}-SO\textsubscript{4}\textsuperscript{2-}. It is suggested that this high binding energy may cause the C\textsubscript{76} to accommodate more pseudocapacitance behavior than the EDL behavior.

Table V-4 Calculated binding energy of C\textsubscript{76} with different ions.

<table>
<thead>
<tr>
<th>The ion adsorbed</th>
<th>Total Energy (eV)</th>
<th>Ionic Energy (eV)</th>
<th>Binding Energy (eV)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non</td>
<td>-78802.93</td>
<td>-</td>
<td>-</td>
<td>1.98</td>
</tr>
<tr>
<td>H\textsuperscript{+}</td>
<td>-78812.65</td>
<td>0.00</td>
<td>9.72</td>
<td>1.36</td>
</tr>
<tr>
<td>Na\textsuperscript{+}</td>
<td>-83214.69</td>
<td>-4410.46</td>
<td>1.31</td>
<td>1.84</td>
</tr>
<tr>
<td>K\textsuperscript{+}</td>
<td>-95123.15</td>
<td>-16319.35</td>
<td>0.86</td>
<td>1.89</td>
</tr>
<tr>
<td>OH\textsuperscript{-}</td>
<td>-80868.19</td>
<td>-2060.62</td>
<td>4.85</td>
<td>1.47</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>-97825.93</td>
<td>-19018.92</td>
<td>4.08</td>
<td>0.96</td>
</tr>
</tbody>
</table>

The GaussSum software was used to calculate the density of states (DOS) of the optimized C\textsubscript{76} as presented in Figure V-16 (B). The DOS reveals a semiconducting nature of C\textsubscript{76} with a bandgap energy of 1.98 eV. Hence, identifying the quantum capacitance (C\textsubscript{Q}) is of great importance as any change in the electronic structure should greatly affect the electrode potential.\textsuperscript{7} C\textsubscript{Q} reflects the contribution of C\textsubscript{76} to the capacitance of the Helmholtz layer at the electrode/electrolyte interface resulting from the electronic response of the material.\textsuperscript{7} The resulted quantum capacitance as a function of applied potential is presented in
Figure V-16 (C). As water-based electrolytes are used in this study, the potential window needs to be between 1 V and -1 V to avoid water splitting. Further calculations of the $C_Q$ in the negative potential window was performed to show that $C_{76}$ can accommodate capacitance for wider potential windows if non-aqueous electrolytes would be used. However, with increasing the negative potential window, the $C_Q$ tend to slightly reduce as well. Note that the $C_Q$ is very low in the positive potential window, while it can reach up to 370 F/g in the negative potential window.

5.3.2 Structure and hybridization

The morphology of $C_{76}$ was investigated using transmission electron microscopy (TEM), as presented in Figure V-17 (A). The TEM image showed $C_{76}$ to have a unified ball shape with a diameter of 0.9 nm. The $C_{76}$ nanoparticles were stacked together randomly as the diameter of the Buckyball is less than 1 nm, which makes it hard to be recognized separately.\textsuperscript{247,248} The porosity and surface area of $C_{76}$ were investigated using N$_2$ gas adsorption/desorption isotherm at 77 K. As shown in Figure V-18, the adsorption/desorption isotherm is of type III with H3 hysteresis loop, according to the IUPAC classification, reflecting the presence of micro and mesopores in the $C_{76}$ sample.\textsuperscript{97} The isotherm was fitted using both the Brunauer–Emmett–Teller (BET) and the non-local density functional theory (NLDFT) equations. The BET fitting showed a surface area of 33.8 m$^2$/g, which is much higher than that reported for $C_{60}$ counterpart.\textsuperscript{92,97} The NLDFT fitting used the cylindrical-shaped pores model to indicate a surface area of 26.7 m$^2$/g. The
distribution of the pore diameters reveals pore diameters that are more likely < 5 nm with most commonly pore diameter size of 2.84 nm, as depicted in Figure V-17 (B), indicating microporous structure. The functional groups on the surface of C_{76} were identified using FT-IR, as presented in Figure V-17 (C). The FT-IR showed a clear broad peak ascribed to O-H vibrations at 3411 cm\(^{-1}\), while the small peaks of C=O and C=C stretching vibrations appeared at 1647 and 1577.7 cm\(^{-1}\), respectively. Some other peaks indicate the existence of O-H stretching of the COOH group at 2378 cm\(^{-1}\), the C-OH bonding vibration of the COOH group at 1384.8 cm\(^{-1}\), and the band at 1440 cm\(^{-1}\) ascribed to the \(\delta(O-H)\) mode.\(^{85,201,205,206}\) As each carbon atom in C_{76} bonds to three other carbon atoms, it is expected that the major hybridization is sp\(^2\). However, due to the presence of the single-bonded pentagons and the double-bonded hexagons, the stretching and the distribution of electrons in the cloud of C_{76} may be affected. The Raman spectroscopy in Figure V-17 (D) showed almost the same intensity peaks for both the G and the D bands. The G-band at 1578 cm\(^{-1}\) represents the in-plane bond stretching of the sp\(^2\) C-C bonds with E\(_{2g}\) symmetry, which can exist in both pentagons and double-bonded hexagons of the C\(_{76}\). However, the D-band represents the disorder in the perfect graphitic hexagons due to the breathing mode of the A\(_{1g}\) symmetry.\(^{207}\) Since C\(_{76}\) has a relatively disordered hexagon, the D-band appeared clearly at 1343.5 cm\(^{-1}\). The calculated I\(_D\)/I\(_G\) was 0.92, which for amorphous carbon (non-graphitic hexagonal carbons) indicates the high ordering of the carbon atoms in the structure.\(^{207}\) Hence, the Raman spectroscopy in non-graphitic materials cannot be a good indication for the sp\(^2\) content in the structure. However, the XPS can give a better insight instead. The XPS of the C 1s of the C\(_{76}\) was investigated as presented in Figure V-17 (E). The XPS showed three peaks at 284.3, 284.9, and 288.8 eV as the binding energy sites of the sp\(^2\) C-C, the sp\(^3\) C-C, and the C-O bonds, respectively.\(^{249}\) The XPS peak analysis showed that the bonding in C\(_{76}\) is 60.6 % sp\(^2\) hybridized. The UV-Vis absorption of C\(_{76}\) was fitted using the Tauc plot as presented in Figure V-17 (F), indicating a bandgap energy of 1.85 eV, matching that of our calculated bandgap of the D\(_2\)-C\(_{76}\) and the previously reported bandgaps.\(^{244}\)
5.3.3 Electrochemical performance

The electrochemical performance of C\textsubscript{76} was investigated in three different media covering a wide range of pH, the acidic H\textsubscript{2}SO\textsubscript{4}, the neutral Na\textsubscript{2}SO\textsubscript{4}, and the basic KOH solutions in a three-electrode electrochemical cell. The applicability of using C\textsubscript{76} as a positive and/or negative electrode was investigated. In the positive potential window, C\textsubscript{76} showed different responses in the three electrolytes, as indicated via the cyclic

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**Figure V-17** Structural characterization of C\textsubscript{76}: (A) HR-TEM, (B) NLDFT pore volume distribution, (C) FT-IR, (D) Raman spectroscopy, (E) C 1s XPS spectra, and (F) Tauc plot of C\textsubscript{76} thin-film.

**Figure V-18** Adsorption/desorption isotherm.
voltammograms (CVs) at a scan rate of 10 mV/s shown in Figure V-19 (A). While C_{76} showed clear reversible peaks in H_{2}SO_{4} electrolyte for the oxidation and reduction processes at ~0.45 V_{SCE} (~0.69 V_{SHE}), it showed an equirectangular shape reflecting either an EDL behavior or a surface pseudocapacitive behavior in Na_{2}SO_{4} and the KOH electrolytes.\textsuperscript{22,124} Therefore, C_{76} seems to undergo redox reactions in H_{2}SO_{4} electrolyte only. The redox reaction may be attributed to the keto-enol tautomerism of the functional groups on the surface of the C_{76}, which usually occur at 0.699 V_{SHE}\textsuperscript{208} and the peak separation may be attributed to the resistance in the cell. Upon charging C_{76} in the positive potential window till 1 V, it attracts the negatively charged SO_{4}^{2-} groups and undergo the adsorption/desorption as well. Moreover, the XPS analysis of the working electrode after 20 cycles showed a negligible ratio of the deposited sulfur proving the full reversibility of the charging/discharging process. On the other hand, the CVs at different scan rates are presented in Figure V-20 (A-C), indicating the stability of C_{76} between 1-150 mV/s in the three electrolytes. As the most important feature of any charge storage device is its ability to charge and discharge, the galvanostatic charge/discharge (GCD) behavior of the material in the positive potential window in different electrolytes is presented in Figure V-19 (B). The GCDs show good Coulombic efficiency in the three electrolytes at a current density of 1 A/g. The GCD of C_{76} in H_{2}SO_{4} electrolyte showed a typical redox behavior, while in the Na_{2}SO_{4} and KOH, the GCD showed a pseudocapacitor behavior. The variation of the rate capability with scan rate and current density in the positive potential window is presented in Figure V-19 (C-D). Note that the rate capability in H_{2}SO_{4} is higher than that in both Na_{2}SO_{4} and in KOH electrolytes and that C_{76} can keep high specific capacitance values of 50.7 F/g and 25 F/g at 150 mV/s and 10 A/g, respectively. In the negative potential window, the CVs in Figure V-19 (E) and the GCDs in Figure V-19 (F) show the same behavior in all tested electrolytes. However, the potential window varied greatly between the three electrolytes. The potential window in Na_{2}SO_{4} was the widest followed by KOH and the lowest potential window was observed in H_{2}SO_{4} electrolyte. This behavior can be attributed to the different catalytic effect of the acidic and basic media on the hydrogen evolution reaction. On the
other hand, the rate capability with both scan rate and current density in the negative potential window were relatively low as presented in Figure V-19 (G-H). This can be attributed to the charge storage mechanism as can be interpreted via electrochemical impedance spectroscopy (EIS) analysis. In the EIS analysis, the x-intercept represents the electrode resistance ($R_E$) whereas the slope indicates the charging process. Generally, the $45^\circ$ linear spectrum in the low frequency regime of the Nyquist plot signifies a balanced charging process between the EDL and diffusion processes.
Figure V-19 Electrochemical characterization of C76: (A) CVs in different electrolytes in the positive potential window (scan rate = 10 mV/s), (B) GCDs in different electrolytes in positive potential window (current density= 1A/g), (C) The change of the specific capacitance with scan rate in positive potential window, (D) The change of the specific capacitance with current density in positive potential window, (E) CVs in different electrolytes in negative potential window (scan rate = 10 mV/s), (F) GCDs in different electrolytes in positive potential window (current density= 1A/g), (G) The change of the specific capacitance with scan rate in negative potential window, and (H) The change of the specific capacitance with current density in positive negative window.
The behavior of C\textsubscript{76} in the three electrolytes was investigated using EIS measurements as presented in Figure V-21 (A). Concerning the electrode resistance, the calculated resistances are in the order: H\textsubscript{2}SO\textsubscript{4} (0.98 $\Omega$) < KOH (4.59 $\Omega$) < Na\textsubscript{2}SO\textsubscript{4} (6.9 $\Omega$), which can be attributed to the differences in ionic mobility as H$^+$ ions have the highest ionic mobility while Na$^+$ ions have the least ionic mobility.\textsuperscript{250} Besides, the DFT calculations revealed the C\textsubscript{76}-H$^+$, and C\textsubscript{76}-SO\textsubscript{4}\textsuperscript{2-} have the lowest bandgaps. Note that the EIS graphs measured in H\textsubscript{2}SO\textsubscript{4} and KOH showed semicircles, indicating a relatively slow ion diffusion.
and charge transfer resistance. However, the disappeared semicircle in Na$_2$SO$_4$ electrolyte indicates fast electron transfer at the electrode/electrolyte interface. The 45° line in the low frequency region indicated the presence of the diffusion-controlled process in all three electrolytes. The supercapacitor electrode materials can store charges in three different mechanisms, the electrical double layer mechanism (EDL), the pseudocapacitance mechanism, and the battery-like mechanism. Usually charge storage in carbon materials depends greatly on the adsorption/desorption of the electrolyte ions, known as EDL mechanism. However, carbon materials have dangling bonds, and previous reports have pointed out that even carbon materials can accommodate a portion of the diffusion-controlled charge storage mechanism. Thus, the data from the CV were used to estimate the diffusion-controlled process percentage in the different carbon structures. The charge storage mechanism was explored using Randles–Sevcik’s equation. The Randles–Sevcik’s slope ($b$) was calculated from 1-10 mV/s and from 15-150 mV/s in both positive and negative potential windows as presented in Figure V-21 (B-C). In the positive potential window, the $b$ value for the H$_2$SO$_4$ and KOH electrolytes is ~0.6 while it is 0.75 for Na$_2$SO$_4$, indicating higher diffusion-controlled charge storage mechanism in the acidic and basic electrolytes than in the neutral electrolyte. However, in the negative potential window, the three electrolytes showed a surface charge storage mechanism $b$ value for the scan rates 1-10 mV/s. However, upon increasing the scan rate, the charge storage-mechanism turned into diffusion-controlled process. This surface reaction can be attributed to the intercalation of the positive H$^+$, Na$^+$, and K$^+$ ions, while with increasing scan rate, the surface intercalation cannot occur, resulting in a drop in the specific capacitance. Regarding the change in the charge storage mechanism, it was reported that with increasing scan rate, the reliability of this method fades. To further investigate the process, the Donne’s method was used. For the positive electrodes, both H$_2$SO$_4$ and KOH electrolytes showed close diffusion current percentage at 1 mV/s while the Na$_2$SO$_4$ showed a lower diffusion controlled current, in agreement with the calculated $b$ value from Randles–Sevcik’s plot. For the negative electrodes, the diffusion controlled current was much lower than that in the positive
electrode in the order $\text{H}_2\text{SO}_4 > \text{Na}_2\text{SO}_4 > \text{KOH}$, which can be attributed to the relative difficulty of the diffusion of ions due to the differences in their ionic radii. It was also observed that with increasing scan rate, the diffusion controlled current percentage decreases, in agreement with the literature. On the other hand, Trasatti’s method was used to calculate the EDL and diffusion-controlled capacitance. However, the results were not accurate due to the shift from linearity. Figure V-21 (D) summarizes the percentages of the EDL and diffusion controlled current. The binding energies calculated using the DFT can explain the obtained high diffusion-controlled current in both the positive and negative potential windows in the $\text{H}_2\text{SO}_4$ electrolyte and the positive potential window in the $\text{Na}_2\text{SO}_4$ and KOH electrolytes. On the other hand, the binding energies of $\text{C}_{76}$ with $\text{Na}^+$ and $\text{K}^+$ ions were very low allowing easy adsorption/desorption processes and EDL characteristics. Also, the high binding energy results in narrowing the bandgap energy, which may be attributed to the partial bonding formed due to the merging of the electronic clouds of $\text{C}_{76}$ and adsorbed ion. Table V-5 summarizes the obtained specific capacitance values in different electrolytes and in different potential windows. Note that $\text{C}_{76}$ can work as a positive electrode in all electrolytes, with the highest performance in $\text{H}_2\text{SO}_4$. On the other hand, it can work better in $\text{Na}_2\text{SO}_4$ electrolyte as a negative electrode. The high contribution of the $C_Q$ in the negative potential window can explain the reason behind the dominated EDL capacitance in the negative potential window. On the other hand, the very low $C_Q$ contribution in the positive potential window can explain the high diffusion controlled capacitance in the positive potential window. However, the $C_Q$ is slightly larger than the capacitance calculated experimentally, which may be attributed to the resistance of the electrolyte and the other cell parts in the experimental setup. For example, upon the use of $\text{Na}_2\text{SO}_4$ electrolyte with a potential window of -1 V, the achieved capacitance was ~346 F/g at 0.5 A/g, which is very close to the calculated $C_Q$ using DFT. The power density (P) and energy density (E) were calculated for the three-electrode system.
While the calculated energy densities at 0.5 A/g in the positive electrodes are 23.3, 15.15, and 2.86 Wh/Kg, they are 1.16, 48.14, and 6.72 Wh/Kg in the negative electrodes for the H$_2$SO$_4$, Na$_2$SO$_4$, and KOH electrolytes, respectively. On the other hand, the power density ranged between 250 W/Kg for the negative electrode in Na$_2$SO$_4$ electrolyte and 75 W/Kg for the negative electrode in H$_2$SO$_4$ electrolyte. The real device “two-electrode system” usually delivers 25% of the capacitance of the three-electrode system. Thus, it is expected that a symmetric device of C$_{76}$ can deliver energy densities of 6.11, 15.8, and 2.4 Wh/Kg at 0.5 A/g in H$_2$SO$_4$, Na$_2$SO$_4$, and KOH electrolytes, respectively.

Table V-5 Specific capacitance values for C$_{76}$ in different electrolytes.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Positive potential window (V)</th>
<th>Negative potential window (V)</th>
<th>Cs (F/g) at 1 mV/s (+Ve)</th>
<th>Cs (F/g) at 1 mV/s (-Ve)</th>
<th>Cs (F/g) at 0.5 A/g (+Ve)</th>
<th>Cs (F/g) at 0.5 A/g (-Ve)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0 to 0.9</td>
<td>0 to -1</td>
<td>171.38</td>
<td>142.51</td>
<td>134.72</td>
<td>346.63</td>
</tr>
<tr>
<td>KOH</td>
<td>0 to 0.55</td>
<td>0 to -0.65</td>
<td>119.74</td>
<td>99.52</td>
<td>68.23</td>
<td>114.60</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>0 to 1</td>
<td>0 to -0.3</td>
<td>257.60</td>
<td>108.50</td>
<td>167.75</td>
<td>93.40</td>
</tr>
</tbody>
</table>

Figure V-21 (A) Impedance spectroscopy in different electrolytes, (B) Randles–Sevcik’s slope in different electrolytes in positive potential window, (C) Randles–Sevcik’s slope in different electrolytes in negative potential window, and (D) The ratio between the EDL current and the Diffusion controlled current in different electrolytes.
5.3.4 Conclusions

Carbon additives have been used to enhance the performance of various classes of supercapacitor electrode materials. However, some carbon materials have limitations in different electrolytes and/or potential windows. Besides, the conductivity of carbon materials differs greatly with their structure. I investigated the potential of using C\textsubscript{76} as supercapacitor electrode material which showed a superior bandgap and quantum capacitance when studied by DFT. C\textsubscript{76} showed excellent capacitive characteristics in the three commonly used aqueous electrolytes; the acidic H\textsubscript{2}SO\textsubscript{4}, the basic KOH, and the neutral Na\textsubscript{2}SO\textsubscript{4}. However, the material showed different charge storage mechanisms over different potential windows. The reasons behind the different charge storage mechanisms were studied using electrochemical methods and further confirmed via DFT calculations. The results revealed that C\textsubscript{76} showed the highest performance as a positive electrode in H\textsubscript{2}SO\textsubscript{4} electrolyte in a potential window of 1 V with a capacitance of 257 F/g at 1 mV/s. However, C\textsubscript{76} showed the highest performance as both positive and negative electrode in the Na\textsubscript{2}SO\textsubscript{4} electrolyte in a potential windows of 0.9 V and -1 V with capacitance values of 171 F/g and 172 F/g in the positive and negative potential windows, respectively. The electrochemical investigation showed that the diffusion-controlled process has a profound impact on the extraordinary performance of the C\textsubscript{76} electrode. Moreover, the DFT study and quantum capacitance calculations showed the reason behind the diffusion-controlled process, the EDL process, and the observed enhancement in conductivity. I think that C\textsubscript{76} can act as the perfect carbon candidate additive to other Faradic materials and the higher fullerenes in general can open the gate for new perspective in carbon electrode materials. I am very optimistic that optimization of this system and related assemblies could lead to a breakthrough in the field.
Chapter VI: Development of Faradic-Based Electrodes

6.1 Mono-sulfide-based electrodes

6.1.1 Deciphering the EDL behavior in MoS$_2$: The interplay of Quantum Capacitance with the number of layers, Van der Waals forces, Intercalation, and Co-intercalation

Researchers exploited Li-ion electrode materials in developing supercapacitor electrodes. One of the main graphene-like structures is the transition metal dichalcogenides (TMDs) such as MoS$_2$. MoS$_2$ exists in three main phases, each phase has its unique capacitance performance.$^{123,124,177}$ The 1T-MoS$_2$ phase can offer a very high conductivity due to its metal-like behavior, however, its cycling stability is not as high as the 2H phase. On the other hand, the 2H phase can provide a stable but lower capacitance value.$^{124}$ While the 3R phase usually gives moderate stability and capacitance performance.$^{124}$ The in-depth study of the electronic structure of the three phases of the MoS$_2$ and their intercalation process can give insights on the route to develop a high performance energy storage device based on MoS$_2$ and other TMDs. Herein, for the first time, the quantum capacitance was studied for the TMDs to unravel the role of the number of layers, and the effects of VdW in the capacitance performance, and to shade the light on the origin of the capacitive behavior of the intercalation process. Also, the energetics of the thermodynamic phase transformation was computed upon the intercalation with different cations. Besides, the co-intercalation of Li$^+$/Na$^+$ was addressed to highlight the possibility of exploiting the small Li$^+$ radius and the abundance of the Na$^+$ at the same time. The study illustrated the different co-intercalation sites and their effects on enhancing the quantum capacitance. The study highlighted the enhancement in the quantum capacitance that outperformed the reported quantum capacitance of graphene and doped graphene.

6.1.1.1 Electronic Performance of pristine MoS$_2$

MoS$_2$ is a 2D material that exists in the form of S-Mo-S stacking layers. The stacking order changes the symmetry and the electronic properties of the MoS$_2$; developing unique phases. Usually there are three main phases that can be easily synthesized.$^{124}$ In this regard, It
is well-known that the 2H-MoS$_2$ phase is the most stable phase with a stacking order of AbA, BaB with a hexagonal symmetry ($D_{3h}$). While the 3R-MoS$_2$ is a metastable phase with a stacking order of AbA, CaC, BcB with a rhombohedral symmetry ($C_{3v}$). The only metallic phase is the metastable 1T-MoS$_2$ with a stacking order of AbC with a tetragonal symmetry ($D_{3d}$). Since quantum capacitance is more reliable for few layered structures and the lowest number of layers to identify the 3R phase is three layers, our study focused on the three-layered structures of the 1T, 2H, and 3R MoS$_2$. However, the one-layer, and the two-layer structures of 1T and 2H phases were studied for investigating the effect of the number of layers on the C$_Q$. The optimized structures revealed that the interlayer spacing of the 1T phase was ~6.40 Å, while it was 6.56 Å and 6.57 Å for the 2H and 3R phases, respectively, in agreement with the reported values. With respect to the interlayer spacing, the Mo-Mo distance were 3.25 Å for the 1T phase and 3.16 Å in case of the 2H and 3R phases, respectively. The resemblance between the 2H and 3R phases is due to the fact that both of them have a metal coordinate of trigonal prismatic, whereas the 1T phase has an octahedral metal coordinate. The calculated total energies of the layered structures of the three phases demonstrated that; on increasing the number of layers, the total energies tend to become more negative indicating more stable structures. In this context, it was found that the 1T phase had the lowest stability, while both 2H and 3R had almost the same total energies ($E_{Tot}$) in presence of three layers; matching literature results. The close energies between the 2H and the 3R phases indicate the stability of the 3R phase in its low dimension. Concerning the bandgaps, the results in Table VI-1 reflected the metallic nature of the 1T phase, which presented an overlapped conduction band (CB) and valence band (VB) as shown in Figure VI-1. In case of the 2H phase, the wide semiconducting bandgap decreased on increasing the number of layers. This can be attributed to the quantum confinement of the electrons as the dimensions decrease, which causes quantization of the electronic density in both the CB and VB leading to an increment in the bandgap. For the 3R phase, results showed a higher bandgap than that of the 2H phase. All the studied phases exhibited direct bandgaps due to the low number of layers in agreement with literature.
Table VI-1 The calculated energy parameters of the pristine MoS$_2$ phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th># layers</th>
<th>Bandgap (eV)</th>
<th>E$_{Tot}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1T</td>
<td>1</td>
<td>---</td>
<td>-20.93</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>---</td>
<td>-27.06</td>
</tr>
<tr>
<td></td>
<td>3</td>
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<td>-40.70</td>
</tr>
<tr>
<td>2H</td>
<td>1</td>
<td>1.64</td>
<td>-21.80</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.49</td>
<td>-28.38</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.32</td>
<td>-42.65</td>
</tr>
<tr>
<td>3R</td>
<td>3</td>
<td>1.34</td>
<td>-42.65</td>
</tr>
</tbody>
</table>

The density of states (DOS) of the pristine MoS$_2$ was calculated as presented in Figure VI-1. The position of the Fermi level (E$_F$) manifests that both 2H and 3R phases are semiconductors as expected, while 1T phase is metallic.$^{260}$ From Figure VI-1, the coincidence of the peaks and the similarity between the DOS trend for Mo atoms and for S atoms can be observed in all of the DOS plots; implying the occurrence of the hybridization of Mo-4d and S-3p orbitals. Importantly, the DOS around the E$_F$ is the most significant factor contributing to the overall C$_Q$ values. In this aspect, the 1T-MoS$_2$ excelled the other two phases in terms of the C$_Q$ performance over the whole range of the potential window as presented in Figures VI-1 (E) and (F). In Figure VI-1 (B), the DOS showed that on increasing the number of layers, the E$_F$ was shifted towards the conduction band in 1T-MoS$_2$. This effect was reflected in the resulting C$_Q$. Also, it was noticed that the three-layered structure of the 1T phase provided a C$_Q$ as high as 2080 F/g. On the other hand, the two-layered structure of the 1T phase provided a very low C$_Q$ in the negative potential window. For the C$_Q$ of 2H-MoS$_2$ presented in Figure VI-1 (D), it can be observed that on decreasing the number of layers, the C$_Q$ is more pronounced in the negative potential window since the PZC is near the valence band. The C$_Q$ of the three phases of MoS$_2$ in Figure VI-1 (F) explains the experimental superior capacitance performance of the 1T-MoS$_2$ in light of the huge contribution of the C$_Q$ to the total capacitance of the 1T-MoS$_2$. Further, the 3R-MoS$_2$ showed a slightly higher C$_Q$ than that resulted from the 2H-MoS$_2$, which agrees well with the experimental findings.$^{124}$ It is crucial to point out that the capacitance resulted from the experimental results are usually lower than those resulted from pure C$_Q$ calculations for several reasons. These reasons include the resistance in the circuit and the electrolyte, and the contribution from other reactions such as the adsorption/desorption of intercalated ions. Nevertheless, in the 2D materials, the C$_Q$ is still essential and valid to elucidate
the origin of the EDL capacitance and the possible enhancement routes. In summary, the study showed that on decreasing the number of layers in the semiconducting 2H phase, the quantum effect is more pronounced and the $C_Q$ is higher. However, for the metallic 1T phase, the effect is different, since the electronic response is not as high as the semiconductors and only a shift in the PZC occurs.

