As scientists, we have an affinity for order: repeating crystal structures, Euclidean space, continuous functions. Even concepts such as defects are discussed in the context of distracting from order. Things are most logical and best described in straightforward, taxonomical fashion. But what happens when the very application desired is dependent on the lack of order?

In many ways, the effective use of amorphous materials is the next frontier in material science. Whereas crystalline based materials, have very defined structures and properties, amorphous materials are not beset but such rigidities. Due to the wide range of possibilities in structure, properties, and complexities, they open up a whole new world of applications.

However, for all the promises offered by amorphous materials, they also come with
a significant amount of challenges: synthesis, characterization, structure-property relationships, and repeatability all come to mind. Furthermore, the very nature of the word, amorphous coming from the Greek \textit{amorphe} symbolizing ”without shape”, indicates there is no clearly defined way of classifying the structure. Different versions of the same amorphous materials lead to different properties, yet they all earn the same designation, as there are no straightforward ways of telling them apart. In a way, these are very much a double-edge sword: the very thing that makes them useful, is also what makes them difficult to work with – and thus the reason you assign them to a graduate student!

As such, the following work deals with two seemingly disparate issues, yet very much inextricably linked: amorphous carbon and Na-ion batteries (NIBs). More specifically, the two are connected due to the role of amorphous carbon as an NIB anode material.

The NIB topic was of particular interest, as there currently exists an unmet need for scalable electrochemical energy storage systems. Current solutions in this domain are either too expensive due to material costs, or do not meet to requisite performance requirements to be an effective option. But, NIBs, with their low overall material costs, and adequate electrochemical performances offer a path forward.

However, there still remains underlying challenges before commercially viable NIBs become a reality. One of the key concerns is the state of the negatively charged electrode – anode for short – material. Typical alkali ion batteries such as Li-ion batteries (LIBs) or K-ion batteries (KIBs), use graphite as an anode material due to its ease of forming reversible graphite intercalation compounds (GICs). Unfortunately, due to thermodynamic constraints, Na atoms are not afforded the
same possibilities. They cannot form reversible GICs, let alone form GICs to begin with. Thus for this reason, other candidate anode materials must be explored.

To that end, amorphous carbon is one of the most promising. The wider spacing and presence of defects in the structure eliminate much of the spatial and thermodynamic constraints that beset the use of graphite. Additionally, the material is cheap, abundant, easy to synthesize – at least on the lab-scale – and non-toxic, which makes it an ideal candidate for further exploration.

Herein, this dissertation addresses two main topics. The first one focuses on the electrochemistry, and structure property relationships linking amorphous carbon and NIBs. In that work, issues such as surface area, porosity, Na-atom storage mechanism, and electrochemical performance are discussed. This newly discovered information is of interest to the battery community, as many of its discoveries can be used to build better batteries, and battery materials proceeding forward.

The second topic is that of amorphous carbon itself, and discoveries on its synthesis process, as well as novel ways of exploring its structure and characterizing it. As stated before, one of the key challenges in working with amorphous materials, is to find unbiased and straightforward methods of characterizing them. In a way, one has to make order from chaos. Thus, new models and approaches to doing this are discussed, which should be a topic of interest to any researcher that primarily works with amorphous materials.

The subsequent work presented was conducted in the years ranging from 2013 to 2017, and was carried out using both experimental methods, as well as computational/numerical methods to test some of the theories that were proposed in the
experimental work. It is the intention of the author that those who should complete the reading of this manuscript should come away with a better understanding of amorphous carbon, its characterization, and how it pertains to NIBs.
Venturing Beyond Crystallinity and Into Amorphous Space: A Na-ion Battery Perspective

by

Clement Bommier

A DISSERTATION

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

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Commencement June 2017

APPROVED:

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Major Professor, representing Chemistry

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Chair of the Department of Chemistry

_________________________________________
Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

_________________________________________
Clement Bommier, Author
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Chapter 1: Motivation

1.1 The Need for Energy Storage

As of the year 2017, current trends in worldwide energy consumption are untenable. The world is consuming energy at an ever growing rate, with much of that energy being generated from CO$_2$ intensive sources – namely the hydrocarbons (Figure 1.1).[6] Environmental effects of this are already being felt worldwide. It is no coincidence that the previous three years of my graduate school tenure, 2014-2016, have all consecutively earned the title of ”hottest year” in recorded history.[7] Unless actions are taken, this trend will continue to be exacerbated, and the consequences on life as we know it are bound to become more and more severe.