**Figure VI-1** The electronic properties of pristine MoS$_2$ (A) DOS of 1T MoS$_2$ with 1, 2, and 3 layers, (B) $C_Q$ of 1T MoS$_2$ with 1, 2, and 3 layers, (C) DOS of 2H MoS$_2$ with 1, 2, and 3 layers, (D) $C_Q$ of 2H MoS$_2$ with 1, 2, and 3 layers, (E) DOS of different phases of MoS$_2$, and (F) $C_Q$ of different phases of MoS$_2$.

MoS$_2$ is considered a Van der Waals (VdW) 2D material. Since the current research trend is directed towards the formation of VdW heterostructures between the MoS$_2$ and carbon materials, it is critical to study the effect of the accurate consideration of VdW forces on the
DOS and the $C_Q$ of the materials. The TDOS and the corresponding $C_Q$ was calculated for the three phases of the MoS$_2$ with and without the VdW-DF2 correction. In comparison with the experimental data, VdW-DF2 proved its accuracy in calculating the lattice parameters, the interlayer spacing, and the mechanical properties of the 2D materials.$^{120,262,263}$ As the absence of the VdW increased the intensity of DOS as observed in Figure VI-2, this was reflected in the $C_Q$ values calculated. As for 1T-MoS$_2$, the absence of VdW caused a high $C_Q$ in the positive potential window, which implies that the presence of VdW induced localization of the free electrons of the metallic 1T phase. In case of 2H and 3R-MoS$_2$, the absence of the VdW overestimated the bandgap and shifted the $E_F$, resulting in a higher $C_Q$ in the negative potential window. In this work, the results emphasized the importance of VdW corrections in the accurate predictions of the bandgap of the semiconductor 2H and 3R-MoS$_2$, and, hence, their conductivities.$^{264}$ In contrast, the absence of the VdW consideration may lead to an overestimation of the $C_Q$ and misleading data.

Figure VI-2 The effect of VdW forces consideration (A) DOS of 3 layers 1T MoS$_2$, (B) $C_Q$ of 3 layers 1T MoS$_2$, (C) DOS of 3 Layers 2H MoS$_2$, (D) $C_Q$ of 3 layers 2H MoS$_2$, (E) DOS of 3 layers 3R MoS$_2$, and (F) $C_Q$ of 3 layers 3R MoS$_2$. 
The alkali metal ions (Li\textsuperscript{+}, Na\textsuperscript{+}, and K\textsuperscript{+}) along with the H\textsuperscript{+} were investigated as intercalants in three phases of MoS\textsubscript{2} using ab-initio methods. The intercalants were modelled with the formula of X\textsubscript{0.17}MoS\textsubscript{2}, and were bonded to MoS\textsubscript{2} in the octahedral site (most stable binding site), where the alkali metal ions can bind to 6 sulfur atoms.\textsuperscript{118,265} The structures were optimized to reach their lowest total energies. The optimized lattice parameters and interlayer spacing is illustrated in Table VI-2 and demonstrated in Figure VI-3. The results showed that all of the alkali metal intercalants increased the interlayer spacing (d') while their effects were minor in the intralayer spacing (d). Furthermore, the alkali metal interlayer expansion in the 1T phase was lower than that in the 2H and 3R phases providing an evidence on the facile insertion of the cations in the interlayer spacing. However, the effect of H\textsuperscript{+} intercalation was completely different. It can be noticed that although H\textsuperscript{+} has a relatively small diameter, it has over expanded the interlayer spacing in the 1T phase. On the other hand, the H\textsuperscript{+} intercalation shrunk the interlayer spacing in the 2H and 3R phases. This can be attributed to the direction of the optimized S-H bond. In the 1T phase, the S-H bond prefers being perpendicular to the bonded S atom in the MoS\textsubscript{2} layer.\textsuperscript{266} Whereas, in the 2H and 3R phases, the S-H bond prefers being parallel to the Mo-S bond and did not impose any significant change in the interlayer spacing. However, the expansion in the alkali metal intercalation will not result in any bond breaking since it occurs in the VdW spacing\textsuperscript{118} and hence, it will not affect the stability through the charging/discharging process. The calculated total energy (E\textsubscript{Tot}) in Table VI-2 confirms the thermodynamic stability of the intercalated phases. Thus, the study validated that the intercalation process stabilizes all the MoS\textsubscript{2} phases. Interestingly, the 1T phase was stabilized to reach E\textsubscript{Tot} values lower than those of the pristine 2H and 3R phases. This may be attributed to the easy insertion of cations in the 1T phase of MoS\textsubscript{2} which explains why the Li intercalation is the most stable intercalation in the study in terms of E\textsubscript{Tot}. In addition, the thermodynamic stability of the intercalation process was investigated using the binding energy and the formation energy as presented in Table VI-2. For the 1T phase, all the intercalation processes
are thermodynamically stable. However, the Li⁺ possessed a very high negative binding energy value reflecting hard reversibility in comparison to K⁺ intercalation, which explains the high cycling stability of the K⁺ in the experimental work. On the other hand, this high negative binding energy promotes phase stabilization. Although H⁺ intercalation provided a negative binding energy for the 1T phase, it provided positive values for both 2H and 3R phases which express hard endothermic formation of the intercalated structures. The high negative value of binding energy in the 1T phase can be attributed to the transfer of the valence electron of the intercalant ion to the low-energy frontier orbitals of 1T-MoS₂ (4dₓ₀, 4dₓᵧ, and 4dᵧz). In case of 2H, the orbital splitting is different, where the valence electron of the intercalant occupies the high-energy orbitals (4dₓ₀ and 4dₓ²−y²). Noteworthy, the cohesive energy of all alkali metals in the study are larger than their binding energies; driving the cations to adsorb within the MoS₂ interlayer spacing. Also, the formation energy of the intercalated 2H and 3R phases are higher than their counterparts in the 1T phase pinpointing to the possible thermodynamic phase transformation from the 2H and 3R phases to the 1T phase. To provide insights on the charge transferred by the intercalated ions, the Bader analysis was used in this study. It was found that the alkali metals (Li⁺, Na⁺, and K⁺) transferred more than 0.8 |e| to the MoS₂ forming ionic bonds with 6 sulfur atoms as illustrated in Table VI-2. On the other hand, the H⁺ only transferred 0.02 |e| to the MoS₂ forming a covalent bond with one S atom. The charge transfer was confirmed with the charge density difference as depicted in Figure VI-4. From the figure, it can be observed that the charges accumulated on the S atoms, where the bonds were formed, while there is a charge depletion on the alkali metal ions. Regarding the partial charge accumulation on the H ion, this is due to the formation of covalent bond and the negligible charge transfer to the S atom.
Figure VI-3 The optimized crystal structures of the intercalated polymorph MoS$_2$.

Table VI-2 The optimized lattice parameters of the intercalated MoS$_2$ phases. (d’) is the interlayer spacing, and (d) is the intralayer spacing.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>d$_{Mo-Mo}$ (Å)</th>
<th>d’$_{Mo-Mo}$ (Å)</th>
<th>d$_{S-S}$ (Å)</th>
<th>d'$_{S-S}$ (Å)</th>
<th>a &amp; b (Å)</th>
<th>E$_{Tot}$ (eV)</th>
<th>E$_b$ (eV)</th>
<th>E$_f$ (eV)</th>
<th>q [e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1T</td>
<td>Pristine MoS$_2$</td>
<td>3.25</td>
<td>6.41</td>
<td>2.48</td>
<td>6.41</td>
<td>6.50</td>
<td>-162.80</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>H-MoS$_2$</td>
<td>3.22</td>
<td>7.32</td>
<td>2.45</td>
<td>6.58</td>
<td>6.84</td>
<td>-174.24</td>
<td>-2.17</td>
<td>-0.35</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Li-MoS$_2$</td>
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<td>6.45</td>
<td>2.56</td>
<td>6.46</td>
<td>6.77</td>
<td>-174.51</td>
<td>-5.80</td>
<td>-0.97</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>Na-MoS$_2$</td>
<td>2.81</td>
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<td>2.55</td>
<td>7.10</td>
<td>6.59</td>
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<tr>
<td></td>
<td>K-MoS$_2$</td>
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<td>2.55</td>
<td>8.14</td>
<td>6.77</td>
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<td>-3.19</td>
<td>-0.53</td>
<td>0.84</td>
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<td>3.16</td>
<td>6.81</td>
<td>2.44</td>
<td>7.51</td>
<td>6.32</td>
<td>-170.60</td>
<td>----</td>
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<td>----</td>
</tr>
<tr>
<td></td>
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<td>3.25</td>
<td>6.80</td>
<td>2.50</td>
<td>6.81</td>
<td>6.60</td>
<td>-176.09</td>
<td>0.81</td>
<td>0.15</td>
<td>0.02</td>
</tr>
<tr>
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<td>3.33</td>
<td>6.99</td>
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<td>7.75</td>
<td>6.63</td>
<td>-176.99</td>
<td>-3.14</td>
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</tr>
<tr>
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<td>2.48</td>
<td>8.21</td>
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<tr>
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<td>8.50</td>
<td>2.48</td>
<td>9.10</td>
<td>6.64</td>
<td>-172.44</td>
<td>-0.79</td>
<td>-0.13</td>
<td>0.84</td>
</tr>
<tr>
<td>3R</td>
<td>Pristine MoS$_2$</td>
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<td>6.82</td>
<td>2.44</td>
<td>6.82</td>
<td>6.33</td>
<td>-170.60</td>
<td>----</td>
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<tr>
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<td>H-MoS$_2$</td>
<td>3.49</td>
<td>6.80</td>
<td>2.47</td>
<td>6.84</td>
<td>6.60</td>
<td>-176.09</td>
<td>0.81</td>
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<td>6.63</td>
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<td>6.64</td>
<td>-172.47</td>
<td>-0.81</td>
<td>-0.13</td>
<td>0.84</td>
</tr>
</tbody>
</table>
Figure VI-4 The charge density difference distribution for the intercalated MoS$_2$ phases. (The black color represents charge accumulation, and the gray color represents the charge depletion).

The projected density of states (PDOS) of the studied intercalated MoS$_2$ phases are illustrated in Figures (V-5-V-7) in comparison to their pristine counterparts. It can be observed that the contribution of the intercalated ion is very minor towards the total density of states (TDOS) in all studied structures. However, they affected the intensity and the profile of the DOS. For the 1T phase, the H$^+$ and Li$^+$ intercalations gave close DOS profiles, while the Na$^+$ and K$^+$ had similar DOS profiles. Interestingly, the intercalation in the semiconductor phases (2H and 3R) caused a thermodynamic phase shift towards the metallic phase since the $E_F$ was shifted into the conduction band and the gap in the DOS was reduced dramatically. The intercalation process increased the $C_Q$ of the 1T phase up to 35% upon Na$^+$ intercalation. For the 2H and the 3R phases the enhancement was mainly in the positive potential window, where
the $C_Q$ reached 2.5 times the pristine counterpart in case of the Na$^+$ intercalation in the 2H phase. And the $C_Q$ was doubled in case of the K$^+$ intercalation in the 3R phase relative to the pristine case. Hence, it is expected that the Na$^+$ and K$^+$ intercalation would enhance the overall performance of the MoS$_2$ through increasing conductivity of the semiconductors and stabilizing the metastable 1T phase. The results showed the enhancement in the quantum capacitance that outperformed the reported quantum capacitance of graphene and doped graphene by more than two to three folds.$^{67,73,268}$

**Figure VI-5** (A) The PDOS of the pristine 1T-MoS$_2$ supercell, (B-E) The PDOS of the intercalated 1T MoS$_2$, and (F) The effect of intercalation on the $C_Q$ of the pristine 1T-MoS$_2$.

**Figure VI-6** (A) The PDOS of the pristine 2H-MoS$_2$ supercell, (B-E) The PDOS of the intercalated 2H MoS$_2$, and (F) The effect of intercalation on the $C_Q$ of the pristine 2H-MoS$_2$. 
6.1.1.3 Li⁺/Na⁺ co-intercalated MoS₂

Since the 2H-MoS₂ is the predominant synthesized phase, it was the focus of our further study. From the previous section it was concluded that both K⁺ and Na⁺ provided the highest C₀ enhancement to the 2H-MoS₂, however, K salts have a low solubility in comparison to its Li and Na counterparts.²⁰⁸ Besides, the Li⁺ intercalation provided the best thermodynamic stability and phase stabilization. Moreover, Li⁺ and Na⁺ have close diffusion coefficients.²⁶⁹ Thus, the co-intercalation of Na⁺/Li⁺ was accommodated to the 2H-MoS₂ to combine the advantages of both ions. As illustrated in Figure VI-8, the co-intercalation study included the three possible co-intercalation configurations, which are the horizontally-aligned similar ions (HASI), the diagonally-aligned similar ions (DASI), and the vertically-aligned similar ions (VASI). From Table VI-3, it can be observed that the interlayer spacing in the LiNa-MoS₂ (HASI) structure is not homogeneous between layers, in contrast to the two other configurations. Interestingly, the interlayer spacing of the co-intercalated configurations lies in the middle between the interlayer spacings of the 2H Li-MoS₂ and 2H Na-MoS₂; indicating a better insertion of ions. However, it was found that the LiNa-MoS₂ (HASI) structure is the most stable in terms of E_{Tot} value with a very low energy difference between the three configurations;
indicating the possibility of formation of all configurations in the experimental work. Also, all the co-intercalated structures enhanced the binding energies of Li\(^+\) and Na\(^+\) ions with the Li\(^+\) binding energy reaching \(-4.99\) eV, and Na\(^+\) binding energy reaching \(-4.98\) eV, indicating more thermodynamically stable structures. Furthermore, the formation energy of the co-intercalated structures is higher than that of the Li\(^+\) intercalation and lower than that of the Na\(^+\) intercalation indicating an enhancement in the reversibility over that of 2H Li-MoS\(_2\) and improved the stability over 2H Na-MoS\(_2\). Additionally, the charge density difference of the co-intercalated structures are illustrated in Figure VI-9 indicating charge accumulation on the S binding sites.

To quantitatively analyze the charge transfer, Bader analysis demonstrated a higher charge transfer from the Li\(^+\) than Na\(^+\), as illustrated in Table VI-3. The effect of the co-intercalation on the \(C_Q\) values of the three structures (Figure VI-10) showed enhancement in the \(C_Q\) over that of 2H Li-MoS\(_2\) reaching values close to those of 2H Na-MoS\(_2\). The \(C_Q\) of the co-intercalation configurations reached values of 3163 F/g, 3111 F/g, and 3143 F/g for LiNa-MoS\(_2\) (HASI), LiNa-MoS\(_2\) (DASI), and LiNa-MoS\(_2\) (VASI), respectively.

**Figure VI-8** The optimized structure of the co-intercalated Li\(^+\)/Na\(^+\) MoS\(_2\) cells.

**Table VI-3** The energy parameters of the co-intercalated MoS\(_2\).

| Structure       | Ion | \(d_{Mo-Mo}\) (Å) | \(E_{Tot}\) (eV) | \(E_b\) (eV) | \(E_f\) (eV) | \(q|e|\) |
|-----------------|-----|------------------|-----------------|-------------|-------------|--------|
| LiNa-MoS\(_2\) (HASI) | Li   | 6.96             | -351.3          | -4.99       | -0.40       | 0.869  |
|                 | Na   | 7.58             |                 | -4.98       |             | 0.805  |
| LiNa-MoS\(_2\) (DASI) | Li   | 7.23             | -351.1          | -4.89       | -0.39       | 0.880  |
|                 | Na   | 7.33             |                 | -4.88       |             | 0.788  |
**Figure VI-9** The charge density difference distribution for the co-intercalated 2H-MoS$_2$. (The black color represents charge accumulation, and the gray color represents the charge depletion.)

**Figure VI-10** The $C_Q$ of the co-intercalated Li$^+$/Na$^+$ MoS$_2$ structures.
6.1.1.4 Conclusions

Since MoS$_2$ exhibits a pseudocapacitive behavior upon its analysis using electrochemical methods, it was mandatory to investigate the capacitive character of the energy storage in MoS$_2$. To this end, quantum capacitance (C$_Q$) has been an instrumental tool to characterize the EDL character of the 2D materials such as graphene and doped-graphene. Herein, the C$_Q$ was used to shed light on the EDL part of the intercalation process and the effect of number of layers, VdW forces, intercalation, and co-intercalation in upgrading the overall capacitance performance for the polymorph MoS$_2$-based electrodes. The study revealed that on decreasing the number of layers, the quantum effect is more pronounced and the C$_Q$ is higher. However, for the metallic 1T phase, the effect is different since the electronic response is not as high as the semiconductors and only a shift in the PZC occurs. Also, the effect of VdW correction indicated that the absence of VdW correction overestimates the bandgap, the interlayer spacing and the C$_Q$ values. For the intercalation effect, all the alkali-metal intercalation stabilized the 1T-MoS$_2$ phase and shifted the 2H and 3R-MoS$_2$ phases towards the metallic phase. On the other hand, the H$^+$ intercalation was not thermodynamically favored and its impact on the C$_Q$ enhancement was minor in comparison to the alkali metals intercalation. Importantly, the Li$^+$ intercalation caused a more stable structure, while Na$^+$, and K$^+$ intercalations resulted in more reversible charge/discharge process with higher C$_Q$ values. For this reason, the co-intercalation of Li$^+$ and Na$^+$ was investigated in 2H-MoS$_2$; resulting in a more charge/discharge reversibility with higher C$_Q$ value than 2H Li-MoS$_2$ and more thermodynamically favorable structural formation than 2H Na-MoS$_2$. Finally, the intercalation process enhanced the quantum capacitance value to outperform the reported quantum capacitance of graphene and doped graphene. In summary, for positive electrodes, the study recommends using 2H-MoS$_2$, whereas for negative electrodes and symmetric devices, the study recommends using 1T-MoS$_2$. Also, it is recommended to use the K$^+$ intercalation for the best C$_Q$ values, and the Li$^+$/Na$^+$ co-intercalation for the best overall performance.
6.1.2 Rb intercalation extraordinarily enhances the electrochemical capacitance performance of 2D-based electrode Materials

Li has been the ideal intercalated ion in batteries and supercapacitors due to its low ionic radius and fast kinetics. Yet, Li is not abundant in the Earth’s crust, necessitating the search for alkali-metal ion alternatives that are earth-abundant. In this regard, Rb-ion intercalation seems to be very promising and worth of investigation, especially that the diffusion coefficients and motilities of alkali cations increase with increasing the atomic number. Moreover, the low electronegativity of Rb should enable stronger intercalation with 2D materials such as MoS$_2$. Further, Rb is more abundant in the Earth’s crust than Li. Besides, Rb salts such as the Rb$_2$SO$_4$ are highly soluble in water in comparison to its K counterpart. However, to the best of our knowledge, the intercalation of Rb ion in 2D materials is yet to be reported. Herein, I investigated the effect of the intercalation of Rb ion on the three main phases of MoS$_2$ as a model 2D material, demonstrating insights on their quantum capacitance, stability, and binding energy. The results revealed that Rb ion intercalation increased the quantum capacitance of the three phases, stabilized the 1T phase of MoS$_2$, and increased the conductivity of the 2H and 3R phases. It is worthy to note that the ab-initio calculations were proven to provide insights on the capacitance performance of a plethora of electrode materials and to model alkali metals intercalation.

The density functional theory (DFT) tool was used to perform geometry optimization and the total energy calculations for the three-layered structures of the three pristine MoS$_2$ phases. Although the number of the available tetrahedral binding sites are twice those of the octahedral sites, it was reported that alkali metals prefer to bind to the octahedral sites in MoS$_2$. In this study, Rb ions were inserted into the VdW interlayer spacing in the octahedral site with a concentration of Rb$_{0.17}$MoS$_2$. The structure was then re-relaxed to its minimum energy. The structure of the optimized cells is illustrated in Figure VI-11. MoS$_2$ is a layered-2D material, which exists in three main phases according to the arrangement of the S-Mo-S sandwich structure. The metallic 1T phase (AbC) can be identified using only one layered
structure, the semiconductor 2H phase (AbA, BaB) can be identified using two layered structures, while the 3R phase (AbA, CaC, BcB) should be classified using a three layered structures. For that reason, the study was unified to three layered structures as a minimum number of layers allowed for comparison and for accurate quantum capacitance calculations. The lattice parameters of the relaxed cells are presented in Table VI-4. For benchmarking, it was found that the bond length, the lattice parameters, bandgaps, and total energies for the pristine MoS$_2$ phases perfectly matched those reported in the literature$^{271,272,277,278}$, confirming the accuracy of our calculations.

Figure VI-11 Unit cells of the DFT optimized structures of pristine MoS$_2$ and Rb-intercalated MoS$_2$ phases.

Table VI-4 Structural parameters of the DFT optimized cells. $d'$ is the interlayer spacing and $d$ is the intralayer spacing.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>d$_{Mo-Mo}$ (Å)</th>
<th>d'$_{Mo-Mo}$ (Å)</th>
<th>d$_{Mo-S}$ (Å)</th>
<th>d'$_{S-S}$ (Å)</th>
<th>a &amp; b (Å)</th>
<th>a (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>$E_{\text{tot}}$ (eV)</th>
<th>$E_{\text{ad}}$ (eV)</th>
<th>$E_{F}$ (eV)</th>
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<tr>
<td>1T</td>
<td>Pristine MoS$_2$</td>
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<td>2.48</td>
<td>6.41</td>
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<td>120.00</td>
<td>-162.80</td>
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<td></td>
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<td>8.93</td>
<td>2.40</td>
<td>7.46</td>
<td>6.78</td>
<td>90.13</td>
<td>89.24</td>
<td>120.16</td>
<td>-169.44</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Pristine MoS$_2$</td>
<td>3.16</td>
<td>6.81</td>
<td>2.44</td>
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<td>6.32</td>
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<td></td>
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<td>89.98</td>
<td>119.95</td>
<td>-172.46</td>
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<tr>
<td>3R</td>
<td>Pristine MoS$_2$</td>
<td>3.16</td>
<td>6.82</td>
<td>2.44</td>
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<td>6.33</td>
<td>90.00</td>
<td>90.00</td>
<td>120.00</td>
<td>-170.60</td>
<td>-0.80</td>
<td>-0.13</td>
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<tr>
<td></td>
<td>Rb-MoS$_2$</td>
<td>3.33</td>
<td>9.97</td>
<td>2.48</td>
<td>7.50</td>
<td>6.64</td>
<td>90.24</td>
<td>89.76</td>
<td>120.00</td>
<td>-172.48</td>
<td></td>
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</tr>
</tbody>
</table>

Note that Rb intercalation resulted in an expansion of the interlayer spacing as 39.3%, 47.43%, and 46.19% for the 1T, 2H, and 3R phases, respectively. The expansion in the 1T phase is much lower than that of the 2H and 3R phases, indicating an easier insertion of Rb ion. Noteworthy to mention that this expansion is attributed to the enlargement in the VdW spacing.
not due to bond breaking, hence the material can maintain its stability over long charging
cycles. The calculated total energy of the three pristine phases reflects the metastability of
the 1T phase, which has an energy that is ~8 eV higher than that of the 2H phase. Although Rb
intercalation stabilized the energy of the three phases, surprisingly, the stabilization in the 1T
phase was very high that it reached a value equivalent to that of the pristine 2H phase. This may
be attributed to the easy insertion of the Rb atom that bonded with 6 bonds in the interlayer
spacing and stabilized the structure of the 1T phase. Additionally, Rb intercalation stabilized
the 1T phase and the other phases more than Li and Na ions. Moreover, the binding energy per
adsorbed Rb atom was calculated, where the more negative binding energy refers to a more
thermodynamically stable reaction (exothermic reaction) that favors the formation of the
intercalated structure over the decomposition of MoS$_2$ and Rb ion. It was found that Rb
intercalation into the 1T phase possesses a relatively high binding energy compared to that with
the 2H and the 3R phases, indicating a stabilization of the metastable metallic phase. This high
binding energy in the Rb-1T MoS$_2$ structure can be attributed to the different orbital splitting
in the different MoS$_2$ phases. The electrons from Rb ion can occupy the low energy partially-
filled $4d_{xy}$, $4d_{yz}$, and $4d_{xz}$ orbitals of the 1T phase instead of the high energy $4d_{x^2-y^2}$ and
$4d_{xy}$ orbitals of the 2H phase. It is also noticed that the binding energy of the Rb-1T is lower than
the cohesive energy of the Rb ion, revealing a high driving force for Rb to adsorb in the
interlayer of the 1T-MoS$_2$ phase and the high electrode stability. Importantly, Rb intercalation
exhibited a lower formation energy (per formula cell) than those reported for other alkali metals
with the same concentration. Furthermore, since the formation energy of the 1T phase is
much lower than that of the 2H and 3R phases, it is assumed that the 2H and 3R phases can be
thermodynamically transformed into the 1T phase.

The projected density of states (PDOS) for the pristine and Rb-intercalated structures
are depicted in Figure VI-12. It can be observed that the $d$ orbital of the Mo atom and the $p$
orbital of the S atoms have the major contribution towards the total density of states (TDOS).
Moreover, for the 1T phase, the intercalated Rb ion resulted in an enlargement in the overall
intensity of the DOS. However, the arrangement of the intensity of the DOS around the fermi level ($E_F$) was different. Interestingly, for the 2H and 3R phases, the intercalated Rb ion resulted in a thermodynamic phase shift from semiconducting to metallic behavior. The bandgap of the pristine 2H and 3R were 1.32 and 1.34 eV, respectively. On the other hand, after Rb intercalation, the DOS intensity increased, and the $E_F$ was shifted towards the valence DOS and the phases exhibited metallic nature with no bandgap.

The 2D dichalcogenides can store charges via intercalation/deintercalation process with adsorbed ions. In addition, the dichalcogenides as 2D materials have quantum characters that affect their overall capacitance. The capacitive behavior of the dichalcogenides can be divided into the classical EDL capacitance represented as the accumulation of charges on the surface of the material and the quantum EDL capacitance (quantum capacitance) represented as the electronic response of the working electrode material upon applying a specific voltage.\textsuperscript{7,279} To this end, the quantum capacitance ($C_Q$) can provide insights on the enhancement of the overall capacitance of the MoS$_2$ phases. The $C_Q$ was calculated using a potential window between -0.5 to 0.5 V, which is the usual potential window of MoS$_2$ capacitance in aqueous non-reactive electrolytes.\textsuperscript{26,124} One of the most important aspects in performing a high operating voltage supercapacitor device with high stability is the potential of zero charge (PZC).\textsuperscript{280} The PZC is identified as the potential at which the working electrode does not accommodate either a positive or negative charges.\textsuperscript{7} However, in $C_Q$ calculations, the $E_F$ is considered the PZC of the working electrode and it can identify the positive and negative potential windows at which the electrode can operate when the PZC is identified experimentally. Noteworthy to mention that the computational calculations of the PZC can explain the presence of capacitance at no applied voltage since working electrodes can accommodate charges if their DOS provided rich occupied states at the fermi level.\textsuperscript{281} For Rb intercalation in 1T, the $C_Q$ has significantly increased from ~2000 F/g (1T pristine) to ~2700 F/g in the working potential window. This can be attributed to the high contribution of the DOS around the PZC. On the other hand, since the 2H and 3R phases were shifted from semiconductors to metals, their $C_Q$ have changed.
dramatically. The $C_Q$ of the 2H and the 3R phases reached ~3250 F/g and 3400 F/g, respectively. Nevertheless, this enhancement was in the positive potential window only, while in the negative potential window, the superiority was for the pristine counterparts. It can be observed that the $C_Q$ resulted from Rb-intercalated MoS$_2$ is significantly higher (up to 120% increment) than the reported $C_Q$ for graphene and doped graphene.\(^{67,73,268}\)

![Figure VI-12](image)

**Figure VI-12** PDOS and related $C_Q$ for the pristine and Rb-intercalated MoS$_2$ phases. (The yellow horizontal line represents the $E_F$).

To further explore the nature of the adsorption process, the charge density difference was estimated as presented in **Figure VI-13**. It can be clearly observed that the charge is transferred from the Rb atom towards the MoS$_2$ accumulating on the S atoms, where the adsorption is taking place. Moreover, Bader analysis\(^ {282}\) was performed to qualitatively identify the amount of charge transferred in the three MoS$_2$ phases. It was found that Rb ion transfers a charge of 0.842 $|e|$, 0.846 $|e|$, and 0.844 $|e|$ to the MoS$_2$ system in the 1T, 2H, and 3R phases, respectively, proving the formation of ionic bonding.
In conclusion, Rb is an attractive alkali metal intercalant for enhancing the capacitance performance of 2D layered materials. Rb intercalation stabilizes the metastable 1T phase of MoS$_2$ without altering its metallic character. Also, Rb intercalation results in shifting the 2H and 3R semiconducting phases -thermodynamically- to the metallic 1T phase while maintaining their stability. Moreover, Rb intercalation improves the quantum capacitance that can enhance the EDL capacitance and increase the overall capacitance of the supercapacitor electrode material. This enhancement in the quantum capacitance renders Rb intercalated MoS$_2$ a better 2D candidate for supercapacitor devices than graphene and doped graphene. Finally, the charge transferred from Rb ion to the MoS$_2$ stabilizes the adsorption process and is expected to increase the stability of the electrode over high number of charging cycles.

### 6.13 Towards Cs-ion Supercapacitors: Cs Intercalation in 2D Electrode

In this regard, MoS$_2$ is considered the prototypical TMDC host material with Li ion being the prototypical intercalant for chargeable electrodes either in batteries and/or supercapacitors. However, Li$^+$ has low diffusion coefficient and was proven to exhibit low capacitance performance in comparison to K$^+$ intercalation. Consequently, a great deal of research was devoted towards Na$^+$ and K$^+$ intercalation instead of Li$^+$. However, the
performance of K\(^+\) and Na\(^+\) intercalation is hindered by the limited solubility of their salts, leading to poor electrolyte conductivity and slow charging process.\(^{14}\) Sulphate salts are well known for stabilizing the MoS\(_2\) through charging/discharging process as well as offering high potential window for supercapacitor applications.\(^{124,273}\) To this end, Cs\(_2\)SO\(_4\) salt can be a perfect candidate for Cs\(^+\) intercalation due to its superior solubility (~ 4 M/L) compared to Li\(_2\)SO\(_4\) (3.11 M/L), Na\(_2\)SO\(_4\) (1.97 M/L), K\(_2\)SO\(_4\) (0.69 M/L), and Rb\(_2\)SO\(_4\) (1.9 M/L).\(^{208}\) Furthermore, Cs\(^+\) as a high atomic number species would provide larger diffusion coefficient and higher motility.\(^{270}\) Herein, I conduct an \textit{ab-initio} approach to elucidate the opportunity of using Cs ion intercalation in MoS\(_2\) polymorph supercapacitor electrodes. It was found that Cs-intercalation stabilizes the metallic 1T phase of MoS\(_2\) and increases the conductivity of the stable 2H phase by converting it into the 1T phase. It is worth mentioning that the capacitance performance of MoS\(_2\), as a typical TMDC material, can be described in terms of intercalation (pseudocapacitance performance) and quantum capacitance (EDL performance).\(^{7,177}\) In this study, the EDL character of pristine MoS\(_2\) and Cs\(^+\)-intercalated MoS\(_2\) was investigated in the light of quantum capacitance (C\(_Q\)). The results showed enhanced EDL character of the three MoS\(_2\) phases by shifting the potential of zero charge (PZC). The C\(_Q\) of the 2H-MoS\(_2\) was increased from ~750 F/g to ~3200 F/g. Since graphene and doped graphene are the typical materials investigated for their C\(_Q\) performance, they were compared to the Cs-MoS\(_2\) and it was found that the C\(_Q\) of Cs-MoS\(_2\) is 200\% that of doped graphene.\(^{67,73,268}\)

The \textit{ab-initio} method was utilized for geometry optimization of the Cs-MoS\(_2\) structures. The optimized structures are illustrated in Figure VI-14 and the structural parameters are compared to the pristine phases in Table VI-5. The Cs was intercalated to the 1T, 2H, and 3R phases of MoS\(_2\) in the concentration of Cs\(_{0.17}\)MoS\(_2\) at the octahedral site since as is the most favoured binding site in alkali metal-MoS\(_2\) structures.\(^{118,265}\) As C\(_Q\) is related to the 2D material surfaces, it was important to study the minimum number of layers. Here, only three layers of MoS\(_2\) were used as the 3R phase can be identified by a minimum of three layers with an order of AbA, CaC, BcB. The bond lengths, lattice parameters, and bandgaps resulted from our calculations
were compared to pristine MoS$_2$ and Cs-MoS$_2$ in literature proving the accuracy of our work.$^{271,272,277,278}$

![Figure VI-14 Optimized structures of the Cs-MoS$_2$ in different phases.](image)

Cs intercalation resulted in the expansion of the interlayer spacing of MoS$_2$. The expansion in 2H was lower than that in 1T and 3R phases, revealing an easier intercalation process in 2H. Moreover, the data in Table VI-5 show that pristine 1T phase is a metastable phase as indicated by its high energy compared to the 2H and 3R phases. However, Cs intercalation stabilized the 1T-MoS$_2$ and reduced its energy dramatically to reach an energy that is equivalent to that of the pristine 2H phase. Furthermore, the binding energy of the Cs ion and the formation energy of the Cs-MoS$_2$ were calculated. It can be observed that Cs intercalation in the 1T phase resulted in a more negative binding energy than binding to the 2H and 3R phases, revealing an exothermic reaction and a more thermodynamically stable formation of Cs-1T MoS$_2$.\textsuperscript{118,122} The high stability of the Cs-1T MoS$_2$ can be attributed to the low energy partially-filled 4d$_{xy}$, 4d$_{yz}$, and 4d$_{xz}$ orbitals of the 1T phase in comparison to the high energy 4d$_{xy}$ and 4d$_{x^2-y^2}$ orbitals of the 2H phase.\textsuperscript{118} Moreover, the cohesive energy of the Cs ion is higher than the binding energy with the 1T phase\textsuperscript{267}, indicating high affinity for Cs to bind to the 1T-MoS$_2$ and hence preserving the electrode stability. Interestingly, the formation energy of the Cs-MoS$_2$ is lower than the Na$^+$ and Li$^+$ counterparts.\textsuperscript{118} Besides, the formation energy of the 1T phase is found to be much lower than that of the 2H and 3R phases, proposing the possibility that the 2H and 3R phases can be thermodynamically transformed into the 1T phase.\textsuperscript{118}
Table VI-5 Structural parameters of the DFT optimized cells. \(d'\) is the interlayer spacing, \(d\) is the intralayer spacing.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>(d_{Mo-Mo}) (Å)</th>
<th>(d'_{Mo-Mo}) (Å)</th>
<th>(d_{Mo-S}) (Å)</th>
<th>(d'_{S-S}) (Å)</th>
<th>(a &amp; b) (Å)</th>
<th>(\alpha (\degree))</th>
<th>(\beta (\degree))</th>
<th>(\gamma (\degree))</th>
<th>(E_{Tot}(eV))</th>
<th>(E_{ad}(eV))</th>
<th>(E_{F}(eV))</th>
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</thead>
<tbody>
<tr>
<td>1T</td>
<td>Pristine MoS(_2)</td>
<td>3.25</td>
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<td>2.48</td>
<td>6.41</td>
<td>6.50</td>
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<td>120.00</td>
<td>-162.80</td>
<td>-3.13</td>
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<td>90.00</td>
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<td>-170.60</td>
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Figure VI-15 PDOS of pristine and Cs-intercalated MoS\(_2\) and the corresponding quantum capacitance (\(C_Q\)).

Figure VI-15 presents the projected density of states (PDOS) of the pristine MoS\(_2\) phases and their Cs-intercalated counterparts. Note that the d orbital of the Mo atom has the major contribution towards the total DOS, while the Cs atom has very minor (negligible) contribution. However, the effect of Cs atom was clear in reformation of the DOS of the three phases. The Cs-intercalation caused an increase of the TDOS of the three phases. Moreover, the Cs intercalation resulted in a thermodynamic phase shift for the 2H and 3R phases as the
fermi level was shifted towards the valence band turning the semiconductor phases into metallic. Since the DOS reflects the quantum nature of materials, the $C_Q$ of the Cs-intercalated MoS$_2$ can be estimated from DOS as illustrated in Figure VI-15. Estimating the $C_Q$ is important in designing supercapacitor electrodes as it gives information on the electronic response of the material upon applying voltage$^{7,279}$ and affects the EDL behaviour of the electrode. In this study, the applied potential window used was -0.5 V to 0.5 V, which is the experimentally accepted potential window for MoS$_2$ in aqueous neutral electrolytes.$^{26,124}$ In $C_Q$ calculations, the fermi level is considered the potential of zero charge (PZC) at which the supercapacitor electrode does not accommodate any charges.$^7$ To this end, the computationally determined PZC reveals the capacitance at no applied voltage since rich occupied states at the fermi level can accommodate charges as reflected in their $C_Q$.$^{281}$ The Cs intercalation increases the $C_Q$ of the three phases to 2530 F/g, 3180 F/g, and 3257 F/g for the 1T, 2H, and 3R phases, respectively. The dramatic enhancement in the $C_Q$ of the 2H and 3R phases is attributed to the shift in their DOS towards the metallic nature. Moreover, the $C_Q$ enhancement was in the positive potential windows only, recommending the use of the 2H-MoS$_2$ as a positive electrode in asymmetric supercapacitor devices. The obtained $C_Q$ of Cs-MoS$_2$ is 200% greater than that reported for doped graphene.$^{67,73,268}$

**Figure VI-16** Charge density difference of the Cs-intercalated MoS$_2$. (Cyan is charge depletion and yellow is charge accumulation).

To further investigate the intercalation process, the charge density difference was calculated and illustrated in Figure VI-16. Note that the charges are accumulated in the bonds between the Cs atom and the S atom, confirming the adsorption and charge transfer between the Cs atom and MoS$_2$. The charge transfer was quantitatively investigated using Bader Charge Analysis.$^{282}$ It was found that Cs ion transfers a charge of 0.85 $|e|$, 0.86 $|e|$, and 0.86 $|e|$ to the MoS$_2$ system in the 1T, 2H, and 3R phases, respectively, revealing the formation of ionic bonding.
In Conclusion, Cs intercalation is very promising to boost the capacitance of TMDCs. For example, Cs intercalation was found to stabilize the metastable 1T-MoS$_2$ phase and enhance the conductivity of the 2H and 3R phases. Furthermore, Cs intercalation enhanced the DOS of the MoS$_2$ phases and hence their C$_Q$, allowing higher EDL contribution and overall high capacitance. The high C$_Q$ values made Cs-intercalated MoS$_2$ a better 2D material than graphene and doped graphene for supercapacitor applications. Moreover, the adsorption of Cs ion on MoS$_2$ should be stable over a large number of charging/discharging cycles as the binding energy and charge transfer indicated stable and reversible adsorption process. These findings demonstrate the potential of Cs ions intercalation to boost the performance of 2D materials for energy storage devices.
6.1.4 Untapped potential of polymorph MoS$_2$: tuned cationic intercalation for high-performance symmetric supercapacitors

Although potential window is related to the nature of the reaction or intercalation process on the surface of the electrode material, it is also limited by the electrolyte used as it might decompose under the applied voltage. For aqueous electrolytes, it is very hard to reach a potential window higher than 1.23 V due to the splitting of water. Although the use of ionic liquids may overcome the potential window limitation, they reduce the Faradic behavior of the electrode material and limit the capacitance to the EDL mechanism due to the inert large ions of the ionic liquids. In this regard, it is better to identify an aqueous electrolyte that withstands the decomposition and a material that is compatible with that electrolyte in the operating potential window. Transition metal dichalgonides such as MoS$_2$, and WS$_2$ have been the target as supercapacitor electrode materials due to their 2D layered structure that provides high surface area for EDL capacitance. Besides, the presence of empty orbitals and large interlayer structure would provide the possibility of intercalation of ions. However, dichalgonides are not conductive in all their possible structures. was studied in 1T MoS$_2$ upon changing morphology and mixing with carbon materials. Herein, I demonstrate a facile hydrothermal fabrication method of flower-shaped 2D structures of the three phases of MoS$_2$. The work sheds the light on the electrochemical performance of polymorph MoS$_2$ as supercapacitor electrode materials in the presence of different cations in the electrolyte solution. Moreover, the cheap carbon sheet substrate is used instead of the expensive Ni-foam substrate to exclude the possibility of any contribution from the substrate and to provide accurate results regarding the charge storage behavior of MoS$_2$.

6.1.4.1 Morphological characterization

The morphology of the as-synthesized MoS$_2$ phases was identified using FESEM as presented in Figure VI-17 (A-C). The FESEM images showed that all synthesized MoS$_2$ samples have flower-shaped morphology with different diameters. The1T/2H mixed MoS$_2$
sample (Figure VI-17 (A)) has the lowest diameter of the flowers (400-700 nm), while the 3R/2H mixed MoS$_2$ sample (Figure VI-17 (B)) has the largest diameter of the flowers (1-3 µm). However, their wettability (inset in Figure VI-17) shows very close contact angles for the three samples, indicating hydrophobic nature of the fabricated MoS$_2$ samples. The surface area of the fabricated MoS$_2$ samples was measured using BET isotherm (Table VI-6), indicating very close surface area. The 3R/2H MoS$_2$ sample showed the largest surface area of ~5 m$^2$/g and the 2H MoS$_2$ sample showed the smallest surface area of ~3.5 m$^2$/g. As the MoS$_2$ was shown to have a very low wettability, the surface charge was measured using the zeta potential to identify the possibility of intercalation of ions and electrosorption upon the use of those materials as electrodes in electrochemical capacitors. The surface charge of the three materials presented in Table VI-6 showed the three samples to have high negative charge on their surfaces, indicating the potential to attract positive ions for intercalation.

**Table VI-6** BET surface area and Zeta potential of the as-synthesized MoS$_2$ phases.

<table>
<thead>
<tr>
<th>Polymorph MoS$_2$</th>
<th>1T/2H-MoS$_2$</th>
<th>3R/2H-MoS$_2$</th>
<th>2H-MoS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m$^2$/g)</td>
<td>4.712</td>
<td>5.024</td>
<td>3.553</td>
</tr>
<tr>
<td>Zeta potential (mV)</td>
<td>-36.900</td>
<td>-28.000</td>
<td>-36.000</td>
</tr>
</tbody>
</table>

Figure VI-17 FESEM images of (A) 1T/2H MoS$_2$, (B) 3R/2H MoS$_2$, and (C) 2H MoS$_2$ samples. Contact angle measurements of (D) 1T/2H MoS$_2$, (E) 3R/2H MoS$_2$, and (F) 2H MoS$_2$ samples.

Figure VI-18 (A) shows the diffraction pattern of the synthesized MoS$_2$. The diffraction peaks are all broad and noisy due to the formation of nanosize domains and few layers of MoS$_2$ making it difficult to identify the exact phase of the MoS$_2$ crystals. However, the
2H MoS$_2$ showed sharper peaks than the 1T/2H MoS$_2$ and the 3R/2H MoS$_2$ counterparts. The (002) plane showed a clear peak in the three samples with $2\theta$ at 14.04° for both 2H MoS$_2$ and 3R/2H MoS$_2$ and at 13.26° for the 1T/2H MoS$_2$. The d-spacing of the (002) plane indicates an interlayer spacing between the adjacent layers of ~6.1 Å for all samples. The 2H MoS$_2$ showed diffraction peaks at 25.9°, 33.4°, 39.6°, 44.9°, and 58.3° that can be ascribed to the (004), (100), (103), (105), and (110) planes, respectively, matching the hexagonal lattice of MoS$_2$. All peaks of the 1T/2H MoS$_2$ were shifted due to the distorted lattice structure that can be attributed to the mixed 1T/2H phases. It is usually hard to differentiate experimentally between the phases of the MoS$_2$ using the XRD since the peaks usually appear in the same position or overlap, besides being noisy and broad. Therefore, the vibrational modes of the MoS$_2$ samples were characterized using the Raman spectroscopy, Figure VI-18 (B). The 1T/2H MoS$_2$ sample showed vibrations at 239 cm$^{-1}$, 281 cm$^{-1}$, and 335 cm$^{-1}$ attributed to the Raman active $J_2$, $E_{1g}$, and $J_3$ vibrations of the 1T MoS$_2$ lattice, respectively. The peaks at 407 cm$^{-1}$ and 378 cm$^{-1}$ can be attributed to the out of plane $A_{1g}$ vibration and the in-plane $E_{12g}$ vibration of the 2H MoS$_2$, respectively. For the 3R/2H MoS$_2$ and 2H MoS$_2$ samples, the Raman spectra were not distinguishable due to the similar vibration modes of the 2H MoS$_2$ phase and the 3R MoS$_2$ phase. The 3R/2H MoS$_2$ sample and the 2H MoS$_2$ sample both showed active peaks at 382 cm$^{-1}$ and 407 cm$^{-1}$ corresponding to the $E_{12g}$ and $A_{1g}$ vibration modes. The difference in Raman shift ($\Delta$) between the $E_{12g}$ and $A_{1g}$ was 29 cm$^{-1}$ for the 1T/2H MoS$_2$ and 25 cm$^{-1}$ for both 3R/2H MoS$_2$ and 2H MoS$_2$, indicating bulk thickness of the MoS$_2$ sheets for all samples. Therefore, Raman spectroscopy is a good tool to confirm the presence of the 1T phase, however, it was not very successful to identify the 3R phase.
Figure VI-18 (A) X-ray diffraction peaks and (B) Raman spectra of the studied phases of the MoS$_2$. (I: 1T/2H MoS$_2$, II: 3R/2H MoS$_2$, III: 2H MoS$_2$).