Aside from an overall reduction in energy consumption, an ideal solution would be to switch to low CO$_2$ energy generation sources. Examples of such sources include hydropower, solar, wind, and geothermal power sources. Such sources, while having a higher CO$_2$ initiation cost, lead to negative emissions if kept in operation long enough.[8]

The benefits of other non-CO$_2$ generating sources, such as nuclear and biomass, are more debatable. Nuclear waste, proliferation of nuclear weapons, and availability of nuclear fuels remain issues, with many of such issues posing global risks.[9]
Figure 1.1: Energy generation sources as of 2013.

Biofuels, while technically a carbon neutral source, as they can be harvested and consumed within a generation, have a more limited energy potential due to a disparity between the energy they can provide, and the energy that is demanded.[10] Thus for energy generation, hydro, solar, wind and geothermal power, are the best options – at the very least from a climate perspective.

As of the current day, hydropower is currently the biggest contributor to environmentally friendly energy sources(Figure 1.1). Yet developing it past what is today poses many challenges. First off, the resource is geographically dependent. Not every region has access to hydropower sites. Additionally, even were such resources can be developed, it often comes at the opposition of many local and environmental groups, which have managed to stopped proposed dams. Lastly,
their viability is under threat from climate change. Shifts in weather and precipitation patterns, as were experienced in the American West in the mid 2010’s greatly reduced to power capabilities of those dams.[11] If such weather anomalies occur more frequently, it will be at the detriment of hydropower.

However, solar and windpower face fewer obstacles. Solar panels can be mounted nearly anywhere, and can operate in environments devoid of water. The same goes for windpower, which can be mounted with little disturbance to the local land area, aside from the visual & auditory disturbances – along with a few unfortunate birds. This is not to say that solar and windpower don’t face constraints in their developments: they do, but those constraints are more manageable than the ones for hydropower, as well as nuclear power and biofuels.

One of the main issues with solar and wind power is their intermittent nature. Unlike other sources of energy that operate ‘on command’, the latter two can hardly be controlled. The sun doesn’t always shine, and the wind doesn’t always blow. Furthermore, even when the sources are plentiful, there is no guarantee that they match the demands of the electric grid, with this being illustrated in Figure 1.2.[12] Excess capacity is produced at a time where it is not needed, while it comes are a shortfall when capacity is needed. Similar patterns hold true for wind power.

The solution to this is fairly obvious: store the energy when it is in excess, and disburse it when there is a deficit. Of course, this is only possible under the condition that we possess effective, and low cost energy storage technologies – and we don’t. Thus, unless such technologies are developed, the wide scale adoption of wind and solar power will be difficult, and fraught with problems and higher costs.
1.2 The Need to Understand Amorphous Carbon

At the beginning of this research, this was not a main motivation. The initial goal of the ARPA-E project that I started working on was simply to improve NIB anodes. However, it quickly became evident that in order to do so, a fundamental understanding of structure-property relationships was needed. If materials were
going to be designed properly, their functions had to be known. However, this was
nearly impossible considering that the many intricacies of the amorphous carbon
structure were not able to be characterized.

As such, a new characterization method is necessary in order to better understand
the amorphous carbon structure. Achieving this goal will allow countless advances
in diverse concentrations, much beyond that of the energy storage field, such as
catalysis, sensing, gas storage, and absorption materials.
Chapter 2: Background Information

2.1 Current Energy Storage Technologies

Current state-of-the-art energy storage technologies can be classified into two categories: mechanical and chemical. Mechanical solutions include pump-hydro storage (PHS), compressed-air storage (CAES), and flywheel storage (FES) (Figure 2.1), which make use of either potential, or kinetic energy, as a storage medium.