The morphology and the phases of the fabricated samples were further identified using HRTEM as presented in Figure VI-19 (A-C). The HRTEM images showed the formation of inhomogeneous structure with some parts being more crystalline than the others and the edges are not curled indicating non-defected MoS$_2$ sheets. The HR-TEM images were further analyzed using imageJ to determine the d-spacing and to identify the phases. The 1T/2H-MoS$_2$ sample (Figure VI-19 (A)) showed multi d-spacing areas indicating multi-phases of MoS$_2$. The 0.63 nm d-spacing represents the (002) plane of the 2H MoS$_2$ while the 0.31 nm and 0.42 nm represent the distances between the adjacent atoms in the 1T phase. It is observed that the distances between atoms in the 1T phase is elongated than normal (0.29 and 0.34 nm, respectively), which can be attributed to the insertion of solvent molecules between layers or intercalation of some residual atoms from the precursor used during synthesis. The selected area electron diffraction (SAED) patterns of the 1T/2H-MoS$_2$ sample was identified using the CrystBox software, based on the reported crystal structures for the three MoS$_2$ phases from the Crystallography Open Database and the Cambridge Crystallographic Data Centre. The SAED image in Figure VI-19 (A) shows that the diffraction patterns represent both the 2H and 1T planes with high accuracy. For the 3R/2H-MoS$_2$, the HR-TEM presented in Figure VI-19 (B) showed that the interlayer spacing has two main values, one is the original 0.63 nm and the other is the elongated 0.83 nm. It was observed that the interlayer spacing near the edges tend to be more elongated, which can be attributed to the adsorption and intercalation of
impurity atoms either during the synthesis or from the environment. The SAED patterns of the 3R/2H-MoS$_2$ sample, Figure VI-19 (B), showed perfect match of the 3R planes$^{300}$ of the MoS$_2$ in some areas and the 2H planes of MoS$_2$ in other areas.$^{298}$ For the 2H-MoS$_2$ sample, the interlayer spacing was homogeneous with some elongation (0.67 nm) and a mixed crystalline-amorphous part. The SAED of the 2H-MoS$_2$ sample presented in Figure VI-19 (C) showed the existence of only 2H patterns.

**Figure VI-19 HR-TEM and SAED:** (A) 1T-MoS$_2$, (B) 3R/2H-MoS$_2$, and (C) 2H-MoS$_2$.

In addition to the HRTEM, the X-ray photoelectron spectroscopy (XPS) is a very useful tool to distinguish between the 1T and 2H phases and to give insights on the ratio of the different phases or other forms of MoS$_2$.$^{102,301}$ Figure VI-20 shows the XPS spectra of the different MoS$_2$ samples. The Mo 3d peak of the 1T/2H MoS$_2$ (Figure VI-20 (A)) can be deconvoluted into four peaks. The peaks at 232.9 eV and 229.9 eV can be attributed to the 3d$_{5/2}$ and 3d$_{3/2}$ orbitals of Mo in the 2H MoS$_2$, respectively.$^{102,105,302}$ However, other two peaks with larger intensity and lower energy are observed at 228.28 eV and 231.8 eV corresponding to 3d$_{5/2}$ and 3d$_{3/2}$ orbitals of the Mo in the 1T MoS$_2$, respectively.$^{102,286,303}$ Another peak at 235.6 eV was observed corresponding to the Mo-O bond due to the presence of impurities of MoO$_3$. The analysis of the XPS peaks showed that MoO$_3$ is as low as 10% while the 1T phase is 70% of the 1T/2H MoS$_2$ sample. The S 2p peak of the 1T/2H MoS$_2$ sample can be deconvoluted into three peaks as shown in Figure VI-20 (B). The peaks at 161.25 eV and 161.42 eV can be attributed to the 2p$_{3/2}$ of the 1T MoS$_2$ and the 2p$_{3/2}$ of the 2H MoS$_2$, respectively, while the peak at 162.55 can be attributed to the 2p$_{1/2}$ of the 1T and/or the 2H MoS$_2$.$^{102,303}$ For the 3R/2H MoS$_2$ sample, Mo
3d peaks can be seen at 228.9 and 232.0 eV (Figure VI-20 (C)), while S 2p peaks were shown at 161.8 eV and 162.9 eV (Figure VI-20 (D)), which are the peaks characteristic of both 2H and 3R MoS₂ phases. However, the 2H MoS₂ sample showed another peak for the impurity MoO₃ (Figure VI-20 (E)) with a ratio less than 5%.

![Figure VI-20 XPS peaks of the MoS₂ phases: (A-B) 1T/2H MoS₂, (C-D) 3R/2H MoS₂, and (E-F) 2H MoS₂.](image)

6.1.4.2 Electrochemical performance of the polymorph MoS₂

The zeta potential measurements presented in Table VI-6 indicate negatively charged potential, suggesting high affinity of the material to intercalation with cations such as Li⁺, Na⁺, and K⁺. Consequently, the MoS₂ electrodes were tested in different electrolytes, namely Li₂SO₄,
Na$_2$SO$_4$, and K$_2$SO$_4$. For the 2H MoS$_2$, the calculated specific capacitance in different electrolytes from both cyclic voltammograms (CV) and GCD showed the same trend of Li$_2$SO$_4$ > Na$_2$SO$_4$ > K$_2$SO$_4$. This trend may be attributed to the fact that Li$^+$ ions are smaller in size, allowing them to diffuse easily into the interlayers of MoS$_2$ forming new electronic states in the band structure of MoS$_2$ due to the formation of Li$_x$MoS$_2$. The three electrolytes showed the same shape of both CVs (Figure VI-21 (A)) and GCDs (Figure VI-21 (B)), which gives insights on the charge storage mechanism. Both the shape of CVs and GCDs show that the 2H MoS$_2$ has a pseudocapacitive along with EDL capacitive behavior. The 2H MoS$_2$ showed a very high stability with retention of ≥100% in the three electrolytes after 2000 cycles (Figure VI-21 (C)), which may be attributed to the fact that the 2H MoS$_2$ phase is the most stable polymorph. Despite the high stability of the 2H MoS$_2$, it showed significantly low specific capacitance. However, to show the effect of adding the metastable 3R phase to the 2H phase, the 3R/2H MoS$_2$ was studied in the three electrolytes. The 3R/2H MoS$_2$ showed a different behavior than that of pristine 2H MoS$_2$. The 3R/2H MoS$_2$ electrode showed almost similar capacitance in K$_2$SO$_4$ and Li$_2$SO$_4$ electrolytes with partial peaks started to appear in the CV (Figure VI-21 (D)) indicating extra redox and/or diffusion process. The new behavior of the 3R/2H phase in K$_2$SO$_4$ may be attributed to the packing structure of the 3R MoS$_2$ (ABCA) that allows the intercalation of the large K$^+$ cation between its layers. Although the packing structure of the 2H MoS$_2$ (ABA) has almost the same interlayer spacing as the 3R MoS$_2$, the sulfur atoms result in a steric effect, making it difficult for the large K$^+$ cations to diffuse. The redox peaks in the CV of the 3R/2H MoS$_2$ in K$_2$SO$_4$ indicate not only the surface pseudocapacitive behavior but also electron transfer between the localized valence electrons of MoS$_2$ and that of the K$^+$ ion. On the other hand, testing the material in Na$_2$SO$_4$ electrolyte did not show any redox peaks, indicating no electron transfer process from the Na$^+$, hence lower capacitance than that obtained in K$_2$SO$_4$. The GCD of the 3R/2H MoS$_2$ electrode also showed similar capacitance upon testing in Li$_2$SO$_4$ and the K$_2$SO$_4$ electrolytes as presented in Figure VI-21 (E). However, the capacitance retention of the 3R/2H MoS$_2$ electrode increased dramatically during the first 1000 cycles then stabilized at a retention of ≥120% (Figure VI-21 (F)), this
may be attributed to the increase in the diffusion of ions to the 3R structure of MoS$_2$. This increase in capacitance may be attributed to the activation of the electrodes until all active sites are subject to the diffused cations.$^{27,177}$ As the 1T MoS$_2$ has the highest conductivity due to its metallic bandgap, the 1T/2H MoS$_2$ has been studied in the three electrolytes as well. The behavior of the 1T/2H MoS$_2$ was found to be different than those of the 2H MoS$_2$ and the 3R/2H MoS$_2$ counterparts. The 1T/2H MoS$_2$ showed a capacitance trend that depends on the electrolyte used as K$_2$SO$_4$ > Na$_2$SO$_4$ > Li$_2$SO$_4$ with only the electrodes tested in K$_2$SO$_4$ showing redox peaks in the CV scans as presented in Figure VI-21 (G). The steric effect of sulfur atoms in the packed structure of the 1T MoS$_2$ is very low, which explains the possibility of diffusion of both K$^+$ and Na$^+$ ions. However, the very low capacitance of Li$^+$ intercalation can be explained by its larger hydrated radius, low transference number, and ionic conductivity in comparison to the K$^+$ and the Na$^+$ ions.$^{308}$ The 1T/2H MoS$_2$ showed a drop in capacitance retention after the first 50 cycles then stabilized at ~72%, 50%, and 80% in the Li$_2$SO$_4$, Na$_2$SO$_4$, and K$_2$SO$_4$ electrolytes, respectively since the 1T phase is a metastable structure of the 2H MoS$_2$ and usually turn back to the stable 2H MoS$_2$ structure. The Coulombic efficiency of all MoS$_2$ phases in all electrolytes is very low but it increases to 100% after ~100 cycles due to the activation and stabilization of the diffusion and intercalation process. In general, the 2H MoS$_2$ electrode prefers the cations with small size to easily intercalate due to the steric effect of the sulfur atoms in its packing structure. However, the 3R MoS$_2$ can allow larger ions to intercalate but only reactive cations with high transference number will have an observable effect. On the other hand, the electrodes with the lowest steric structures such as 1T MoS$_2$ will allow the intercalation of larger cations with higher ionic conductivity.
Electrochemical behavior of the polymorph MoS$_2$ in different electrolytes. (A) cyclic voltammograms of the 2H MoS$_2$ at 10 mV/s, (B) GCD of the 2H MoS$_2$ at 0.5 A/g, (C) cycling stability of the 2H MoS$_2$ at 2 A/g, (D) cyclic voltammograms of the 3R/2H MoS$_2$ at 10 mV/s, (E) GCD of the 3R/2H MoS$_2$ at 0.5 A/g, (F) cycling stability of the 3R/2H MoS$_2$ at 2 A/g, (G) cyclic voltammograms of the 1T/2H MoS$_2$ at 10 mV/s, (H) GCD of the 1T/2H MoS$_2$ at 0.5 A/g, and (I) cycling stability of the 1T/2H MoS$_2$ at 2 A/g.

The rate capability is an important metric for the material to be used in advanced electronic devices. The specific capacitance was calculated from both CV and GCD data at different scan rates and current densities, respectively. For the 2H MoS$_2$ electrode (Figure VI-22 (A-B)), the highest specific capacitance is 63 F/g in the Li$_2$SO$_4$ electrolyte at 5 mV/s that is decreased to 26.6 F/g at 0.5 A/g, 9 F/g at 300 mV/s, and 1.5 F/g at 10 A/g. Although the stability of the 2H MoS$_2$ electrode increases with increasing cycling, its rate capability is very low. For the 3R/2H MoS$_2$ electrode (Figure VI-22 (D-E)), the specific capacitance in the Li$_2$SO$_4$ electrolyte is 107.5 F/g and 62.2 F/g at 5 mV/s and 0.5 A/g, respectively that were reduced to 19.8 F/g and 6.9 F/g at 300 mV/s and 10 A/g, respectively. The presence of the 3R phase enhanced the rate capability of the 2H MoS$_2$, however, the enhancement is still limited. For the 1T/2H MoS$_2$
electrode (Figure VI-22 (G-H)), the specific capacitance in K$_2$SO$_4$ electrolyte is 590.6 F/g and
193 F/g at 5 mV/s and 0.5 A/g, respectively that were reduced to 80.13 F/g and 17.22 F/g at
300 mV/s and 10 A/g, respectively. Although the rate capability of the 1T/2H MoS$_2$ is still not
very high, it is acceptable due to the high starting capacitance. To identify the charge storage
mechanism, Randles–Sevcik’s plot was constructed for MoS$_2$ in different electrolytes as
presented in Figure VI-22 (C,F,I). It was found that Randles–Sevcik’s slope is between 0.54
and 0.65, indicating a pseudocapacitive behavior with equirectangular shape of the CVs. Table VI-7 lists the recent development in the capacitance behavior of MoS$_2$ for supercapacitor
application showing that different electrolytes and different substrates can result in different
capacitance values. Our current work shows that K$_2$SO$_4$ can be a good electrolyte that can be
used to assemble 1T MoS$_2$-based supercapacitor devices.

Figure VI-22 Electrochemical behavior of the polymorph MoS$_2$ in different electrolytes (a) rate
capability of the 2H MoS$_2$ at different scan rates, (b) rate capability of the 2H MoS$_2$ at different current
densities, (c) Randles–Sevcik’s’s representation of the 2H MoS$_2$, (d) rate capability of the 3R/2H MoS$_2$
at different scan rates, (e) rate capability of the 3R/2H MoS$_2$ at different current densities, (f) Randles–Sevcik’s’s representation of the 3R/2H MoS$_2$, (g) rate capability of the 1T/2H MoS$_2$ at different
scan rates, (h) rate capability of the 1T/2H MoS$_2$ at different current densities, and (i) Randles–Sevcik’s’s representation of the 1T/2H MoS$_2$.

Table VI-7 Chosen comparative capacitance data of MoS$_2$ electrodes studied between 2017-2019.

<table>
<thead>
<tr>
<th>Material</th>
<th>Substrate</th>
<th>Potential window</th>
<th>Electrolyte</th>
<th>Specific Capacitance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammoniated 1T/2H MoS$_2$</td>
<td>Ni Foil</td>
<td>0.6 to -0.1</td>
<td>2.0 M KOH</td>
<td>346 F/g at 1 A/g</td>
<td>104</td>
</tr>
<tr>
<td>Water coupled 1T MoS$_2$</td>
<td>Glassy Carbon</td>
<td>0.2 to -1</td>
<td>0.5 M Li$_2$SO$_4$</td>
<td>380 F/g at 5 mV/s</td>
<td>310</td>
</tr>
<tr>
<td>1T/2H MoS$_2$</td>
<td>Filter Paper</td>
<td>0.8 to -0.8</td>
<td>1 M KCl</td>
<td>259 F/g at 5 mV/s</td>
<td>102</td>
</tr>
<tr>
<td>2H MoS$_2$/GNF/CNT</td>
<td>Graphite Sheet</td>
<td>0.6 to -0.6</td>
<td>1 M Na$_2$SO$_4$</td>
<td>104 F/g at 0.5 A/g</td>
<td>177</td>
</tr>
<tr>
<td>High defect density 1T MoS$_2$</td>
<td>Ni-foam</td>
<td>0.0 to 0.5</td>
<td>1 M KOH</td>
<td>379 F/g at 1 A/g</td>
<td>311</td>
</tr>
<tr>
<td>MoS$_2$ flakes</td>
<td>Carbon Papers</td>
<td>0.0 to 1.0</td>
<td>1 M H$_2$SO$_4$</td>
<td>283 F/g at 1 A/g</td>
<td>312</td>
</tr>
<tr>
<td>1T MoS$_2$</td>
<td>TiO$_2$/Ti</td>
<td>0.2 to -0.7</td>
<td>1M Na$_2$SO$_4$</td>
<td>428 F/g at 0.2 A/g</td>
<td>313</td>
</tr>
<tr>
<td>Carbon nanoparticle/MoS$_2$</td>
<td>Stainless Steel</td>
<td>0.2 to -0.8</td>
<td>1 M Na$_2$SO$_4$</td>
<td>394.2 F/g at 5 mV/s</td>
<td>314</td>
</tr>
<tr>
<td>1T MoS$_2$ hydrogel</td>
<td>Filter Paper</td>
<td>0.0 to 0.7</td>
<td>1 M H$_2$SO$_4$</td>
<td>147 F/g at 0.1 A/g</td>
<td>315</td>
</tr>
<tr>
<td>1T MoS$_2$ flowers</td>
<td>Graphite Sheet</td>
<td>0.5 to -0.4</td>
<td>0.5 M K$_2$SO$_4$</td>
<td>590 F/g at 5 mV/s</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 M Na$_2$SO$_4$</td>
<td>208 F/g at 0.5 A/g</td>
<td></td>
</tr>
</tbody>
</table>

6.1.4.3 Electrochemical performance of the symmetric device

To test the real behavior of the 1T/2H MoS$_2$ electrode in K$_2$SO$_4$ electrolyte, a symmetric device was assembled and tested. The CVs of the device presented in Figure VI-23 (A) show a stable quasi-rectangular behavior that maintained its shape up to 300 mV/s. For the charge/discharge curves at different current densities (Figure VI-23 (B)), it was found that the Coulombic efficiency is enhanced from that measured in the 3-electrode system and the GCD behavior is stable up to 10 A/g. The electrochemical impedance spectroscopy measurements were performed for the device before and after 2000 cycles, with the Nyquist plot fitted to the circuit shown in Figure VI-23 (C). It was found that the electrolyte resistance (R$_1$) increased from 2.5 Ω to 2.56 Ω after 2000 cycles, while the diffusion resistance (R$_2$) increased from 1.188 Ω to 1.659 Ω after 2000 cycles. The specific capacitance of the device was 79.4 F/g and 37.2 F/g at 5 mV/s and 0.5 A/g, respectively that was reduced to 31 F/g and 13.44 F/g at 300 mV/s and 10 A/g, respectively indicating a dramatically increase in rate capability than that obtained in the 3-electrode system as presented in Figure VI-23 (D-E). The power density and the corresponding energy density are presented in the Ragon’s plot shown in Figure VI-23 (F). The obtained energy densities are 4.18 and 1.5 Wh/Kg at power densities of 225 and 4500.
W/Kg, respectively. The stability of the device is very close to that of the 3-electrode system maintaining 82% capacitance after 1000 cycles and 72% after 2000 cycles. Figure VI-23 (G) shows the time of each 500 cycles in different color. The enhanced behavior of the device over that of the 3-electrode system may be attributed to the adjustment of the weight of the active material in both the positive and negative electrodes and due to the absence of resistance of other parts in the 3-electrode system.

**Figure VI-23** Electrochemical behavior of the 1T/2H MoS$_2$ symmetric device in K$_2$SO$_4$ electrolyte: (A) CVs at different scan rates, (B) GCDs at different current densities, (C) Nyquist plot of the electrode before and after 2000 cycles, (D) rate capability of the at different scan rates, (E) rate capability at different current densities, (F) Ragone plot of the device at different power densities, (G) stability of the device over the 2000 cycles.

### 6.1.4.4 Conclusions

High-performance supercapacitor devices are urgently needed for our modern technology. Although transition metal dichalcogenides are promising for supercapacitor applications, there have been some problems that need optimization. Herein, I demonstrated a hydrothermal method to fabricate different phases of MoS$_2$. XRD was used to prove the
presence of the 2H phase in the three MoS$_2$ samples, while Raman spectroscopy and XPS were used to identify the 1T phase of MoS$_2$. The 3R MoS$_2$ phase was proven using the SAED images of the samples. The electrochemical behavior of the three phases was studied using 3-electrode system. It was found that the 2H MoS$_2$ prefers the small sized cation intercalation due to the steric effect of the sulfur atoms in its packing structure. The 3R MoS$_2$ allows the intercalation of larger ions but only the ions with high transference number showed an observable effect. On the other hand, the lowest steric structures such as the 1T MoS$_2$ preferred the larger cations with a higher transference number and higher ionic conductivity. A symmetric device of 1T/2H MoS$_2$ was assembled and tested in K$_2$SO$_4$ electrolyte. The overall electrochemical behavior of the symmetric device was better than the 3-electrode system behavior. The device can deliver a specific capacitance of ~80 F/g at 5 mV/s, an energy density of 4.19 Wh/Kg, and a power density of 225 W/Kg, with cyclic stability of 82% after 1000 cycles.
6.1.5 Unveiling the effect of the structure of carbon material on the charge storage mechanism in MoS$_2$-based supercapacitors

Layered materials such as MoS$_2$ has the ability to intercalate with the ions in the electrolyte forming a Faradic process (diffusion) and acts as a pseudocapacitor. Unfortunately, pseudocapacitors have a limitation of losing stability over time and consequently losing one of the benefits of the supercapacitors.\textsuperscript{316} To overcome the drawbacks of the two types of materials researchers are using hybrid electrode of both carbon and MoS$_2$ together. Understanding the charge storage mechanism is the primary step to enhance the capacitance performance of the material, which can be elucidated from the relation between the applied voltage and the scan rate, the shape of the cyclic voltammogram (CV) and the discharge curves, and other electrochemical measurements such as Randles–Sevcik and Trasatti methods.\textsuperscript{24–26} Although a plethora of studies have focused on the performance of carbon/MoS$_2$ composites, the effect of the shape and amount of the carbon material on the charge storage mechanism is yet to be explored. Herein, the charge storage mechanism in 2H MoS$_2$ with and without carbon additives was explored in details. The 2H MoS$_2$ was mixed with different proportions of either 8 nm-diameter carbon nanotubes (CNTs) or graphene nanoflakes (GNFs) and the effect of the structure and content of the carbon material on the charge storage performance and mechanism in MoS$_2$ was explored in details.

6.1.5.1 Characterization of the as-fabricated MoS$_2$ and the composites

Figure VI-24 (A) shows the X-ray diffraction pattern of the as-fabricated MoS$_2$, revealing diffraction peaks at $2\theta$ of 14.25°, 33.3°, 39.7°, 58.68°, and 69°, which can be attributed to the (002), (100), (105), (110) and (201) planes, respectively. This indicates the 2H hexagonal structure of the as-fabricated MoS$_2$ (JCPDS 37-1492).\textsuperscript{317} The high intensity of the (002) peak reveals a well-crystalline layered structure along the $c$-axis with a calculated interlayer spacing of 0.62 nm, which is the ideal spacing in the MoS$_2$ hexagonal crystals.\textsuperscript{104,317} To further investigate the crystal structure of the MoS$_2$, Raman spectroscopy was performed as shown in Figure VI-24 (B). The Raman spectra showed two main peaks at 376 cm$^{-1}$ and 404
cm$^{-1}$, corresponding to the in-plane E$_{2g}^{1}$ vibration and the vertical plane A$_{1g}$ vibration that occur in the Mo-S bond of the hexagonal 2H-MoS$_2$ phase, respectively.$^{105,108}$ The composition and chemical states of the elements of the synthesized MoS$_2$ were investigated using XPS. The XPS survey of MoS$_2$ (Figure VI-24 (A)) showed a predominance of the elements Mo, S, C and O. The high resolution spectra of the O 1s (Figure VI-25 (D)) revealed a main peak at a binding energy of 531.8 eV, which can be attributed to adsorbed oxygen from air.$^{318}$ The high resolution spectra of Mo (Figure VI-25 (B)) showed two peaks at binding energies of 232.8 eV and 229.6 eV corresponding to the Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$, respectively, with a spin orbit splitting of 3.2 eV indicating Mo(IV) valence state.$^{108}$ The high resolution spectra of S (Figure VI-25 (C)) showed two peaks at binding energies of 162.46 eV and 163.63 eV corresponding to the S 2P$_{3/2}$ and S 2P$_{1/2}$, respectively, with a spin orbit splitting of 1.17 eV correspond to the S$^{2-}$ valence state.$^{108,319,320}$ The further investigation showed that the ratio between Mo and S in the sample was 1:2.28, which proves the enrich sulfur content in the sample. The XPS elemental mapping (Figure VI-25 (E-F)) showed a uniform distribution of both Mo and S atoms in the synthesized MoS$_2$.

![Figure VI-24 Characterization of MoS$_2$: (A) XRD patterns, (B) Raman spectroscopy.](image)
The morphological structure of the fabricated MoS$_2$ was investigated using HR-TEM as shown in Figure VI-26 (A,B). The HR-TEM images confirm the layered structure of the MoS$_2$ and the lattice fingers were found to be 0.26 nm (Figure VI-26 (C)), matching the d-spacing calculated from the XRD spectra. The selected area electron diffraction (SAED) patterns of the MoS$_2$ showed clear rings representing the (002), (100), (105) and (110) planes of the hexagonal MoS$_2$ structure (Figure VI-26 (C)).
Figure VI-26 (A,B) TEM images, (C) HR-TEM image, and (D) SAED patterns of the as-fabricated MoS$_2$.

The morphology of MoS$_2$/CNTs and MoS$_2$/GNF composites was investigated using FESEM. Figure VI-27 (A) reveals flower-like structure of pure MoS$_2$, with different flower sizes ranging from 1 µm to 5 µm. The FESEM image of the MoS$_2$/CNTs composite (Figure VI-27 (B)) shows the CNTs to be imbedded between the layers of the MoS$_2$ flowers, which can be ascribed to the very small diameter (8 nm) of the used CNTs. With increasing the amount of the added CNTs, the MoS$_2$ surface becomes almost completely covered with CNTs, Figure VI-28. For the MoS$_2$/GNF composite (Figure VI-27 (C)), the GNFs (1.0-2.5 µm) sandwiched the MoS$_2$ flowers. Upon reducing the ratio of the added GNF, the MoS$_2$ accumulated on the surface of the GNF and the flower shape started to deform and collapse into a ball-like shape as shown in Figure VI-28. For the MoS$_2$/CNTs/GNF composite with equal weights (Figure VI-27 (D)), both the MoS$_2$ and the impeded CNTs were sandwiched into the GNF. The BET analysis of the active materials, Table VI-8, revealed a specific area of ~7 m$^2$/g for the pure MoS$_2$, which is enormously increased with increasing the amount of CNTs to reach 180.6995 m$^2$/g for the MCNT 1:3. In contrary, the addition of GNF did not have a relatively significant effect on the
surface area of the prepared MoS$_2$/GNF composites. By measuring the contact angle for the composites, it was found that the added CNTs decreased wettability along with diffusion of ions inside the MoS$_2$ flowers while the GNFs increased the wettability along with the possibility of diffusion of ions into the MoS$_2$ flower. The insets in Figure VI-27 show the contact angles for the composites MCG, MCNT 1:1 and MGNF 1:1.

Figure VI-27 FESEM images of the studied materials: (A) MoS$_2$, (B) MCNT 1:1, (C) MGNF 1:1, and (D) MCG 1:1:1. The insets show the corresponding contact angles.
Figure VI-28 SEM images of: (A) MCG, (B-C) CNT, (D-F) GNF, (G) MCNT 1:1, (H) MCNT 1:3, (I) MCNT 3:1, (J) MGNF 1:1, (K) MGNF 1:3, (L) MGNF 3:1.

Table VI-8 Active surface area of the studied composite active materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET value (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS₂</td>
<td>6.9851</td>
</tr>
<tr>
<td>MCNT1:1</td>
<td>128.6986</td>
</tr>
<tr>
<td>MCNT1:3</td>
<td>180.6995</td>
</tr>
<tr>
<td>MCNT3:1</td>
<td>35.3578</td>
</tr>
<tr>
<td>MGNF1:1</td>
<td>4.4570</td>
</tr>
<tr>
<td>MGNF1:3</td>
<td>5.8126</td>
</tr>
<tr>
<td>MGNF3:1</td>
<td>6.0841</td>
</tr>
<tr>
<td>MCG</td>
<td>95.3127</td>
</tr>
</tbody>
</table>

6.1.5.4 Electrochemical performance of the studied materials

To investigate the electrochemical performance of the prepared composites as potential supercapacitor electrodes, the cyclic voltammograms (CV) and charge/discharge characteristics were studied using a 3-electrode system in 0.5 Na₂SO₄ electrolyte solution. Figure VI-29 shows
the CVs of the studied materials at different scan rates (from 10 mV/s to 1000 mV/s). Note that all studied materials were able to maintain the semi-rectangular shape up to 500 mV/s.

Figure VI-29 CV of the studied materials at different scan rates.
Figure VI-31 (A) compares the CVs of the studied materials at a scan rate of 100 mV/s. Note that the more the added CNTs or GNF to the MoS$_2$, the more ideal the rectangular shape appears, with the peaks starting to be more flattened. The ideal rectangular shape of the CV indicates the pure EDL capacitance charge storage mechanism, while the deviation from the rectangular shape indicates the Faradic pseudocapacitive mechanism of the charge storage.$^{22}$

The specific capacitance of the prepared materials was calculated from the CVs and depicted in Figure VI-31 (B). At a scan rate of 10 mV/s, the specific capacitance of the pure MoS$_2$ was 58.35 F/g and that of the MCG composite was 123.18 F/g. To investigate the origin of such increase in capacitance, the capacitance of MCNT and MGNF with different ratios was also calculated. The MCNT 1:3 showed a specific capacitance of 98.5 F/g, which was decreased to 90.3 F/g and 83.77 F/g for MCNT 1:1 and MCNT 3:1, respectively. On the other hand, the MGNF 1:3 showed a specific capacitance of 74.68 F/g that was decreased to 69.98 F/g and 55.33 F/g for MGNF 1:1 and MGNF 1:3, respectively. The results suggest that the CNTs may have the leading role in the increment of the charge stored in the MCG, which can be due to the large surface area of CNTs as estimated via the BET measurements. Although the calculated active surface area was larger for the CNTs composites than for the MCG, the MCG specific capacitance was larger than that of the CNTs composites. I believe the reason is that CNTs are hindering the diffusion of ions into MoS$_2$ layers. At scan rates higher than 10 mV/s, the capacitance of the MoS$_2$/CNTs composites kept the same trend, Figure VI-31 (B). On contrary, the MoS$_2$/GNF showed a reverse trend, where the MGNF 1:1 shows higher capacitance than MGNF 1:3. The charge/discharge analysis showed a similar trend to the CVs data. Figure VI-30 shows the charge/discharge plots of the prepared materials at different applied current densities (from 0.5 A/g to 10 A/g). The selected charge/discharge plots for the prepared materials at 1 A/g are presented in Figure VI-31 (C), revealing ideal behavior of the pseudocapacitive charge storage mechanism. The pseudocapacitive behavior is believed to be due to the intercalation process between the MoS$_2$ and the Na ions in the electrolyte since MoS$_2$ has empty orbitals that can intercalate with ions and the layered structure of the MoS$_2$ allow the diffusion of ions in between the layers. However, the discharge line is more flattened for the 1:3
MGNF and MCNT, indicating that the charge storage mechanism is more directed towards the ideal EDL charge storage mechanism. The calculated capacitance from the discharge curve shows a similar trend to those calculated from the CV scans. The MoS$_2$ specific capacitance was 56 F/g at 0.5 A/g and increased to 104 F/g for the MCG. Upon increasing the applied current density, the capacitance of MoS$_2$ decreased, while that of MoS$_2$/CNTs composites showed the trend MCNT 1:3 > MCNT 1:1 > MCNT 3:1. Similar to those calculated from the CV scans, the MoS$_2$/GNF composites showed a different trend such that at low applied current density, the MGNF 1:3 showed the highest capacitance value between the three tested MoS$_2$/GNF composites. However, upon increasing the applied current density, the MCNT 1:1 initially shows higher capacitance then returned back to the normal trend at very high applied current density (10 A/g). The energy density shows the same trend as the capacitance calculated from the discharge plots (Figure VI-31 (D)) with the energy density of MoS$_2$ at 0.5 A/g reaching 40.32 Wh/kg, which increased to 74.97 Wh/kg for the MCG. Figure VI-31 (E) shows the plots of the capacitance retention over 1000 cycle of charge/discharge at 1 A/g current density. The coulombic efficiency increased dramatically after the first 100 cycles and reached up to 95 % after the first 500 cycles. The retention increased above 104 % after the first 10 cycles and continued to increase until the 100th cycle due to the diffusion of ions in the pores of the materials and possible improvement of the wettability of the material over time. The retention started to decrease after the 200th cycle and stabilized between the 700th and the 800th cycle. The retention of the MoS$_2$ after 1000 cycle was 62.34 % and increased to 82.37 % for the MCNT 1:3. For the MCG, the retention reached 75.15 % after 1000 cycle with a capacitance of 61.32 F/g at 1 A/g.
Figure VI-30 Charge/discharge diagrams for the studied materials at different current densities.
Figure VI-31 (A) CV of the studied composites at 100 mV/s vs. SCE, (B) The change of specific capacitance with scan rate for the studied materials, (C) Charge/discharge curves for the studied materials at 1 A/g, (D) Change of energy density of the studied materials, (E) Retention of the studied materials, the mentioned percentage is after 1000 cycle, (F) Nyquist blot for the studied materials in frequency range (10 kHz- 100 mHz).

Electrochemical impedance spectroscopy (EIS) is a good tool to elucidate the resistance of the working electrodes and investigate the working mechanisms. Figure VI-31 (F) shows the Nyquist plots of the studied materials, revealing a small semicircle in the high frequency regime and a tilted line in the low frequency regime. The smaller the semicircle, the higher the
The conductivity of the material will be. The tilted line is due to the Warburg impedance resulted from the diffusion of Na\(^+\) ions into the MoS\(_2\) sheets.\(^{108}\) The effect of the intercalation in the MoS\(_2\) affected the ideal shape of the Nyquist plot.\(^{108}\) The Nyquist plot was fitted using the equivalent electrical circuit shown in Figure VI-31 (F), with the detailed fittings represented in the inset. The R1 represents the resistance of the solution, R2 represents the surface resistance, and W represents the Warburg impedance. Note that, at high frequency, the Warburg is small due to the low diffusion, while at low frequency, the Warburg resistance increases due to the increase of the diffusion of ions into the materials.\(^{8}\) Table VI-9 lists the fitting parameters, where R1 does not vary between the different materials. However, the Warburg impedance is lower for pure MoS\(_2\) and increases with increasing the amount of the added carbon material (CNTs or GNF).

**Table VI-9** Resistance parameters of the fitted equivalent circuit for the studied materials. R1 is the resistance of the solution, R2 the resistance of the surface, and W is the Warburg impedance.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MoS(_2)</th>
<th>MCG</th>
<th>MCNT 1:1</th>
<th>MCNT 1:3</th>
<th>MCNT 3:1</th>
<th>MGNF 1:1</th>
<th>MGNF 1:3</th>
<th>MGNF 3:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>5.858</td>
<td>4.999</td>
<td>4.944</td>
<td>4.15</td>
<td>6.858</td>
<td>3.655</td>
<td>4.979</td>
<td>5.314</td>
</tr>
<tr>
<td>R2</td>
<td>94.23</td>
<td>98.37</td>
<td>105.4</td>
<td>476.4</td>
<td>89.77</td>
<td>181.2</td>
<td>65.64</td>
<td>240.9</td>
</tr>
</tbody>
</table>

The in-depth understanding of the obtained results could be possible via the analysis of the contribution of both EDL charge storage and the diffusion intercalation charge storage to the obtained capacitance. Figure VI-32 (A) shows a schematic representation of the MCG charge storage mechanism in which the small diameter (8 nm) CNTs are surrounding the MoS\(_2\) and the large GNF are sandwiching the MoS\(_2\). This structure would result in maintaining both the large surface area (EDL capacitance) and allowing the diffusion of ions to intercalate within the layers of the MoS\(_2\). To this end, Randles−Sevcik’s relation was used to estimate the EDL contribution. All tested materials resulted in \(b\) values (the intercept of the \(\log i\) versus \(\log v\) plot) that are ~0.6, indicating the predominance of the diffusion charge storage mechanism.\(^{24,26}\) Moreover, using Trasatti’s method\(^{25}\), the total capacitance (EDL and the diffusion) was calculated. It is worth mentioning that due to the used neutral electrolyte and the high scan rate, the relations were not entirely linear.\(^{25}\) Thus, the fitting was done in the low scan rate regime.
**Figure VI-32 (B)** shows a representation of the percentage EDL capacitance and the diffusion capacitance. It can be noticed that CNTs have the highest effect on increasing the EDL contribution in the capacitance performance, which can be related to their small size that favour the EDL mechanism. However, GNFs only surround the MoS$_2$ layers and contribute their surface area to the original EDL of MoS$_2$. From the BET analysis, it was found that the GNFs did not increase the surface area of MoS$_2$ that much when added to it, this is why the GNFs did not show a significant change in the contribution of the EDL capacitance. In general, it was observed that the more contribution of EDL capacitance over the diffusion capacitance led to higher overall capacitance. The plot of $v^{-1/2}$ *versus* $i(v)/v^{1/2}$ was used to estimate the percentage of the diffusion current at different scan rates. Note that the linearity of the graph increases with increasing the amount of added carbon material, indicating a more ideal behavior and reduction in the Ohmic drop.$^{24}$ The results (**Figure VI-32 (C)**) showed that increasing the scan rate resulted in a decrease in the percentage of the diffusion current. Also, upon increasing the percentage of added carbon material, the percentage of the diffusion current is greatly reduced. However, at lower sweep voltage, the contribution of the diffusion current is almost the same irrespective of the amount of added carbon material. The contribution of the diffusion current becomes significant at high sweep voltages, which can be ascribed to the possibility that, at high sweep voltage, the ions can reach the interior of the CNTs and the GNF, increasing the participation of the EDL capacitance in the charge storage mechanism.
Figure VI-32 (A) Schematic diagram for possible charge storage in MCG, (B) the percentage of EDL capacitance and diffusion capacitance estimated from Trasatti’s method, and (C) variation of diffusion current with scan rate.

6.1.5.5 Conclusions

I demonstrate the successful fabrication of 2H MoS$_2$ and its composites with CNTs and GNFs. The capacitance of the fabricated composites was found to depend on the structure of the carbon material. The MoS$_2$/CNTs/GNFs (1:1:1) composite showed a capacitance retention of 75% after 1000 cycle at a scan rate of 10 mV/s. In-depth analysis of the origin of the charge storage mechanism was investigated. The analysis indicated that by increasing the content of the carbon material in the composite, the charge storage behavior is more directed towards the EDL charge storage mechanism. The added CNTs to MoS$_2$ increased the capacitance, the EDL capacity and reduced the percentage of diffusion current more than the added GNFs counterpart. The positive effects of CNTs were ascribed to their small diameters and large surface area. Besides, CNTs enhanced the EDL contribution more than the diffusion counterpart. On the other hand, the GNFs only surrounded the MoS$_2$ with limited surface area and without interference with the diffusion of the ions into the MoS$_2$.
6.2 Di-sulfide-based electrodes

6.2.1 3D Interconnected Binder-Free Mn-Ni-S Nanosheets for High-Performance Asymmetric Supercapacitors with Exceptional Cyclic Stability

Transition metal sulfides, such as CoS, MnS and NiS, have been widely investigated with very promising results reported.\textsuperscript{322–328} More recently, mixtures of those sulfides, such as Ni-Mn-S, have also been investigated. However, the reported fabrication methods are tedious multistep processes and non-environmental friendly. Moreover, the reason behind the higher capacitance of mixed sulfide than their individual counterparts is not well-identified and explained. One more important point is to identify a means to achieve high power density, the main advantage of supercapacitors, along with high capacitance. As the power density is directly affected by the operating potential window, identifying counter electrodes that maintain both capacitance and high power density should be one of the main targets to enable the design of high performance supercapacitor devices.\textsuperscript{329} In this contribution, I report a facile and green one-step method to fabricate disulfide materials to overcome the above mentioned limitations. Specifically, hierarchically 3D interconnected Mn-Ni-S sheets with controlled composition were grown via electrochemical co-deposition on Ni-foam.

6.2.1.1 Morphological characterization

The electrodeposition of Mn-Ni-S was performed using cyclic voltammetry by sweeping the potential from -1.2 to 0.2 V to allow Mn\textsuperscript{2+}, Ni\textsuperscript{2+}, and S\textsuperscript{2-} ions in solution to be deposited onto the Ni-foam substrate, resulting in Mn-Ni-S 3D interconnected sheet-like structure. Note that cyclic voltammetry allows the deposition of uniform film over the electrode surface, where the thickness can be controlled by limiting the number of sweeping cycles.\textsuperscript{138} The color of the Ni-foam turned yellow once the film is deposited, which is a characteristic of Mn-Ni-S. To confirm the growth of Mn-Ni-S on Ni-foam, different characterization techniques have been employed. Figure VI-33 (A) shows the XRD pattern of the fabricated electrode, all the observed diffraction peaks, demonstrate that the Mn-Ni-S composed of Cubic MnS (ICCD card no. 01-076-6011), Hexagonal NiS\textsubscript{2} (ICCD card no. 01-079-9982), and NiS (ICCD card
no. 00-003-1170). Also, there are characteristic peaks related Ni-foam substrate (ICDD card no. 04-001-0091). Therefore, the composition and surface electronic states of the as-prepared Mn-Ni-S electrodes were investigated by X-ray photoelectron spectroscopy (XPS). Figure VI-33 (B) shows the Mn 2p photoelectron spectrum, where doublet peaks of Mn 2p$^{1/2}$ and Mn 2p$^{3/2}$ were detected at 654.3 eV and 642.8 eV, respectively. Using Gaussian fitting, the overlapped Mn 2p$^{3/2}$ peak was deconvoluted into three peaks at ~642 eV, ~643.9 eV, and ~647.5 eV, which are characteristic of Mn(II), Mn(III), and Mn(IV) species,$^{330-332}$ respectively. Similarly, the coexistence of Ni(II) and Ni(III) species was evident from the deconvolution of the Ni 2p peaks (Figure VI-33 (C)), with the Ni(II) peak being more intense than Ni(III). Furthermore, intense satellite peaks (marked as Sat.) were observed, indicating that Ni(II) is the main oxidation state present.$^{333,334}$ For the XPS spectrum of Sulfur (Figure VI-33 (D)), the S 2p spectrum revealed two peaks, one satellite peak (~168.1 eV), and a main peak (~163 eV). The former peak is assigned to the surface-adsorbed oxidized sulfur species such as sulfates and hydrogen sulfates. The other overlapped main peak was deconvoluted into two peaks; S 2p$^{3/2}$ (~161.9 eV), which is assigned to metal-sulfur bonds (Mn–S bond and Ni–S bond), and S 2p$^{1/2}$ (~163.4 eV), which is attributed to sulfur ions at low coordination numbers.$^{335-337}$

![Figure VI-33 (A)](image1.png) XRD pattern for Mn-Ni-S, (B-D) HR-XPS of Mn 2p, Ni 2p, and S2p, respectively.
Figure VI-34 (A,B) shows FESEM images of the film grown on the Ni-foam substrate. Note the formation of a homogenous 3D interconnected sheets-like structure. The thickness of the grown Mn-Ni-S film is estimated to be only approximately 300 nm as shown in Figure VI-34 (C), and the sheet thickness ranged from 12 to 18 nm as shown in Figure VI-34 (D). Besides, the EDX analysis (Figure VI-34 (E)) shows the coexistence of Ni, Mn and S with no other peaks of foreign elements, indicating the successful formation of the Mn-Ni-S with high purity. The EDX mapping (Figure VI-34 (F-H)) clearly shows that Mn, Ni, and S are evenly distributed.

Figure VI-34 FESEM images of the electrodeposited Mn-Ni-S nanosheets: (A), and (B) represent top view scan at low and high magnification, respectively, (C), and (D) represent side view scan at low and high magnification, respectively (E) EDS spectrum of Mn-Ni-S, and the EDS mapping of: (F) Ni, (G) Mn, and (H) S.
6.2.1.2 Electrochemical performance of the fabricated materials

The electrochemical performance of the deposited Mn-Ni-S was compared to that of NiS, MnS and Mn-Ni-S that have been deposited under the same conditions, Figure VI-35. The electrochemical test was performed in a 3-electrode cell in 1.0 M KOH as the electrolyte with the sulfide material acting as the positive electrode. All tested electrodes showed clear redox peaks in the cyclic voltammograms, Figure VI-35 (A), which originate from the reaction between KOH and the sulfide material. The reactions can be described by the reactions below:\textsuperscript{23}:

\[ \text{NiS} + \text{OH}^{-} \rightarrow \text{NiS-OH} + \text{e}^{-} \]

\[ \text{NiS}_2 + \text{OH}^{-} \rightarrow \text{NiS}_2\text{-OH} + \text{e}^{-} \]

\[ \text{MnS} + \text{OH}^{-} \rightarrow \text{MnS-OH} + \text{e}^{-} \]

At a scan rate of 5 mV/s, the CV curve showed two peaks that are characteristic of secondary sulfides.\textsuperscript{338} While the higher current peak can be ascribed to the participation of NiS, the lower current peak can be related to the participation of the MnS. Upon increasing the scan rate to 50 mV/s (Figure VI-35 (B)), the behavior of the Mn-Ni-S maintained its behavior and the two peaks were better matching the peaks of NiS and MnS, respectively. A comparison between the specific capacitance values of the tested sulfide materials at different scan rates is presented in Figure VI-35 (C). At all scan rates, the specific capacitance of Mn-Ni-S was higher than that of both NiS and MnS. For example, the specific capacitance of Mn-Ni-S at 5 mV/s was as high as 3205 F g\textsuperscript{-1}, which is higher than that of both NiS (1829.27 F/g) and MnS (1363 F/g). The exceptionally high capacitance of the mixed sulfide electrode can be related to the synergism between the two high capacitance metal sulfides. Note that the obtained specific capacitance is higher than those reported in literature for the same composition but prepared by other methods, see Table VI-10. Although the specific capacitance of Mn-Ni-S decreases at higher scan rates, the material maintained its higher overall capacitance with a specific capacitance of 1188 F/g. As the charge and discharge characteristics of the electrodes is the
main factor to identify the good charge storage and delivery, GCD measurements were performed for the fabricated sulfide electrodes at different current densities. Figure VI-35 (D) illustrates the comparative GCD curves of the sulfide electrodes at 1.0 A/g. The GCD curves show symmetric charge and discharge behavior that resembles the typical battery-like supercapacitor behavior, which is maintained even at a higher current density of 20 A/g (Figure VI-35 (E)). The specific capacitance calculated from the GCD showed also a great enhancement upon the combination of Mn and Ni sulfides. The comparison between the specific capacitance of the fabricated sulfide electrodes is presented in Figure VI-35 (D). The specific capacitance of Mn-Ni-S at a current density of 1 A/g (2841.25 F/g) was much higher than that of NiS, MnS, and previously reported values in literature, Table VI-10. At high current density of 20 A/g, the Mn-Ni-S electrode maintained its excellent specific capacitance of 1334 F/g.

**Figure VI-35** Electrochemical performance of sulfide electrodes in a 3-electrode cell, (A) CVs of sulfide materials at a scan rate of 5 mV/s, (B) CVs of sulfide materials at 50 mV/s, (C) variation of the specific capacitance with the scan rate, (D) GCDs of sulfide materials at 1 A/g, (E) GCDs of sulfide materials at 20 A/g, and (F) variation of the specific capacitance with current density.

**Figure VI-36** (A) shows the CV curves of the Mn-Ni-S at different scan rates. Upon increasing the scan rate, the anodic peaks were shifted to higher potentials while the cathodic peaks were shifted to lower potentials. This shift in the redox peaks can be ascribed to the difference in the diffusion rate of the electrolyte (OH⁻) at high scan rate, which is not fast
enough to fulfill the electrochemical reactions at the active electrode material. The GCD curves of the Mn-Ni-S at different current densities in the potential range from 0 to 0.45 V. All GCD curves exhibited obvious voltage plateaus, indicating the Faradic-type (battery-like) capacitive behavior. The specific capacitance was calculated from each discharging curve. The calculated values of specific capacitance were 2841.25, 2328, 1860, 1608.5, 1334, 1132.5, 951, and 856.25 F/g at current densities of 1, 2, 5, 10, 20, 30, 40, and 20 A/g, respectively. The Mn-Ni-S maintained its behavior and stability over high current densities. To further investigate the charge storage behavior of the Mn-Ni-S, Randles–Sevcik’s plot \( (i = aV^b) \) is illustrated in Figure VI-36 (C), where the slope (b) indicates the predominant charge storage mechanism. While a slope of \( b=0.5 \) indicates diffusion-controlled process, a slope of \( b=1 \) indicates a surface process.\(^{23,177}\) The obtained b value for the Mn-Ni-S electrode was 0.55 and 0.62 for the cathodic and anodic peaks, respectively, which are similar to those obtained for NiS electrode. However, those values were 0.59 and 0.63 for the cathodic and anodic peaks of the MnS electrode. This indicates a predominant diffusion-controlled process of the charge storage mechanism in all sulfide electrodes, giving an insight on the origin of the observed redox peaks of the Mn-Ni-S, which can be ascribed to NiS.
Figure VI-36 Electrochemical performance of Mn-Ni-S electrode in the 3-electrode system: (A) CVs of Mn-Ni-S at different scan rates, (B) GCDs of Mn-Ni-S at different current densities, and (C) Randles–Sevcik’s plot of Mn-Ni-S electrode.