While these are promising in their own right, cost, scalability and safety issues do pose further problems. Much like hydropower, PHS is heavily dependent on location, as it needs an abundance of water, and favorable terrain to be effective. Additionally, the volumetric energy storage it provides is low. CAES is also dependent on location, as it necessitates the use of permeable underground caves, and has the added disadvantage of being effected by geological events, and of needing natural gas heating to prevent the freezing of turbines upon release of the compressed air. FES is the most accessible of the mechanical storage technologies, but unfortunately, it is also the most expensive, and the most dangerous one, as all the energy stored is kinetic.

On the other hand, chemically based energy storage systems, or batteries, manage to alleviate many of these previous concerns. Depending on the technology used, they have the potential to be much cheaper, more scalable, and safer to operate.
than mechanically based storage systems.

As the name would imply, these technologies make use of chemical energy as a storage medium. Energy is released as molecules are converted from one state to another, releasing energy in the process. The electrochemical systems can be further separated into different classes of materials: flow batteries, molten salt batteries, and ionic batteries.

Flow batteries make use of two oppositely charged liquids, an anolyte and a catholyte, as a storage medium (Figure 2.2a). The reaction occurs through an ion exchange across a selectively permeable membrane, as to reduce one of the liquids, while oxidizing the other. These batteries have the advantage of being scalable, and do not face any structural degradation problems. However, the engineering aspect behind the flow batteries is more costly and challenging. The electrolytes used are often very corrosive, proper electrical conductivity between the electrolyte and the graphite felt is key, and the ion membrane expensive. Additionally, the most common type of flow batteries make use of a vanadium salt,
Figure 2.2: Schematic diagrams of a) Flow battery system, where the anolyte and catholytes are designated 'electrolyte A' & 'electrolyte B'. b) Molten NaS battery system.

which also raises the overall cost, as well as the prospect scaling up the technology to meet grid storage needs.

One of the best example of large scale molten salt battery technologies are the Na-Sulfur batteries. In a molten salt battery, a reaction occurs between an alkali metal, which typically have low melting points, and a typically more electronegative element – most often sulfur. In a NaS batteries, the reaction occurs as liquid Na diffuses across a $\beta$-alumina separator, to a molten sulfur cathode (Figure 2.2b). Such batteries also have the advantage of being easily scalable, and unlike the case of Vanadium dependent flow batteries, do not face elemental shortage constraints. On the other hand, these batteries must be operated at elevated temperatures, and the molten salts are highly corrosive, causing them to have a higher operational and maintenance cost.[13]

Ionic batteries share some similarities with the previous two batteries, but also
offer several unique features, which render them more advantageous. Like flow batteries, they also use ion exchange as a means of conducting the chemical reaction, however, unlike flow batteries, the electrodes that are oxidized and reduced are in the solid state. Additionally, like molten salt batteries, many ionic batteries depend on alkali-metals as the anode component. However, unlike molten salt batteries, these batteries can operate at room temperature. The ability to operate at low temperatures, as well as the lack of mechanical equipment needed for their operation make them cheaper, and in some cases, more scalable alternative, to flow batteries and molten salt batteries.

Ionic batteries function by using a positively charged cathode, usually some type of layered oxide structure, and a negatively charged storage medium, such as a carbon material. Using a purely metal anode is possible, but not practical, as it introduces the risk of dendrite formation, which if unchecked, leads to short-circuits, battery failure, and fires. During the operation, ions are shuttled across the electrolyte from the cathode to the anode, and vice versa (Figure 2.3). In the context of this PhD thesis, the ionic battery system that will be discussed at length will be that of NIBs.