Table VI-10 Comparison of previous reports on Mn-Ni-S as an electrode material for supercapacitors with our fabricated material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Synthesis</th>
<th>Substrate</th>
<th>Electrolyte</th>
<th>Capacitance</th>
<th>Condition</th>
<th>Retention</th>
<th>No. of Cycles</th>
<th>Pot. Window, (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Mn-S</td>
<td>Electrodeposition</td>
<td>Ni-foam</td>
<td>1 M KOH</td>
<td>3205 F/g</td>
<td>5 mV/s   1A/g</td>
<td>Device (90%)</td>
<td>Device (11,000)</td>
<td>0 - 0.45</td>
<td>This work</td>
</tr>
<tr>
<td>Ni–Mn-S</td>
<td>Hydrothermal</td>
<td>Ni-foam</td>
<td>6 M KOH</td>
<td>1068 F/g, 2:1 Ni:Mn</td>
<td>1 A/g</td>
<td>90%</td>
<td>1500</td>
<td>0 - 0.55</td>
<td>339</td>
</tr>
<tr>
<td>NiS₂/MnS</td>
<td>Etching and pre-oxidation</td>
<td>Ni-foam</td>
<td>3 M KOH</td>
<td>6.7 mAh/cm²</td>
<td>2 mA/cm²</td>
<td>96.5%</td>
<td>1000</td>
<td>0 - 0.6</td>
<td>340</td>
</tr>
<tr>
<td>Ni-MnS</td>
<td>Hydrothermal</td>
<td>Ni-foam</td>
<td>6 M KOH</td>
<td>1430 F/g</td>
<td>0.5 A/g 10 A/g</td>
<td>---</td>
<td>100</td>
<td>-0.1 - 0.5</td>
<td>341</td>
</tr>
<tr>
<td>Ni-MnS</td>
<td>Self-template</td>
<td>Ni-foam</td>
<td>3 M KOH</td>
<td>1636.8 F/g</td>
<td>2 A/g</td>
<td>95.1%</td>
<td>4000</td>
<td>0 - 0.4</td>
<td>342</td>
</tr>
<tr>
<td>MnS/Ni₅Sₓ</td>
<td>Hydrothermal</td>
<td>Ni-foam</td>
<td>3 M KOH</td>
<td>1073.81 F/g</td>
<td>1 A/g</td>
<td>82.14%</td>
<td>2500</td>
<td>0 - 0.45</td>
<td>323</td>
</tr>
</tbody>
</table>
To further explore the Mn-Ni-S electrode for potential practical applications, asymmetric supercapacitor devices were assembled by combining the Mn-Ni-S as the positive electrode, Fe$_3$O$_4$-GR as the negative electrode, and a filter paper as the separator, Figure VI-37, and tested in 1.0 M KOH solution.

Figure VI-37 Schematic illustration of the assembled asymmetric supercapacitor.

The electrochemical performance of the asymmetric supercapacitor cell was investigated. Figure VI-38 (A) shows the CV scans of the Mn-Ni-S/Fe$_3$O$_4$-GR asymmetric supercapacitor at different scan rates from 5 to 50 mV/s over the potential range of 0 to 1.6 V in an aqueous 1.0 M KOH electrolyte. The redox peaks are feasible in all CV curves, indicating the Faradic-type (battery-like) behavior of the Mn-Ni-S/Fe$_3$O$_4$-GR asymmetric supercapacitor. This Faradic-type feature can also be observed in the GCD curves obtained at different current densities as shown in Figure VI-38 (B). The discharge curves exhibit a small IR drop even at high current densities, indicating a low device resistance. Additionally, the GCD profiles are perfectly symmetric, which indicates a reversible electrochemical process and high Columbic efficiency. Figure VI-38 (C) illustrates the variation of the rate capability of our fabricated device over a broad range of current densities ranged from 1 to 20 A/g. Interestingly, the specific capacitance reaches a maximum of 113.75 F/g at 1 A/g and sustains a capacitance of 47.5 F/g at a high current density of 20 A/g. This high rate capability performance can be attributed to the 3D interconnected structure of the fabricated Mn-Ni-S electrode, which is easily accessible by the electrolyte as well as the excellent charge/discharge
characteristics of the Fe$_3$O$_4$-GR negative electrode. **Figure VI-38 (D)** shows the Nyquist plot of the Mn-Ni-S//Fe$_3$O$_4$-GR device in the frequency that range of 0.01 Hz–100 kHz. Note the low charge transfer resistance in the high frequency regime indicates a facile Faradic behavior of the device. Moreover, the small intercept of the Nyquist curve indicates very low internal resistance of the asymmetric supercapacitor device. The linear part observed at low frequencies reflects the excellent capacitor characteristics.\textsuperscript{329,338} Upon evaluating the stability of the fabricated device, only 10\% capacitance decay was observed with a very high cumbic efficiency reaching 100\% after 11,000 cycles at a current density of 10 A/g, indicating the remarkable reversibility and stability of the device as shown in **Figure VI-38 (E)**. Consequently, the energy density (E) and power density (P) were calculated, based on the total weight of the positive and negative electrodes in the devices.

**Figure VI-38 (F)** shows Ragone plot (E vs. P) for the Mn-Ni-S//Fe$_3$O$_4$-GR asymmetric supercapacitor. The highest obtained energy density was 40.44 Wh kg$^{-1}$ with a power density of 0.8 kW/kg and a power density of 15.831 kW/kg at an energy density of 16.71 Wh/kg. The obtained energy and power densities of our devices are higher than most of the recently reported values for asymmetric aqueous supercapacitor devices: (MnO$_2$/graphene\textsuperscript{344} achieving an energy density of 23.2 Wh/kg at a power density of 1 kW/kg, Ni$_3$S$_2$-MWCNT//activated carbon\textsuperscript{345} achieving an energy density of 19.8 Wh/kg at a power density of 798 W/kg, NiCoS nanowires//activated carbon\textsuperscript{346} with an energy density of 25 Wh/kg at a power density of 447 W/kg, NiCo$_2$O$_4$/graphene//AC\textsuperscript{347} giving an energy density of 7.6 Wh/kg at a power density of 5600 W/kg, MnO$_2$-graphene //graphene\textsuperscript{348} with an energy density of 30.4 Wh/kg at a power density of 100 W/kg, CoO nanowire arrays – polypropylene//AC\textsuperscript{349} showing an energy density of 11.8 Wh/kg at a power density of 5500 W/kg, and Ni(OH)$_2$ free standing nanoporous film//exfoliated graphite oxide\textsuperscript{350} with an energy density of 6.9 Wh/kg at a power density of 44000 W/kg.
Finally, for practical applications, three series-connected ASC devices successfully lighted up a 3 V LEDs. Figure VI-38 (G) shows the glowing LED for 1500 s. These results indicate that the Mn-Ni-S//Fe$_3$O$_4$-GR SC has a great potential for energy storage applications.

6.2.1.3 Conclusions

In summary, 3D interconnected Mn-Ni-S nanosheets (12-18 nm thick) were synthesized by a facile one-step electrodeposition method as confirmed via FESEM imaging, EDS, and XPS analysis. The XPS analysis showed the existence of Mn(II), Mn(III), and Mn(IV) as well as Ni(II) and Ni(III). Due to the unique structure and composition of the interconnected nanosheets, Mn-Ni-S exhibited a very high specific capacitance of 2849 F/g at a current density of 1 A/g with a capacitance retention of 90% after 11,000 cycles. The asymmetric device showed a high energy density of 40.44 Wh/kg and a higher power density of 800 W/kg with 90% capacitance retention and 100% Columbic efficiency. The excellent electrochemical performance of the Mn-Ni-S nanosheets is related to its high conductivity and porosity that can allow rapid electrons/ions transport. These results highlight the promising applications of Mn-Ni-S nanosheets structure as a potential candidate for effective energy storage devices.
Figure VI-38 Electrochemical performance of the Mn-Ni-S//Fe₃O₄-RGO asymmetric supercapacitor: (A) CV curves at different scan rates ranging from 5 to 50 mV/s, (B) GCD curves at various current densities ranging from 7 to 20 A/g, (C) calculated capacitance at different current densities, (D) Nyquist plots of the device, (E) capacity retention and coulombic efficiency for 11,000 cycle at a current density of 10 A/g, (F) Ragone plot comparing the performance of our device with those reported in literature, and (G) glowing LED for 1500 s.
6.3 Tri-sulfide-based electrodes

6.3.1 Rigid Ni-foam or flexible carbon cloth? Effect of substrate on sulfide-based supercapacitor electrode

Electrodeposition is one of the most facile eco-friendly synthesis methods that can provide a fast one step electrode preparation. However, choosing the substrate for the deposition process may lead to a great change in the electrode properties. In supercapacitor application, electrodeposition was used as one of the superior synthesis methods to provide high surface area hierarchical structures. Since transition metal sulfides can provide a 2D structure with high surface area, sulfides were the target materials for the supercapacitor application. Synthesis of sulfides via the electrodeposition method have been reported to give extraordinary performance either mono sulfides or binary sulfides. On the bad side, the stability of the electrodeposited sulfides and their rate capability hindered their commercialization. On the other hand, it was noticed that the Ni-foam (Ni-F) has been extensively utilized as a substrate for the electrodeposition of sulfide supercapacitor electrode materials. Ni-F can provide a very high conductivity, a high surface area and facilitate the formation of layered sulfide structure. However, the reactivity of the Ni-F makes the results somehow suspicious. Besides, the rigidity of the Ni-F hinders many of the applications that requires flexibility in its design. Alternatives to the Ni-F may be metallic substrates or carbon based substrates. Since carbon substrates are usually more stable and inert to many reactions, carbon based substrates were used in some supercapacitor electrodes. In addition, carbon based substrates may add flexibility feature to the electrode mechanical behavior; promoting their usage in the wearable electronics arena. Unfortunately, for electrodeposition, carbon substrates are rarely used due to the low surface area. Yet, some carbon substrates could provide high surface area such as the carbon cloth (CC) that was used as a substrate and proved its excellent performance. Noteworthy to tell that research lacks the systematic comparison of the effect of the substrate on the reactivity and stability of the deposited materials that will affect the overall performance of the supercapacitor electrode. Herein, I have studied the effect of
using the flexible high surface area CC as an alternative substrate for the electrodeposition of sulfide materials vs. the Ni-F. I have electrodeposited the MnS, CoS and the NiS on both Ni-F and CC. The results revealed the high performance and stability of the CC substrated electrodes relative to Ni-F, giving a promising future for flexible wearable electronics.

Although MnS, CoS, and NiS are believed to have a low pseudocapacitive behavior in presence of KOH, they have a great capacitance performance due to their transformation to their hydroxide counterparts upon applying voltage. The three-electrode system was used to examine the electrochemical behavior of the deposited electrodes in terms of cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD). The CVs measured for the three electrodes on both Ni-F and CC gave insights on the nature of the redox reaction occurring through the electrodes as shown in Figure VI-39. Form the redox peaks of the electrodes deposited on Ni-F in Figure VI-39 (A), it can be observed that the three electrodes expressed a peak around 0.3 V vs. SCE (0.54 V vs. SHE) indicating the formation of the NiOOH redox species according to eq. VI-1. Moreover, it can be noticed that the intensity in the case of the NiS deposited electrode was higher than its MnS and CoS counterparts proving that the NiOOH redox was greater in case of the NiS. On the other hand, MnS a peak like deviation at 0.045 vs. SCE (0.286 V vs. SHE) indicating the MnO$_4^-$ species, while the CoS showed another peak at 0.057 V vs. SCE (0.298 V vs. SHE) indicating the formation of the CoOOH redox species according to eq. VI-2, and VI-3 respectively. It can be observed that at higher scan rates (Figure VI-39 (B)), the overall behavior did not change for the three electrodes. The capacitance values for the three electrodes were calculated as 1037, 1947, and 1410 F/g at 5 mV/s for the MnS, CoS, and NiS, respectively. And from Figure VI-39 (C), it can be noted that the three electrodes kept a 62, 75, and 64% of their capacitance with increasing scan rate up to 40 mV/s, respectively.

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (\text{VI}-1)
\]

\[
\text{MnO}_4^- + 4 \text{H}_2\text{O} + 5 e^- \rightleftharpoons \text{Mn(OH)}_2 + 6 \text{OH}^- \quad (\text{VI}-2)
\]
Co(OH)$_2$ + OH$^-$ ⇌ CoOOH + H$_2$O + e$^-$  \hspace{1cm} (VI-3)

Upon examining the electrodes deposited on CC in Figure VI-39 (D), it can be observed that only the NiS showed redox peaks at 0.3 V confirming that those peaks were due to the interference of Ni-F with MnS and CoS. Also, both MnS and CoS showed their original redox peaks at 0.048 vs. SCE (0.289 V vs. SHE) and at 0.1 vs. SCE (0.34 V vs. SHE), respectively. The MnS, CoS, and NiS electrodes deposited on CC gave capacitance of 706, 588, and 1066 F/g at 5 mV/s. Although the capacitance values of the CC deposited electrodes are lower than their Ni-F deposited counterparts, they accommodated higher rate capability at 40 mV/s as presented in Figure VI-39 (F). The comparison between the overall capacitance results indicated that the Ni-F increased the capacitance of the MnS and CoS remarkably, with its effect reaching the maximum with CoS. While for the NiS, the effect was minimum giving the forefront to the NiS when deposited on CC. However, this increment was at the expense of its rate capability. Figure VI-39 (G-I) shows the CV of the electrodes on Ni-F vs. CC. It can be noted that the Ni-F has increased the intensity of the peaks of CoS referring to the catalytic effect of Ni on the redox of the electrode material. While it reduced the intensity of the peak in case of NiS referring to the reduction of the reactivity of the NiS.
Electrochemical behavior of the studied sulfide electrodes: (A) CVs on Ni-F at 5 mV/s, (B) CVs on Ni-F at 40 mV/s, (C) rate capability on Ni-F, (D) CVs on CC at 5 mV/s, (E) CVs on CC at 40 mV/s, (F) rate capability on CC, (G) CV of MnS on Ni-F vs. CC at 5 mV/s, (H) CV of CoS on Ni-F vs. CC at 5 mV/s, and (I) CV of MnS on Ni-F vs. CC at 5 mV/s.

The GCDs of the deposited electrodes was studied for more understanding of the nature of the charging and discharging process of the electrodes. The behavior deduced from the GCDs resembled those resulted from the CVs. It can be observed that three electrodes gave a step in the GCD curve at ~0.2 V on Ni-F (Figure VI-40 (A-B)), while on CC, only the NiS gave this step. On the other hand, the CoS showed two steps on Ni-F substrate while only one step on CC substrate. It is worth mentioning that the MnS, did not show any steps when measured on CC (Figure VI-40 (C)). And the behavior did not change upon increasing the current density up to 20 A/g. The capacitance calculated from the GCDs on Ni-F and CC gave almost the same trend resulted from the CV calculations. Furthermore, the stability of the electrode was calculated up to 1000 cycles as presented in Figure VI-40 (E). It was unfortunate that the Ni-F interference deteriorated the stability of the electrodes significantly relative to the CC. The
MnS, CoS, and NiS experienced a retention of 92, 97, and 73% on CC, respectively, while the retention was decreased to 86, 85, and 30% on Ni-F, respectively. The high decrease in retention may be attributed to the parasitic substrate redox reaction that induced an irreversible corrosion effect on the substrate. Since the NiS has a similar redox reaction nature to the Ni-F substrate, the effect on its stability was the greatest through catalyzing the redox reaction in one direction than the other.

Figure VI-40 Electrochemical behavior of the studied sulfide electrodes (A) GCDs on Ni-F at 5 A/g, (B) GCDs on Ni-F at 20 A/g, (C) GCDs on CC at 5 A/g, (D) GCDs on CC at 20 A/g, and (E) stability of the studied sulfide electrodes on Ni-F vs. CC for 1000 cycles.

Further investigation of the charge storage mechanism was performed using Randles–Sevcik’s equation and Trasatti’s method. The Randles–Sevcik’s slope for the Ni-F deposited electrodes and the CC deposited electrodes are presented in Figure VI-41 (A and B), respectively. It can be noticed that the sulfides deposited on both Ni-F and CC presented almost the same Randles–Sevcik’s slope. From Randles–Sevcik’s, it was observed that both MnS and CoS gave current resulted from the surface EDL and/or surface redox, while the NiS offered current that has contribution from both surface and inner electrode material. However, when treating the results using Trasatti’s method, the results revealed different outcomes for MnS
and CoS (Figure VI-41 (C)). From Trasatti’s treatment, the capacitance of the NiS electrode reflected contribution from both surface (capacitive) and inner (diffusion) origin which matches its Randles–Sevcik’s slope. On the other hand, the MnS and CoS also revealed a high diffusion controlled capacitance origin despite their ~1 Randles–Sevcik’s slope. This can be attributed to origin of the current peak involved in treating Randles–Sevcik’s equation. For the NiS, there is only one sharp peak on both Ni-F and CC substrates, so, the data from Randles–Sevcik’s and Trasatti’s are matching. On the other hand, the CoS, acquired two peaks on Ni-F and one peak on CC, the peak corresponding to the CoS redox was the one adopted in the Randles–Sevcik’s treatment (highest in intensity). Therefore, it gave a ~1 Randles–Sevcik’s slope corresponding to surface redox as presented by Trasatti’s on CC substrate. While it showed a high diffusion contribution in Trasatti’s on Ni-F substrate corresponding to the parasite redox peaks in the CV used in capacitance calculation. For MnS, the redox peaks used in the Randles–Sevcik’s treatment on Ni-F are the ones corresponding to the Ni parasite reaction affected by the contribution of the MnS giving a pseudo effect on the nature of the redox reaction. While in the one used in Randles–Sevcik’s treatment on CC are the ones corresponding to the deviation in the CV curve. For the Trasatti’s treatment, the MnS gave 59% diffusion capacitance on CC, this may be attributed to the contribution of the inner reaction of the MnS that was reflected in the Randles–Sevcik’s slope of 0.9. In the overall observation, the Ni-F substrate increased the contribution of the diffusion process in the capacitance origin.

**Figure VI-41** Charge storage mechanism investigation (A) Randles–Sevcik’s plot on Ni-F, (B) Randles–Sevcik’s plot on CC, and (C) the Trasatti’s capacitance origin of the sulfide electrodes.
Finally, it can be concluded that the Ni-F enhanced the deposition of higher weight of the transition metal sulfides. Furthermore, the Ni-F substrated electrodes gave higher capacitance values than those deposited on CC. Nonetheless, the Ni-F interfered with the redox reactions of the MnS and the CoS giving parasite reactions that reduced the rate capability and the retention of the electrodes. Although Ni-F did not interfere with the redox of the deposited Ni-F, it deteriorated remarkably its stability. This may be attributed to the increased diffusion controlled capacitance that interfered with the electrode bulk. On the other hand, the CC gave a relatively high capacitance values up to 706, 588, and 1066 F/g for the MnS, CoS, and NiS, respectively. Besides, CC provided a high stability of 92, 97, and 73% after 1000 cycles for the MnS, CoS, and NiS, respectively. In summary, CC can provide a flexible wearable stable alternative to the Ni-F substrate for a successful electrodeposition of sulfide materials.
6.3.2 Facile one step synthesis of high performance wearable Ni-Mn-Co-S supercapacitor electrode

Recent researchers have noticed that the double sulfides can give even higher capacitance performance than the single sulfide electrodes. Our previous work reported an enhancement of capacitance when using Ni-Mn-S electrode that gave a 2849 F/g at 1 A/g. However, the triple sulfides also were involved in the recent researches. Herein, I have studied the carbon cloth (CC) substrate for a facile one step electrodeposition synthesis of hierarchal Ni-Mn-Co-S. The electrodeposition on stirring allowed a homogeneous deposition of the material on the CC and showed a high capacitance performance on the flexible substrate. The Ni-Mn-Co-S gave a capacitance of 1250 F/g at 5 A/g which is a high current density proving the stability and high performance of the electrode. The Ni-Mn-Co-S was used in an asymmetric device on the CC as a positive electrode and the graphene hydrogel as the negative electrode.

6.3.2.1 Material characterization

Figure VI-42 (A-D) illustrates typical low and high electron micrographs of the electrodeposited chalcogenides. Figure VI-42 (A) shows very low magnification of the Ni-Mn-Co sulfide on CC (NMCS/CC), revealing rough fibers with a uniform diameter of around 9 μm. The higher magnification images (Figure VI-42 (B-D)) indicate homogenous coverage of the entire CC substrate with a neat 3D interconnected nanosheet arrays with a thickness ranging from 15 to 20 nm. The obtained nanosheets possess high porous structure with high surface area, which are necessary characteristics to ensure high activity upon use for electrochemical energy storage. The energy dispersive X-ray (EDS) spectra reveal coexistence of C, Ni, Co, Mn, S, and O only without any other peaks for traces of impurities, indicating that the fabricated NCMS/CC is of high purity. The EDX mapping (Figure VI-42 (E-J)) confirm the homogenous distribution of the C, Ni, O, Mn, S, and Mn elements in the fabricated NMCS/CC.
Figure VI-42 FESEM images of Ni-Co-Mn-S nanosheets: (A-D) low and high magnification respectively, and EDS mapping of the elements (E) carbon, (F) Nickel, (G) Cobalt, (H) Manganese, (I) sulfur, and (J) oxygen, respectively.

To elucidate the oxidation states and chemical composition of the elements in the fabricated NMCS/CC electrodes, XPS analysis was carried out with the spectra charge-referenced to the O 1s emission line at 532 eV. Figure VI-43 (A) depicts the high-resolution XPS emission spectra of Ni 2p, revealing a doublet broad peaks corresponding to Ni 2p$^{1/2}$ and Ni 2p$^{3/2}$ that can be deconvoluted into 4 peaks at 854.35 eV & 871.4 eV (Ni$^{2+}$) and ~ 858.53 & ~ 874.3 eV (Ni$^{3+}$). Additionally, the observed intense loss (satellite) peaks can be an indication of the dominance of Ni$^{2+}$. Figure VI-43 (B) illustrates the high-resolution XPS emission
spectrum of Co 2p, which was deconvoluted into two peaks and two satellites. While the two fitted peaks at 782.1 and 798.8 eV are characteristic to Co$^{2+}$, the peaks at 779.46 and 794.95 eV correspond to Co$^{4+}$, revealing the presence of both Co$^{4+}$ and Co$^{2+}$. Similarly, Figure VI-43 (C) displays the high-resolution spectrum of Mn 2p, where the Mn 2p$^{3/2}$ peaks were deconvoluted into two peaks at ~641.84 eV and ~638.92 eV that are characteristic of Mn$^{4+}$ and Mn$^{2+}$ species, respectively. Figure VI-43 (D) displays high-resolution XPS emission spectrum of S 2p showing two peaks characteristic of metal–sulfur bonds at the S 2p$^{1/2}$ and S 2p$^{3/2}$ emission lines at 161.997 and 163.518 eV, respectively. However, the satellite peak at 167.363 eV is characteristic of the surface-adsorbed oxidized sulfur species.

Figure VI-43 High resolution XPS spectra obtained for Ni-Co-Mn-S nanosheets: (A-F) HRXPs for C 1s, Ni 2p, Co 2p, Mn 2p, S 2p and O 1s, respectively.
6.3.2.2 Electrochemical performance of the three-electrode system

The electrochemistry of the Ni-Mn-Co-S was studied using the three-electrode system. The CVs between 5 to 50 mV/s are presented in Figure VI-44 (A). It can be observed that the CVs show one clear redox peak in all scan rates indicating the presence of reversible redox reactions that can be attributed to the redox pairs of Ni$^{2+}$/Ni$^{3+}$, Mn$^{2+}$/Mn$^{3+}$, and Co$^{2+}$/Co$^{3+}$/Co$^{4+}$ that react in presence of OH$^-$ group to form the NiMnCoS-OH$^{136,137,362}$. The Ni-Mn-Co-S showed a unique capacitance value of 1976 F/g at 5 mV/s that was reduced slightly to 1713 F/g at 50 mV/s which proves the stability of the material over a wide range of scan rates. The GCDs in Figure VI-44 (B) shows a typical redox behavior as well proving the presence of the reversible reactions. The GCD test was analyzed to give a capacitance of 1284 F/g at 5 A/g and a rate capability up to 20 A/g as presented in Figure VI-44 (C) proving the stability of the material that maintained more than 66% of its capacitance at 20 A/g. The resistance of the flexible electrode was measured using the EIS as presented in Figure VI-44 (D). The Nyquist plot shows a small semicircle with low Faradic charge transfer resistance (R$_{ct}$) and a 45° line proving the small resistance in the electrode and presence of diffusion controlled process. To further investigate the charge storage mechanism in the electrode material, the CV data was used to plot the Randles–Sevcik’s equation and to provide the slope “$b$”. As presented in Figure VI-45 (A), the “$b$” value was found to be 0.87 which means that the electrode tends to be controlled by surface current instead of diffusion current.$^{24}$ However, more investigations were performed to give the percentage of the surface current and the diffusion controlled current at different scan rates. Using the more complex Randles–Sevcik’s equation,$^{24,177}$ it was found that at a scan rate of 5 mV/s, the electrode expressed 42% diffusion controlled current while this number decreased to 19% at 50 mV/s. Furthermore, the Trasatti’s method (Figure VI-45 (C-B)) was used$^{25}$ to provide the percentage of the EDL capacitance which was found to be as high as ~70% as presented in Figure VI-45 (D). The high contribution of the capacitive behavior instead of diffusion controlled process although the presence of the redox reactions can be attributed to the fact that those reactions occurred only on the surface not in
the bulk of the electrode material. Since the CV measurements started at 5 mV/s, it was hard for the electrolyte to diffuse into the bulk of the material and react on a larger scale. However, the surface reactions allowed a more reversibility and stability to the electrode material providing high rate capability over a wide range of scan rates and current densities.

![Figure VI-44](image)

**Figure VI-44** Electrochemical performance of Mn-Ni-Co-S@CC electrode in the 3-electrode system (A) CVs of Mn-Ni-Co-S at different scan rates, (B) GCDs of Mn-Ni-Co-S at different current densities, and (C) rate capability, and (D) Nyquist plot.

Besides, the porous nature of the CC allowed high surface area that provided a high capacitance instead of the presence of the surface reaction only. Our results can be compared to the most recent studies as presented in **Table VI-11**. Previous work was mainly on Ni-F which is rigid and cannot be used in flexible or wearable devices. Moreover, previous work reported their results in very low current densities which does not support the actual application in real working devices. On the other hand, our work used a low concentration of KOH electrolyte and worked on a flexible wearable substrate to give high capacitance values at high scan rate and current density.
Figure VI-45 (A) Randles–Sevcik’s plot, (B) Dependence of 1/q on \(v^{1/2}\), (C) dependence of q on \(1/v^{1/2}\), and (D) Ratio of the capacitive behavior using Trasatti’s method.

Table VI-11 Comparative presentation of capacitive performance of reported tertiary sulfides.

<table>
<thead>
<tr>
<th>Material</th>
<th>Synthesis Method</th>
<th>Substrate</th>
<th>Capacitance</th>
<th>Condition</th>
<th>Electrolyte</th>
<th>Energy density (WhKg(^{-1}))</th>
<th>Stability</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Zn-Co-S</td>
<td>Hydrothermal</td>
<td>Ni-F</td>
<td>1.11 mA h/cm(^2)</td>
<td>10 mA/cm(^2)</td>
<td>3 M KOH</td>
<td>91.7</td>
<td>88% 1000 cycles</td>
<td>135</td>
</tr>
<tr>
<td>Ni-Zn-Co-S</td>
<td>Hydrothermal</td>
<td>GO/Ni-F</td>
<td>627.7 F/g</td>
<td>0.25 A/g</td>
<td>2 M KOH</td>
<td>75.9</td>
<td>97.8% 4000 cycles</td>
<td>134</td>
</tr>
<tr>
<td>Ni-Mn-Co-S</td>
<td>Electrodeposition</td>
<td>Ni-F</td>
<td>2717 F/g</td>
<td>1 A/g</td>
<td>2 M KOH</td>
<td>94</td>
<td>80% 1000 cycles</td>
<td>136</td>
</tr>
<tr>
<td>Ni-Mn-Co-S</td>
<td>Hydrothermal</td>
<td>CNTF</td>
<td>2554 F/cm(^3)</td>
<td>1 mA/cm(^3)</td>
<td>1 M KOH</td>
<td>52.4 mW h/cm(^3)</td>
<td>92.9% 5000 cycles</td>
<td>136</td>
</tr>
<tr>
<td>Ni-Mn-Co-S</td>
<td>Self-templating</td>
<td>Ni-F</td>
<td>1360 F/g</td>
<td>1 A/g</td>
<td>3 M KOH</td>
<td>49.8</td>
<td>98.2% 6000 cycles</td>
<td>137</td>
</tr>
<tr>
<td>Ni-Mn-Co-S</td>
<td>Electrodeposition</td>
<td>CC</td>
<td>4395.27 F/g</td>
<td>5 mV/s</td>
<td>1 M KOH</td>
<td>49.55</td>
<td>86.5% 12000 cycles</td>
<td>This work</td>
</tr>
</tbody>
</table>

This work
6.3.2.3 Electrochemical performance of the device

The real time performance of the fabricated material was further investigated using the two-electrode system. The device was constructed using graphene hydrogel negative electrode and the Ni-Mn-Co-S deposited on CC positive electrode with a separator made of cellulose paper tested in 1.0 M KOH electrolyte as shown in Figure VI-46.

![Figure VI-46](image)

**Figure VI-46** A schematic illustration of the assembled Ni-Co-Mn-S//graphene hydrogel asymmetric supercapacitor device.

The CVs of the device at different scan rates was investigated as in Figure VI-47 (A) to reveal the stability of the device performance up to 100 mV/s. It can be observed that the scan has one characteristic peak at ~0.9 V reflecting the formation of the NiMnCoS in a reversible redox reaction. It worth mentioning that the small peak separation in the CVs indicate a small resistance in the device. Moreover, the semi-rectangular shape in the range of 0-0.6 V refers to the participation of the graphene hydrogel in the current generation. The small IR drop in the GCDs measured between 1-15 A/g as presented in Figure VI-47 (B) also displayed the small resistance in the system. However, the behavior of the GCD curves expressed the Faradic nature of the device. The rate capability presented in Figure VI-47 (C) showed the excellent performance of the device at different current densities. The device measured capacitance was 136 F/g at 1 A/g and decreased to 80 F/g at 15 A/g. That
extraordinary behavior can be attributed to the nature of the porous substrate and interconnected deposited sheets that maintained a great electrolyte accessibility at high current densities. Besides, the negative electrode played a major role in sustaining the high device performance. To further explore the resistance in the device, the EIS was measured in terms of Nyquist plot. The plot in Figure VI-47 (D) reveal that the resistance in the device is mainly due to small Faradic charge transfer resistance represented by the shallow semicircle in the high frequency range and the 45° line in the low frequency range. Additionally, the Ragon’s plot (sketched in Figure VI-47 (E)) gave insights on the energy density and power density of the device. It was found that the device can give up to 49.55 and 28 Wh/Kg energy density at 800 W/Kg and 10 kW/Kg power density, respectively. One extra credit given to our fabricated device was the 100% coulombic efficiency and 86.5% retention after 12,000 cycles as plotted in Figure VI-47 (F).

Figure VI-47 Electrochemical performance of the Ni-Mn-Co-S//Graphene Hydrogel device (A) CVs at different scan rates, (B) GCDs at different current densities, (C) rate capability, (D) EIS Nyquist plot, (E) Ragon’s plot, and (F) Stability and coulombic efficiency.
6.3.2.4 Conclusions

Developing an innovative charging device with high power and energy densities as well as long lasting stability is a substantial endeavor for the research community. Herein, I have developed an easily fabricated flexible device that can satisfy the needed criteria. Our study showed the opportunity to use carbon cloth (CC) as a flexible substrate for the electrodeposition of Ni-Mn-Co-S as the active material. The resulted Ni-Mn-Co-S/CC electrode has been characterized via FESEM, EDX, and XPS. Furthermore, the electrode was electrochemically tested in three-electrode system to get insights on its capacitive behavior. The material exhibited excellent characteristics with a capacitance reaching 1250 F/g at 5 A/g. The capacitance was ascribed to the surface redox reactions as confirmed by Randles–Sevcik and Trasatti methods. The stunning behavior of the electrode encouraged its application in an asymmetric device against a graphene hydrogel negative electrode. The 1.6 V device provided an energy density of 49.55 Wh/Kg with a retention of 86.5% up to 12,000 cycles in a low concentrated (1 M) KOH electrolyte. This outstanding performance makes the Ni-Mn-Co-S deposited on CC a unique candidate for the design and assembly of a long lasting high-performance flexible charge storage devices.
Chapter VII : Sustainable Supercapacitor

7.1 Recycling of Li-Ni-Mn-Co Hydroxide from spent batteries to produce high-performance supercapacitors with exceptional stability

The global market of LIBs was reported to be $30,186.8 million in 2017 and is estimated to increase to $100,433.7 million by 2025. However, despite the utility of LIBs in many applications such as cell phones, iPods, PDAs, laptops, digital cameras, and electric vehicles, the chemical composition of LIBs is problematic, especially after their expiration due to the reactive metals and organic materials used. Every battery has a limited lifetime and may be bulging, leaking or otherwise damaged or defective after repeated use.\textsuperscript{172,363} The main structure of Li-ion batteries contains graphite or graphene as the anode, Li oxide for cathode, lithium salts dissolved in organic solvents as an electrolyte, and a separator from polyethylene (PE) or polypropylene (PP). LIBs are very dangerous if not disposed properly and can seriously cause damages to the human health and the environment.\textsuperscript{187,364,365} Some essential metals used in LIBs like lithium, cobalt, and graphite are extracted in few countries with limited quantities.\textsuperscript{366} Therefore, it is extremely essential to develop a plethora of recycling methods of the active components of LIBs for reuse in various applications. Moreover, although previous reports showed the reasonable capacitance of the reused metals, they were tested only in 3-electrode cells and not in real 2-electrode devices, making it questionable whether the recovered materials can be reused in constructing new devices. Herein, I demonstrate a simple, but optimized, protocol to recycle lithium ion batteries (LIBs) to recover complex Li-Ni-Mn-Co nanostructured films by one-pot electrodeposition method as confirmed via FESEM, EDX, XRD and XPS analyses. For real life application, asymmetric supercapacitor devices were constructed comprising the recycled Li-Ni-Mn-Co as the positive electrode and graphene as the negative electrode.
7.1.1 Morphological characterization

Figure VII-1 (A and B) shows the FESEM images of the electrodeposited films on Ni-foam as recovered from Li-ion battery, revealing the formation of nanoflowers-like structure. Figure VII-1 (C) shows the cross-sectional view, indicating the thickness of the film to be ca. 850 nm. Note that the CV deposition yields a uniform film thickness over the electrode surface, which can be controlled by limiting the number of sweeping cycles and potential limits. However, the chronoamperometric technique results in a non-uniform structure (islands) with significant aggregation as shown in Figure VII-2. The EDX analysis of the deposited material, Figure VII-1 (D), reveals an elemental ratio of 0.27: 0.16: 0.001: 0.46 for the elements Co: Ni: Mn: O, which is compatible with the inductively-coupled plasma (ICP) results listed in Table VII-1. Note that Co is the predominant component in the deposited films. This was also confirmed via EDS mapping, indicating a homogeneous distribution of the corresponding Co, Ni, Mn, and O elements as shown in Figure VII-3.

![FESEM images of the electrodeposited material](image)

Figure VII-1 FESEM images of the electrodeposited material: (A, B) top-view image at low and high magnification, (C) cross-sectional view of the deposited films, and (D) EDX spectrum of the fabricated material. Scale bars are 1 µm and 300 nm for (A) and (B), respectively.
Figure VII-2 FESEM images of the electrodeposited material using two different deposition techniques: (A) Cyclic voltammetry, and (B) Chronoamperometry.

Figure VII-3 EDX mapping of O, Mn, Co, and Ni for the fabricated material.

Table VII-1 ICP-OES analysis of the recovered solution from spent Li-ion battery.

<table>
<thead>
<tr>
<th>Metal</th>
<th>C (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>990</td>
</tr>
<tr>
<td>Li</td>
<td>57</td>
</tr>
<tr>
<td>Ni</td>
<td>0.2</td>
</tr>
<tr>
<td>Mn</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Figure VII-4 (A) shows the x-ray diffraction (XRD) pattern of the electrodeposited films, revealing characteristic peaks at 44.65°, 51.96°, and 76.45°, which are related to (111),
(200), and (220) of the Ni-foam substrate (ICDD: 04-001-0091). Note the absence of any peaks related to hydroxide-based materials, indicating the amorphous nature of the fabricated Li-Ni-Mn-Co films. Therefore, the composition and surface electronic states of the as-prepared Li-Ni-Mn-Co films were investigated by X-ray photoelectron spectroscopy (XPS). Figure VII-4 (C) shows the Mn 2p photoelectron spectrum, where doublet peaks of Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ were detected at 645 and 642.8 eV, respectively. Using Gaussian fitting, the overlapped Mn 2p$_{3/2}$ peak was deconvoluted into two peaks at 640.16 and 645.15 eV corresponding to Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$, respectively, indicating the co-existence of Mn (III) and Mn (IV) species in the form of Mn(OH)$_2$. Similarly, the coexistence of Ni (II) and Ni (III) species was evident from the deconvolution of the Ni 2p peaks (Figure VII-4 (B)) with the Ni (II) peak being more intense than Ni (III). Furthermore, intense satellite peaks (marked as Sat.) were observed, indicating that Ni (II) is the predominant oxidation state. The Co 2p spectrum (Figure VII-4 (D)) can be deconvoluted into two spin-orbit doublets and two shake-up satellite peaks. Whereas the spin-orbit peaks appear at binding energies of 780.6 and 795.8 eV, the satellite peaks appear at 784.9 and 804.5 eV, corresponding to Co (II) species, being attributed to Co (OH)$_2$ species. Figure VII-4 (E) shows the XPS spectrum of Li, revealing the existence of Li–OH and Li–O bonds at 59.96 and 66.7 eV, respectively. Finally, Figure VII-4 (F) shows the O 1s spectrum, indicating a main peak centered at a binding energy of 530.52 eV and another secondary peak at 532.08 eV, which can be assigned to bound hydroxide groups (OH$^-$) ascribed to the formation of M–OH species (M: Li, Ni, Mn, or Co). Hence, XPS analysis confirms the successful formation of Li-Ni-Mn-Co mixed hydroxide.
Figure VII-4 (A) XRD pattern of the deposited film on Ni-foam, and (B-F) HR-XPS of Co 2p, Mn 2p, Ni 2p, Li 1s, and O 1s, respectively.

7.1.2 Electrochemical behavior

The electrochemical behavior of the recycled materials was investigated using cyclic voltammetry (CV) and the constant current charge-discharge (CCCD) measurements. Figure VII-5 (A) shows the obtained CVs at different scan rates (5-50 mV s\(^{-1}\)), indicating battery-like charge storage mechanism as evident from the well-separated oxidation and reduction peaks. To confirm the charge storage behavior of our recycled material, Randles–Sevcik’s plot was demonstrated as shown in Figure VII-5 (B) according to the relation \( i = a v^{b} \), where \( i \) is the current, \( v \) is the scan rate, and \( b \) is the slope. The slope was found to be \( \sim 0.5 \), revealing diffusion-controlled process as supported by the redox peaks shown in the CV scans.
Therefore, the electrochemical measurements indicate a battery-like behavior, which can be ascribed by a Faradic process in terms of redox reactions and diffusion of ions. Figure VII-5 (C) depicts the GCD graphs at different current densities (1-4 A/g), showing nonlinear curves of potential versus time, which confirm the battery-like behavior of the recycled material.

Figure VII-5 (D) shows a high specific capacitance ~ 951 F/g (Specific capacity 523.5 C/g) at 1.0 A/g. Figure VII-5 (E) shows the recorded Nyquist plot for the 3-electrode system in the frequency range 0.01 Hz to 100,000 Hz at open circuit potential (OCP) to investigate the charge storage behavior of the fabricated electrodes. The Nyquist plot exhibits a noticeable semicircle in the high frequency region related to charge transfer resistance resulting from electrolyte and a linear line in the low frequency region related to diffusion resistance. Note that the fabricated electrodes show a retention capacitance of ~ 84% even after 2000 cycles of charge/discharge as shown in Figure VII-5 (F). To confirm that the Ni-foam has no contribution to the performance of the recycled material, bare Ni-foam was tested under the same conditions and the current was almost nil compared to the Ni-foam that contains the recycled material. This also was confirmed via EDX analysis, which shows no oxidation of the Ni-foam as shown in Figure VII-6. Our work demonstrates an outstanding performance of recycled Li-ion battery materials as presented in Table VII-2, especially that it was possible to recover more than one metal using a very simple method. Moreover, it was possible to achieve an outstanding performance in low electrolyte concentration compared to those reported in literature as listed in Table VII-2.
Figure VII-5 (A) Cyclic voltammetry for 3-electrode system at different scan rates, (B) Randles--Sevcik’s plot of recycled material, (C) GCD at different current densities, (D) Cs vs. current density, (E) Nyquist plot of 3-electrode system, and (F) stability of 3-electrode system.

Figure VII-6 (A) CV of bare Ni-foam and Co-Li-Ni-Mn hydroxide/ Ni-foam electrodes, and (B) EDX of the tested bare Ni-foam in KOH.
Table VII-2 A comparative capacitance behavior of the recovered Li-ion battery materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>3- electrode system</th>
<th>2- electrode system</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Ni-Co-Mn hydroxides</td>
<td>1 M KOH</td>
<td>1 A/g</td>
<td>951</td>
</tr>
<tr>
<td>LiCoO₂</td>
<td>2 M KOH</td>
<td>1 A/g</td>
<td>754</td>
</tr>
<tr>
<td>CoS</td>
<td>2 M KOH</td>
<td>1 A/g</td>
<td>409.3</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>5 M KOH</td>
<td>0.5 A/g</td>
<td>143</td>
</tr>
<tr>
<td>RGO</td>
<td></td>
<td>0.5 A/g</td>
<td>112</td>
</tr>
<tr>
<td>Mn-Co carbonate</td>
<td>6 M KOH</td>
<td>0.5 A/g</td>
<td>121</td>
</tr>
<tr>
<td>CuFe₂O₄</td>
<td>1 M KOH</td>
<td>10 mV/s</td>
<td>2.4</td>
</tr>
</tbody>
</table>

To test the functionality of the recycled material, an asymmetric supercapacitor device was constructed and tested. The device is comprised of graphene as the negative electrode, the recycled material (Co-Li-Ni-Mn -OH) as the positive electrode, and a filter paper as a separator between the two electrodes tested in 1.0 M KOH solution as the electrolyte. Based on the CV scans of the 3-electrode system, the potential window for the negative and positive electrodes were chosen to ensure the stability of the electrochemical device, see Figure VII-7 (A). According to the cyclic voltammograms, the negative electrode is potentially stable from -1.05 to 0 V while the positive electrode shows a stability in the potential window from -0.1 to 0.45 V. Therefore, the potential window of the device can be as high as 1.5 V. In an asymmetric supercapacitor, the capacity of each electrode can settle the cell voltage. As a result, it is necessary to establish a balance between the charges of the positive and the negative electrodes with the maximum capacitance to get the most suitable voltage. Since the positive and negative potential windows are usually identified from the CV scans of the electrodes, the masses can be easily established, the typical mass loading of the asymmetric supercapacitor of 3.2 mg/cm².

The capacitance performance of the device can be demonstrated through the CVs at different scan rates (5, 10, 20, 30, 40, and 50 mV/s) as shown in Figure VII-7 (B and C). The device shows perfect electrochemical stability within the potential window 0 - 1.5 V. Moreover, the quasi-rectangular CV shape reveals a prominent Faradic /capacitive behavior of the system.
The GCD analysis was carried out at different current densities (0.5, 1, 2, 3, 4, 5, and 6 A/g) in the same potential window (0 - 1.5 V). Figure III-7 (D) reveals symmetry in all curves for GCD, indicating good Columbic efficiency of the device.

Figure VII-7 (A) the potential window of positive and negative electrode in the 2-electrode system, (B) the cyclic voltammetry for 2-electrode system at scan rate 20 mV/s, (C) cyclic voltammetry at different scan rates, and (D) GCD at different current densities.

The charge transfer resistance (R_{ct}) and equivalent series resistance (R_e), which includes the internal resistance of the recycled material, the contact resistance between electrolyte and electrodes and the ionic resistance of electrolyte, are estimated through the Nyquist plot in the frequency range 0.01 Hz to 100 000 Hz at OCV as shown in Figure VII-8 (A). Nyquist plot exhibits a small semicircle in the high frequency regime that can be related to R_{ct} (25.6 Ω) and a linear line in the low frequency region that can be related to the diffusion resistance (R_e). The device shows high specific capacitance (~ 92 F/g at 0.5 A/g) corresponding to specific capacity 138 C/g with good rate capability as shown in Figure VII-8 (B). Figure VII-8 (C) shows that the device succeeds to maintain very high Columbic efficiency (100%) throughout more than 9000 cycles. Moreover, the capacitance drop after the first 9000 cycles retains 89% of its capacitance. Energy density and power density are crucial metrics of the performance of any energy storage device. Figure VII-8 (D) shows the obtained Ragone plot,
revealing a maximum energy density of ~30 Wh/Kg at 0.5 A/g with a power density of 377 W/Kg. The power density increases to 3750 W/kg at 5 A/g with an energy density of 15.7 Wh/kg. Connecting two devices in series with 1.5 V each showed the ability to power a commercial white light emitting diode (LED) that requires a potential difference 3 V, indicating the practical functionality of the fabricated devices made of the recycled materials, see the inset in Figure VII-8 (D).

Figure VII-8 (A) Cs vs. discharge current density, (B) impedance spectroscopy, (C) capacitance retention and columbic efficiency over 9000 CCCD cycles, and (D) Ragone plot of the fabricated device with the inset showing the glowing of white LED using two in series connected devices.

7.1.3 Conclusions

In conclusion, I demonstrated the ability to fabricate a binder-free Li-Ni-Mn-Co hydroxide films directly on Ni-foam from spent Li-ion batteries for supercapacitor device applications. The fabricated electrodes showed flower-like structure with high porosity. Upon their use as supercapacitor electrodes in a three-electrode cell using CV, CCCD, and EIS measurements in 1 M KOH, the fabricated Li-Ni-Mn-Co hydroxides showed battery-like behavior with high specific capacitance of 951 F/g at 1 A/g (Specific capacity 523.5 C/g) and low charge-transfer resistance. Moreover, upon their use as positive electrodes in asymmetric
supercapacitor devices with GHG as the negative electrode, the devices reveal a capacitance retention reaching ~89% and an excellent cycling stability after 10,000 cycles. The device delivered a maximum energy density of 30 Wh/kg. For practical applications, the proposed versatile recycling approach will open a new avenue for the synthesis of electroactive films from spent Li-ion batteries and their use to construct real life devices with reasonable performance.
7.2 Silkworms as a factory of functional wearable energy storage fabrics

In the past few years, enormous efforts have been devoted to developing flexible wearable devices. Specifically, developing fibers for energy generation and storage devices is a tremendous demand. One of the cheapest and commonly used fibers is the natural silk (NS). Through many decades, NS has been used as fabric for many applications. NS consists mainly of a polymerized protein known as fibroin covered with a glue-like material named sericin. It is fabricated through the organisms of silkworms from a liquid combination of polymers at room temperature, resulting in a silk that is insoluble in water. The fibroin of the *Bombyx mori* larvae is a semi-crystalline biopolymer consisting of glycine, alanine and serine. Developments in the structure and properties of the resulting silk occur through additives to the food of the silkworms (usually mulberry leaves). Feeding the worms with special chemical materials, which can be incorporated in the glands of the worms and mix with the fibroin liquid, results in a modified-silk composite that comprises the properties of both NS and the incorporated materials. The fact that NS radiates heat more than it absorbs and self-cool, makes it a good candidate for electronic applications.

Feeding *Bombyx mori* larvae with nanostructured materials such as CNTs, Graphene, \( \text{TiO}_2 \) and other metal oxides have been investigated in recent reports. The feeding process proved that *Bombyx mori* larvae can intake nanostructured materials, which affect the crystallinity of the resulting silk. Feeding the worms with \( \text{TiO}_2 \) was also proved to be nontoxic. However, most of the previous reports were limited to the investigation of the mechanical and photonic properties of such modified silk. Tailoring the properties of the NS to be used in electronic devices, energy generation and energy storage devices is yet to be reported.

Rapid development of modern society has raised the urgent need of clean and sustainable energy conversion as well as efficient storage devices. To this end, flexible supercapacitors are emerging as promising platforms for energy storage. Herein, I
introduce the modification of NS structure through feeding the *Bombyx mori* larvae with four different types of materials (Graphite, TiO$_2$ nanotubes, MoS$_2$, and KMnO$_4$/MnCl$_2$) for use as supercapacitor electrodes. The study shows that modification of the NS enhanced its capacitive behavior, paving the way for their use in flexible supercapacitor applications.

### 7.2.3 Effect of the feeding process

All the studied silkworms started the feeding on their 5th instar, and they did not reject the food. It was observed that the larvae fed with MoS$_2$ were eating more than usual while the ones fed with KMnO$_4$/MnCl$_2$ were eating in a lower rate than usual. The larvae fed with graphite and TiO$_2$ did not show any unusual behavior in the feeding process. While the Cocoons of the blank fed larvae were of homogeneous size and white color, the chemically-modified ones showed a non-homogenous size and off-white color. After degumming, all the fabricated fibers were of a clear white color. The resulted silk was given the names S/B, S/G, S/TiO$_2$, S/MoS$_2$ and S/Mn for the blank silk, the graphite modified silk, the TiO$_2$ modified silk, the MoS$_2$ modified silk and the KMnO$_4$/MnCl$_2$, respectively.