2.2 The Case for NIBs

2.2.1 Uncertainty of the LIB market

It is typically stated in most of the NIB literature, that while LIBs are the best and most developed rechargeable ionic type battery, the shortage of lithium metal
prohibits their scale-up.[14] To some extent, this is true. LIBs are the most developed type of ionic batteries and do offer superior performance. The scale up issue is more dubious. The amount of available lithium is more a function its unevenly distributed resources, and difficulty of extraction, than its sheer amount. This can have the effect of large price swings in times of high demands, the price can climb quickly, only to be followed by steep price drops if the output is increased (Figure 2.4)a. In this manner, lithium metal is not unlike the oil market of the pre-fracking era, with extreme price swings being seen in the late 2000’s & early 2010’s. Thus it would be more sensible to utilize a material which allays the market volatility concerns.

Part of these price swings are due to the way lithium is obtained. The easiest is to extract Li₂CO₃ from a brine source (Figure 2.4)b.[15] Unfortunately, these lithium rich brines are located in high mountain plateaus in underdeveloped regions. While increased development of these brines, or other lithium sources, such as hard rock mining,[16] or seawater extraction are possible,[17] they do increase...
the overall cost.

![Price chart of Li$_2$CO$_3$](image1) ![Picture of lithium rich brines](image2)

**Figure 2.4:** (a) Price chart of Li$_2$CO$_3$ (b) Picture of the lithium rich brines, and their extraction in the high Andean plateaus.

Another issue aside from the use, or cost of lithium, for LIBs is the cost of the other battery components. Modern LIBs routinely make use of cobalt and nickel as part of the cathode material, metals that are both rarer and more expensive – not to mention toxic in the case of cobalt.[18] If LIBs are going to be scaled up, the use of those metals is going to be an issue as well. Additionally, lithium batteries must utilize a copper current collector for its anode, as an aluminum current collector would alloy with the lithium, leading to the failure of the battery. Copper being more expensive than aluminum, this fact also drives up the cost of the battery.

### 2.2.2 Cutting Costs Wherever Possible

On the other hand, NIBs face less of these cost issues. Their cathodes are mostly Fe-based, and they can utilize an aluminum current collector for its anode. This
helps to drive down the cost, which is very crucial to their commercial viability. It is important to remember that, while NIBs underperform LIBs in terms of gravimetric and volumetric energy density, that is not their purpose. In terms of large scale stationary energy storage, gravimetric and volumetric energy matter less. What matters more is the cost, measured in $/kWh. In this regard, NIBs have an advantage.[19]

2.3 NIBs: a Brief History

2.3.1 Setting the Stage for Ionic Batteries

The first battery systems, which came about in the early 1900’s, comprised mostly of Lead Acid type batteries and ‘dry cells’ such as NiFe batteries.[20] While they found initial successes in electric cars, among other uses, their performances precluded them from many applications. As such, throughout the 20th century, there was a keen interest in developing new and improved battery technologies.

In the 1950’s and 1960’s, buoyed by a new era of scientific research, their came to be new push in battery technology, which aimed at developing alkali/halogen batteries. It was well-known that an alkali-halogen couples were on opposite ends of the reduction potential spectrum, thus offering a large voltage window, and with it, a high energy density.[21] Reversibility was another issue altogether, but if that problem could be resolved, a viable battery with high energy density would soon follow.
To that end, there were several key breakthroughs in that time period, which in many ways, laid the foundation for the modern alkali batteries. Several patents in that era detail the use of organic liquid electrolytes in conjunction with alkali metals.[22] These electrolytes were stable enough to not be reduced by the alkali metal, while being effective mass transport mediums for the ions involved in the reaction. The electrolytes we utilize today, are not too much different from the electrolytes that were being explored then.

While the electrolyte problem had been solved, the switch to ionic type batteries took a little longer. For much of the 1950’s and 1960’s, the emphasis was largely on using metal anodes, with halogen cathodes, where the reaction would take place through the formation of a salt. However, this process was inefficient, and often needed higher temperatures to work. This started to change in the early 1970’s. During this time, there was research interest in intercalating layered chalcogenide materials with alkali ions as potential superconducting materials.[23] This concept proved to be short-lived, but its principles spilled over into the battery field. Instead of relying on an alkali/halogen salt couple, researchers began to experiment with the possibility of inserting alkali ions into layered materials electrochemically. This proved to be possible, which led to the first lithium-ion battery cathode material in the mid 1970’s, TiS$_2$.[24] The full commercialization of the LIB would not come until 1991,[25] but never-the-less, its inception dates back to the mid 1970’s.
2.3.2 The Proliferation of LIBs

The publishing of the LIB cathode during that time period spurred much research into similar intercalation type electronic materials. To that end, both Li & Na intercalation materials were actively explored. Putting ourselves in the frame of the time-period, this was a sensible decision. No one could have known at the time that LIBs would become the dominant commercial battery nearly 30 years later. At that time, it was best to explore all options, as the outcomes were unknown. Thus, the late 1970’s for lithium materials, and early 1980’s for sodium materials, are full of publications of cathode materials, such as LiCoO$_2$,[26] LiFePO$_4$,[27] Na$_x$CoO$_2$,[28] Na$_x$CrO$_2$,[29] Na$_x$NiO$_2$,[30] Na$_x$TiO$_2$.[31]

The anode side of the battery was more of a challenge. Utilizing metal anodes, while feasible for half-cells and lab scale testing posed more of a problem for an actual battery, due to the dendrite formation, and all the problems associated with that. Thus, substitutes had to be found. In the case of lithium, it was well known that graphite could act as lithium host, forming a LiC$_6$ GIC,[32] and it was further shown in the mid 1970’s that such a compound could be formed electrochemically by Besenhard et al.[33] The breakthrough behind the commercialization of LIBs by Sony, was that they were able to piece together the main components: the organic electrolyte, the layered oxide cathode, and the graphite anode into a commercial battery. Trivial, but in a way, most batteries technologies are just that.

Unfortunately, NIBs did not have such a straightforward solution for the anode material. The paper by Besonhard et al. from the 1970’s also tried to electrochemically intercalate sodium into graphite, but to no avail. These results were
repeated once again in 1988 by Ge et al. who showed graphite only to have an intercalation stoichiometry of NaC\textsubscript{64}.\cite{34} This translates into a theoretical capacity of 34 mAh g\textsuperscript{-1}, a far cry from the 372 mAh g\textsuperscript{-1} of graphite.

This failure to use graphite as an anode material, along with the difficulty of finding a proper replacement chilled much of the NIB research in the critical lab to market phase of its development. As a result, this relegated NIB research to a niche field, a trend which was exacerbated in the 1990’s following the development of the commercial LIB. Most researchers concentrated their efforts on the LIBs, leaving NIBs by the wayside.

2.3.3 NIBs: a Pilot Light Reignited

This is not to say that research on the NIB was totally abandoned, and the search for a candidate anode material did not progress during that time. Later attempts by Doeff et al. in the 1990’s using petroleum coke, a non-graphitic material raised the capacity to NaC\textsubscript{24}, effectively being 94 mAh g\textsuperscript{-1}, an improvement, but one that still left a lot to be desired.\cite{35}

At the same time, there was a growing research interest in exploring non-graphitic carbon materials as LIB anodes, in hopes of surpassing the theoretical capacity of graphite. This involved the pyrolysis of oxygen rich organic precursors, mostly plant matter, to yield amorphous carbon. Such carbons showed a deviation from the traditional graphite structure, and as such, introduced the potential of achieving higher capacities, and better performance at high current rates than conven-
tional graphite type anodes. These studies, which occured in the mid 1990’s, with a majority of them conducted by Dahn et al. yielded extensive knowledge and data on the storage properties and behaviors of lithium ions inside amorphous carbon structures.[36, 37, 38, 39, 40]

Much like the efforts devoted to the development of lithium based cathodes 20 years prior, the research of amorphous carbon materials as anodes was appropriated from LIBs to NIBs, with a much greater degree of success. This led to a series of seminal papers by Dahn et al. in the early 2000’s, which demonstrate amorphous carbon anodes had the potential of achieving reversible capacities of close to 300 mAh g$^{-1}$ – a substantial improvement over the previous anode using petroleum coke derived carbon.[41, 42, 43] Furthermore, these papers also proposed a sodiation storage mechanism for sodium ions in these materials, with many of the overarching themes being similar to what had previously been elucidated for lithium ion storage in amorphous carbon.

Following the publications of the amorphous carbon anodes in the early 2000’s, the subsequent decades saw a few more publications dedicated to the subject, but nothing too substantial. More papers were published regarding amorphous carbon as a NIB anode material, but most of those papers merely echoed the claims made by the Dahn et al. papers.[44, 45, 46]

However starting in the early 2010’s, right around the time I started graduate school, NIB literature and research really began to take-off. Several influential review papers were published, newer, and better performing cathode materials were produced, and there began to be a genuine effort to commercialize these batteries.
The external reason for the dramatic increase in NIB research is yet unclear, but it could be a conflux of several factors: the increased need for energy storage technologies, a plateauing trend in LIB research, an emphasis on battery funding from government agencies in the U.S. (of which I was a beneficiary), greater visibility in online scientific publications, and the rise of Chinese influence in academic research – a majority of the researched published in the past 10 years on NIBs has occurred in China. Their prominence in this field, among others, has grown exponentially in the past few decades.
Chapter 3: Carbon Materials & NIBs

Carbon is ubiquitous with our physical world. It is the sixth most abundant element in the universe, and is an essential building block to life here on earth. It can be encountered in many forms, ranging from gaseous CO$_2$, clear diamond, and graphite. For the purpose of this work, we will focus mainly on the "solid-state" aspect of pure carbon, which form the basis for the anode materials in NIBs.

3.1 Carbon Materials: a Story of Allotropes

In chemistry, most lighter elements can generally be ascribed to role of electron donor, or electron acceptor. Elements in the first and second columns of the table tend to be electron donors, while electrons in the sixth and seventh column of the period tend to be electron acceptors. Carbon, possessing four out of the eight electrons needed for a full octet, can act as both a donor, and an acceptor. Additionally, the possession of the four valence electrons gives carbon an affinity for forming four covalent bonds, though in many cases, it doesn’t.

The type of allotropre carbon forms depends on the covalent bonding scheme between the carbon atoms which make up the structure. A carbon structure is connected through a combination of covalent bonds, and Van Der Waals forces, both of which determine the final carbon structure, and the taxonomy that we
utilize to label the material.

3.1.1 the $sp$ Allotrope

The first type of allotrope is one dependent on $sp$ type of bonds. Under the hybridization bonding model, two carbon atoms are directly opposed at 180° to each other, while being connected by a triple bond. In the case of carbon, can also be referred to as carbyne bonds. From this initial representation, the carbyne bond can be extended to form a 1D chain. This time of carbon configuration is rather atypical, and has been researched very little in the context of NIB anodes.

3.1.2 the $sp^2$ Allotrope

More common than the $sp$ bond, is the $sp^2$ bond. For small carbon molecules, under the hybridization bonding model, this type of bond consists of a double bond, also called a carbyne bond, and three covalent bonds. Larger $sp^2$ systems are also very common, and come in the form of large organic molecules such as pentacene, perylene, and coronene, among others (Figure 3.1a). These large organic molecules are considered aromatic as the electrons in the $\pi$ orbitals, which comprise of the double bonds, are considered delocalized, meaning that they are free to roam around the surface of the molecule.

However, this is where we begin to run into a conunrdrum with $sp^2$ carbon structures. The organic aromatic molecules discussed before possess double bond, which
lead to delocalized electrons. However, a $sp^2$ carbon structure can also exist without the presence of these double bonds. This is the case of graphene.