### 7.2.4 Structure of the resulted silk

The morphology of the silk fibers was investigated using FESEM imaging as shown in Figure VII-9. Note that the thickness of the fabricated fibers is independent of the type of the chemical additive, having diameters ranging from 9 to 16 µm, in agreement with previous reports.$^{379,383}$ The fed materials appeared as debris on the surface of the fibers and/or within their internal fibroins. While the S/B fibers showed a trigonal shaped cross-section as presented in the inset of Figure VII-9, the S/G and S/TiO$_2$ showed an oval-shaped cross-section with the additives clearly appearing on the surface of the fibers. However, the S/MoS$_2$ and S/Mn showed a flattened oval cross-section and the fibers were more flat than usual, which may suggest that the additives (MoS$_2$, Mn) were interfered with the fiber materials and reconstructed its protein structure.$^{379}$ The elemental composition of the fibers was studied using the EDS technique and the results are presented in Table VII-3. The resulted composition showed that the added
material did not exceed 0.03 at% of the total atoms in the fiber, which is an accepted ratio due to the low concentration (0.5 wt% suspension) used in the diet. The S/B and S/G did not vary greatly due to the fact that graphite is only made of carbon atoms. However, the S/MoS\(_2\) analysis showed 0.03 at% of Mo and 0.05 atom% of S. the S/TiO\(_2\) showed a Ti composition of 0.03 at% and the S/Mn showed 0.02 at% of Mn and 0.01 at% of K “from the added KMnO\(_4\)”, with no signal for Cl atoms at different positions of the S/Mn fibers indicating that Cl\(_2\) gas may have evaporated from the reaction medium during the formation of MnO\(_2\). 384 Although the EDS analysis showed a minor ratio of the added materials, the SEM images showed a major effect on the morphology of the resulted fiber. The investigation of the crystal structure of the silk was performed using XRD as presented in Figure VII-9 (F). The XRD patterns show that all the resulted silk has a mesophase behavior with a broad peak around 20.0°, which can be attributed to the \(\beta\)-sheet of silk II structure. 144,385–388 The mesophase structure of the silk is believed to facilitate the diffusion of ions to the internal parts of the silk fibers.

**Table VII-3** EDS analysis of the spun silk.

<table>
<thead>
<tr>
<th>Material</th>
<th>C (atom%)</th>
<th>N (atom%)</th>
<th>O (atom%)</th>
<th>Mo (atom%)</th>
<th>S (atom%)</th>
<th>Ti (Atom%)</th>
<th>Mn (atom%)</th>
<th>K (atom%)</th>
<th>Cl (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/B</td>
<td>81.94</td>
<td>10.31</td>
<td>7.75</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S/G</td>
<td>82.24</td>
<td>9.84</td>
<td>7.92</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S/MoS(_2)</td>
<td>81.9</td>
<td>10.13</td>
<td>7.89</td>
<td>0.03</td>
<td>0.05</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S/TiO(_2)</td>
<td>85.96</td>
<td>6.86</td>
<td>7.15</td>
<td>N/A</td>
<td>N/A</td>
<td>0.03</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S/Mn</td>
<td>81.36</td>
<td>9.55</td>
<td>9.06</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.02</td>
<td>0.01</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure VII-9 Morphological and structural analysis of the silk: (A-E) FESEM images of the fabricated fibers (inset: cross section in the fiber) “pseudo-color is used for clarity” (A) S/B, (B) S/G, (C) S/MoS₂, (D) S/TiO₂, (E) S/Mn, and (F) the corresponding XRD patterns.

As the Raman spectroscopy has been used as a good tool to investigate the deformation of polymers backbone structure 389, the Raman spectra of the fabricated silk were recorded as shown in Figure VII-10 (A). All fibers showed the same peak position with different intensities, indicating more or less a similar internal structure. The Raman active peaks of the studied fibers are in the range between 800 to 1800 cm⁻¹, in a good agreement with literature. 377,389 The observed Raman peaks of the B. Mori silk appeared at 1085, 1232 and 1669 cm⁻¹ as indicated by red arrows in Figure VII-10 (A). The FTIR spectra in Figure VII-10 (B) showed the typical peaks at 1623, 1515 and 1230 cm⁻¹ characteristic of the silk fibers but with different intensities for different samples. 160,161,379 The peak at 1623 cm⁻¹ indicated the presence of amide I structure, which can be ascribed to the vibration of the C=O bond due to the co-
formation of the α-helix and random coiled structures. The peak at 1515 cm$^{-1}$ indicated the presence of amide II structure, which can be related to the deformation of the N-H bond in the β sheet structure. The Peak at 1623 cm$^{-1}$ indicated the presence of amide III structure and the peak is due to the vibration of the O-C-O bonds and the N-H bond. The positions of the peaks did not change with the chemical additives, which confirm that the chemical additives did not change the original backbone of the silk fibroins and hence the mechanical properties. CasaXPS software$^{390}$ was used to deconvolute the peaks of the FTIR which indicated that the percentage of both α-helix and β sheet structure are almost equal in all samples and the presence of the β-sheet structure was found to be more pronounced in the S/TiO$_2$, the Blank silk and the S/G more than in the S/Mn, and the S/MoS$_2$, the deconvoluted data are presented in Table VII-4. Thermogravimetric analysis was performed to indicate the thermal stability of the resulted silk fibers. Figure VII-10 (C) shows that all the silk fibers were stable up to 200° C then the blank silk started to decompose at ~ 250° C. The modified silk showed enhanced thermal stability. At 500° C, the remaining weight of the silk was 28.18, 26.7, 21.67, 16.13 and 12.27% for S/TiO$_2$, S/G, S/MoS$_2$, S/Mn, and S/B, respectively.

Figure VII-10 The characterized peaks of the spun silk fibers (A) Raman spectroscopy, (B) FT-IR, and (C) TG analysis for the silk fibers.

Table VII-4 Deconvoluted data of the FTIR spectra.

<table>
<thead>
<tr>
<th>Material</th>
<th>Area under the peak of ~1515 cm$^{-1}$ (β sheet)</th>
<th>Area under the peak of ~1623 cm$^{-1}$ (α-helix)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/B</td>
<td>9.37</td>
<td>9.65</td>
</tr>
<tr>
<td>S/G</td>
<td>10.03</td>
<td>11.49</td>
</tr>
<tr>
<td>S/MoS$_2$</td>
<td>6.40</td>
<td>7.26</td>
</tr>
<tr>
<td>S/TiO$_2$</td>
<td>12.15</td>
<td>13.47</td>
</tr>
<tr>
<td>S/Mn</td>
<td>4.24</td>
<td>4.83</td>
</tr>
</tbody>
</table>
7.2.5 Electrochemical performance of the natural silk

To test the capacitive performance of the natural silk, the self-standing silk was tested once as a positive electrode and once as a negative electrode in a 3-electrode system with 6 M KOH as the electrolyte. Although 6 M KOH is a high concentration electrolyte, it is commonly used with the carbon-based materials in supercapacitor applications.\textsuperscript{17,391–395} Usually, the carbon materials show a typical rectangular cyclic voltammogram (CV) reflecting the electrical double layer behavior (EDL).\textsuperscript{7,22,396} However, the CVs of the positive and negative silk electrodes in Figure VII-11 (A and B) did not show an EDL behavior indicating diffusion processes for the ions in the polymeric structure of the silk.\textsuperscript{22} It is expected that the OH\textsuperscript{-} ion from the KOH reacted with the organic polymer of the silk fibers resulting in a diffusion and pseudocapacitive behavior to the silk electrodes. The ions from the KOH can react with MoS\textsubscript{2}, TiO\textsubscript{2}, and MnO\textsubscript{2} to give MoSSOH,\textsuperscript{397} TiOOK\textsuperscript{398} and MnOOK\textsuperscript{399}, respectively. The CVs of the positive silk electrodes at a scan rate of 10 mV/s (Figure VII-11 (A)) show that the redox peaks are more visible in the S/TiO\textsubscript{2} while the other additives did not affect the shape of the CV of the S/B. This can be ascribed to the accumulation of TiO\textsubscript{2} on the surface of the silk fibers while other additives affected the morphological shape of the silk fibers and did not accumulate with high amount on the surface of the fibers. At a scan rate of 10 mV/s and at a positive potential window, the specific capacitance of the S/Mn showed the highest specific capacitance of 778.975 mF/g while the S/TiO\textsubscript{2}, S/MoS\textsubscript{2}, S/G and S/B showed 577.925, 419.767, 247.822, and 157.291 mF/g, respectively. This shows that all the additives dramatically increased the specific capacitance values of silk electrodes. The CVs of the negative silk electrodes at a scan rate of 10 mV/s (Figure VII-11 (B)) show clearer redox peaks than the positive electrodes. The specific capacitance of the negative electrodes calculated at a scan rate of 10 mV/s was 1122.832, 263.047, 131.794, 112.141, and 109.403 mF/g for S/Mn, S/B, S/MoS\textsubscript{2}, S/G and S/TiO\textsubscript{2}, respectively. To make a deeper study with accurate weight of the active material, the strands of the silk fibers were coiled over a glassy carbon (GC) electrode and measured as a positive electrode. The calculated specific capacitance of silk fibers @ GC at 10 mV/s (Figure VII-11
(C) showed a capacitance of 610.911, 604.701, 569.047, 556.923, and 206.650 mF/g for S/MoS$_2$, S/TiO$_2$, S/Mn, S/G and S/B, respectively. The contribution of the GC current collector affected the shape of the CVs and shifted them to the EDL rectangular shape. Also, the GC affected the values of the specific capacitance and the order of the materials in their capacitance values. Therefore, the current collector affects greatly the overall performance of the material and I will focus herein on the self-standing fibers as they are more reliable for the study. As one of the most important metrics of supercapacitors is their ability to store and release charges, the time of the charge and discharge was also studied for the silk fibers. Figure VII-11 (D and E) shows the galvanic charge/discharge (GCD) curves of the self-standing silk fibers at a current density of 0.1 A/g. The GCD curves show a pseudocapacitive behavior. For the positive electrodes, the specific capacitance calculated from the GCD at 0.1 A/g showed the same trend as that calculated from the CVs at 10 mV/s. The specific capacitance values of the positive electrodes calculated at 0.1 A/g were 1222.2, 373.25, 177.2, 54.6, and 29.25 mF/g for S/Mn, S/TiO$_2$, S/MoS$_2$, S/G and S/B, respectively. However, for the negative electrodes, the specific capacitance values calculated at 0.1 A/g were 3114, 108.7, 53.6, 37.05, and 17.8 mF/g for S/Mn, S/TiO$_2$, S/B, S/MoS$_2$ and S/G, respectively. The GCD curves of the silk @ GC positive electrodes at 0.1 A/g are presented in Figure VII-11 (F). The specific capacitance of the positive silk @ GC calculated at 0.1 A/g were 88.3, 85.1, 81.05, 68.1, and 35 mF/g for S/TiO$_2$, S/MoS$_2$, S/Mn, S/G and S/B, respectively. As for the CV results of the silk @ GC, the trend is different, and the effect of the current collector is shifting the shape of the GCD curves to the ideal shape of the EDL capacitor materials. However, the specific capacitance values of the silk with additives are still much higher than this of the blank silk. The CV and GCD results showed that the blank silk (S/B) behaved better as a negative electrode than as a positive electrode and so did the addition of Mn ions (S/Mn) and usually MnO$_2$ acts as a better capacitive material when used as a negative electrode. However, the S/G, S/MoS$_2$ and S/TiO$_2$ enhanced the performance of the silk as a positive electrode than as a negative electrode. Although the amounts of the additives were relatively low, their effect can be attributed to both the nature of
the materials and their effect on the morphology of the silk fiber, which controls the diffusion of ions into the silk fibers.

**Figure VII-11** Electrochemical performance of the silk fibers: (A) CVs of the studied self-standing silk fiber at 10 mV/s in positive potential window (inset: legend of Figure VII-11 (A-F)), (B) CVs of the studied self-standing silk fiber at 10 mV/s in negative potential window, (C) CVs of the studied silk @ GC at 10 mV/s in positive potential window, (D) GCDs of the studied self-standing fibers at 0.1 A/g in positive potential window (inset: enlarged figure), (E) GCDs of the studied self-standing fibers at 0.1 A/g in negative potential window (inset: enlarged figure), (F) GCDs of the studied silk @ GC at 0.1 A/g in negative potential window.

The conductivity is one of the main factors that affects the overall performance of a supercapacitor electrode. **Figure VII-12** (A) shows the Nyquist plots of 10 mg of silk fibers coiled over the same area of a glassy carbon electrode. The resulted curves were fitted to the inset circuit in **Figure VII-12** (A), with R1 representing the electrolyte resistance and R2 representing the charge transfer resistance of the material. As the obtained circle is a depressed semicircle not a perfect semicircle, Q was used in the fitting instead of C and L is used to represent the inductance related to the electrical connections, $Z'$ and $Z''$ represent the real part and the imaginary part of the impedance, respectively. This circuit showed a perfect match with all the Nyquist plots as presented in **Figure VII-13**. The R2 values of the silk fibers were 157.7,
115.7, 104.9, 92.54, and 39.72 Ω for S/B, S/G, S/TiO₂, S/MoS₂ and S/Mn, respectively. Those R² values show that the additives greatly enhanced the conductivity of the silk fibers and hence enhanced their specific capacitance. The supercapacitors should be able to work under different conditions of scan rates and current densities. The value of the specific capacitance of self-standing silk positive electrodes versus the scan rate is presented in Figure VII-12 (B). Note that the specific capacitance values have the same trend except at 500 mV/s. At 500 mV/s, the specific capacitance values are 196.991, 117.22, 87.491, 76.976, and 55.531 mF/g for S/Mn, S/MoS₂, S/TiO₂, S/G, S/B, respectively. On the other hand, from the GCD calculations of the positive self-standing silk electrodes (Figure VII-12 (C)), the trends differed over the high current density. It showed the values of 78.25, 26.5, 9.5, 8.75, and 5.5 mF/g at 0.5 A/g for S/Mn, S/MoS₂, S/G, S/TiO₂, and S/B, respectively. For the negative self-standing silk electrodes, the change of specific capacitance with scan rate is presented in Figure VII-12 (D). The values of the S/Mn and S/B were always much higher than those of the S/G, Si/MoS₂, and Si/TiO₂. At a scan rate of 500 mV/s, the specific capacitance values of the negative self-standing electrodes were 211.009, 60.195, 36.27, 35.729, and 30.272 mF/g for S/Mn, S/B, S/G, S/TiO₂, and S/MoS₂, respectively. The trend of the specific capacitance at different current densities is presented in Figure VII-12 (E), enlarged in Figure VII-14. At a current density of 0.5 A/g, the specific capacitance values of the negative self-standing electrodes were 90.5, 12, 7.75, 6.8, and 5.25 mF/g for S/Mn, S/MoS₂, S/G, S/TiO₂, and S/B, respectively. Although the S/TiO₂, S/MoS₂, and S/G specific capacitance values as negative electrode (from GCD) are higher than that of the S/B but it is lower than their positive electrode values (from GCD). Thus, it is believed that S/TiO₂, S/MoS₂, and S/G act better as positive electrodes than as negative electrodes. Despite the different trends over the different scan rates and current densities, the performance of all silk with additives was better as positive electrodes than the blank silk and the S/Mn was always better as a negative electrode. One of the performance metrics of the supercapacitor materials is their stability upon cycling. Figure VII-12 (F) shows the retention percentage of the self-standing silk as positive and negative electrodes over 1000 cycles. The retention fluctuates at the first 200 cycles and reaches a relative stability after 600 cycles. The
positive electrodes showed retention of 141.88, 90.59, 87.7, 66.63, and 61.3% for S/TiO$_2$, S/MoS$_2$, S/G, S/Mn, and S/B, respectively after 1000 cycles. The negative electrodes showed retention of 80.99, 67.6, 63.45, 46.06, and 42.13% for S/MoS$_2$, S/TiO$_2$, S/Mn, S/B, and S/G, respectively. From the retention results I conclude that the silk fiber has a better retention as a positive electrode in general and that the additives enhanced the retention and cyclability of the electrodes. The above 100% retention values are attributed to the further diffusion of ions into the material and enhancement of reaction over time.\textsuperscript{177,321} Noteworthy to mention that the specific capacitance values in mF are acceptable for self-standing carbon-based materials with no high conductive current collectors.\textsuperscript{400–402}

\textbf{Figure VII-12} Electrochemical stability of the silk fibers (A) Nyquist plots of the studied silk @ GC in the range 1 MHz to 100 mHz (B) Change of specific capacitance with scan rate (10, 50, 100, and 500 mV/s) for the self-standing fiber in positive potential window (inset: legend for Figure VII-12 (A-E)), (C) Change of specific capacitance with current density (0.1, 0.2, 0.4 and 0.5 A/g) for the self-standing fiber in positive potential window, (D) Change of specific capacitance with scan rate (10, 50, 100, and 500 mV/s) for the self-standing fiber in negative potential window, (E) Change of specific capacitance with current density (0.1, 0.2, 0.4 and 0.5 A/g) for the self-standing fiber in negative potential window, (F) Retention of the studied self-standing fiber in both positive and negative potential window.
7.2.6 Conclusions

I demonstrate the ability to fabricate functionalized natural silk fibers by feeding the silkworms with the material of interest. Specifically, this work highlights the possibility of using natural silk fibers as supercapacitor electrodes upon feeding the worms with high capacitive materials such as graphite, MoS$_2$, TiO$_2$, and KMnO$_4$/MnCl$_2$. The study showed that the fed material did not greatly affect the crystallinity of the silk fibroin and all the added materials enhanced the capacitance performance and the thermal stability of the silk fibers. It was observed that both S/B and S/Mn contained more β-sheet silk, have close thermal stability, and both acted better as negative electrodes. The study proved that natural silk can be tuned for use in energy storage devices.
Chapter VIII : Conclusions & Future Outlook

The thesis designed a number of electrode materials based on the three charge storage mechanisms of the supercapacitor electrodes. Moreover, the study illustrated the availability of designing electrode materials and using hybrid electrodes and devices to reach a better performance. Here are the points concluded throughout the thesis:

- The thesis suggests that for reaching a high operating voltage in electrodes of EDL behavior, it is better to use a neutral electrolyte such as Na$_2$SO$_4$. While the use of basic electrolytes should ensure the highest capacitance performance of functionalized carbon-based electrodes.

- The thesis illustrated that CNTs can deliver the highest capacitance in comparison to various carbon allotropes.

- The thesis showed the possibility to reach a potential window of 1.9 V and an energy density of 23.3 Wh/Kg at a power density of 475 W/Kg for symmetric CNTs device.

- Doped graphene can give a better quantum capacitance than graphene and can act as self-hybrid material that deliver both pseudocapacitance and EDL capacitance at the same time combining the benefits of both charge storage mechanisms.

- MoS$_2$ quantum capacitance modeling upon alkali metal intercalation presented the possibility of shifting the 2H phase into the metallic nature and stabilization of the 1T phase. the results showed ion intercalation to enhance the quantum capacitance and stabilize the 1T phase of MoS$_2$ and recommended the use of Cs$^+$ intercalation for concentrated electrolyte supercapacitors and K$^+$ intercalation for the diluted counterpart. Moreover, the 2H and 3R-MoS$_2$ phases should be used only as positive electrodes, while the 1T-MoS$_2$ can be employed as positive and negative electrodes.

- The MoS$_2$ electrochemical investigation proved the accuracy of the DFT calculations and the high capacitance performance upon K$^+$ intercalation. The 1T-
MoS$_2$ symmetric device revealed an energy density of 4.19 Wh/Kg at a power density of 225 W/Kg.

- The hybrid electrode of MoS$_2$/carbon proved that carbon additives can enhance the performance of the pseudocapacitive materials.
- Mono, di, and tri-sulfide can make a redox reaction in presence of alkaline medium and store energy in a battery-like behavior. A hybrid device of metal sulfide//N-doped graphene can give the best capacitance performance, where the hybrid Ni-Mn-Co-S/graphene hydrogel device delivered an energy density of 49.55 Wh/Kg at a power density of 800 W/Kg.
- Electrodeposition is an easy method to recycle the content of spent batteries and synthesize a new supercapacitor electrode. Interestingly, Li-Ni-Mn-Co hydroxides recycled from spent batteries showed a specific capacitance of 951 F/g at 1 A/g.
- In-vivo production of conductive silk is the easiest method to produce wearable electronics. Silk in-vivo chemically-modified electrode exhibited 5 folds of capacitance increase compared to the unmodified silk.

In summary, it is advised to use neutral electrolytes with the EDL electrode materials, and H$_2$SO$_4$ for high performance functionalized carbon electrodes. Also, quantum capacitance and other DFT predictions are useful in screening electrode materials. Besides, sulfide electrodes can exhibit very high capacitance performance either through intercalation or redox processes if combined in hybrid supercapacitor devices. Moreover, it is suggested to use hybrid electrodes and devices for better supercapacitor performance.

On the other hand, more research is needed before moving to market. The study of the ionic liquid electrolytes to enhance the potential window of the EDL-based electrodes is required and a more DFT screening for the carbon allotropes, doped graphene, CNTs, and TMDs may shed the light on new high performance electrode material. Moreover, integrated systems of solar conversion and storage can be reached through the smart design of the electrode materials.
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List of Publications Extracted From Thesis

Published Articles:


Submitted Manuscripts:


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PhD candidate, Nanotechnology  
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BSc. in Chemistry, (Honors)  
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Professional Positions

01/17 – Now  
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Freelance Translator, Coursera website.

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Honors/Awards

- I was recommended by the chemistry department, Alexandria University as the student of the year 2011/2012.
- Mohammed Bin Abdulkarim A. Allehedan Fellowship, PhD fellowship.
Professional Activities

- **Co-Founder and member**: Recycling project at the Faculty of Science, Alexandria University.
- **Co-Founder and R&D director**: The American Chemical Society, Alexandria University Student Chapter.
- **Organizing Committee Member**: The communication skills training course, Faculty of Science, Alexandria University, August 7-11, 2011.
- **Organizing Committee Member**: The 2nd Student Conference, Faculty of Science, Alexandria University, May 23-24, 2011.
- **Conference Coordinator**: Paper Club: Nano Chemistry Conference, Faculty of Science, Alexandria University; Sponsored by Springer Nature.
- **Co-Principle Investigator**: "In-situ Modified Silk for Technological Applications", American University in Cairo, Proof of Concept Grant, Grant amount: **785,000 EGP**, 2019-2020

Teaching Experience:

- C 103: General Practical Chemistry for 1st year students, Science, Pharmacy and Dental students.
- C 244: Qualitative analysis of Organic Samples, 2nd and 3rd year students.
- C 448: Preparation and identification techniques of Organic Materials and research skills, 4th year Honor Chemistry students.

Participations

- Fame Lab, Alexandria 2011.
- NASA’s Space App Challenge, 11-12/4/ 2015.

Publications

I. **Referred Journal Publications**


• Farah A. El Diwany, Basant A. Ali, Ehab N. El Sawy, Nageh K. Allam. "Fullerene C\textsubscript{76} as a novel electrocatalyst for VO\textsuperscript{2+/0} and chlorine evolution inhibitor in all-vanadium redox flow batteries." Chemical Communications, 56 (2020): 7569 - 7572.


II. Conference Posters and Presentations

- **The day of innovation** “4, 5/5/2011” at Alexandria University with a research on “The Birth of Elements”.

- **The Second Student’s Research Conference** for Egyptian faculties of science at The Faculty of Science “18-19/5/2011”.

- **The 6th environmental forum** at The Faculty of Science, Alexandria University “2/5/2012”.

- **The Fourth Student’s Research Conference** for Egyptian faculties of science at The Faculty of Science, 5-6/5/2015.

- ACS Alexandria University: Activities, events and community outreach, **ACS 250th national meeting** abstract, 18/08/2015.

- Displacement Quantization in the Simple Harmonic Motion, **ACS 251th national meeting** abstract, 17/03/2016.


III. NextGen Voices Short essay at Science Magazine (AAAS)

- Value of a young scientist, Science online, Apr. 2016, ISSN: 1095-9203.

- Full speed ahead to the City on the Hill, Science, May 2016, 352(6288), 886-889.


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IV. Book Chapters:

- The DFT+U: Approaches, Accuracy, and Applications (DFT Calculation); Sarah A. Tolba, Kareem M. Gameel, Basant A. Ali, Hossam A. Almossalami, Nageh K. Allam, Density Functional Calculations - Recent Progresses of Theory and Application, InTech publication.

V. Patents: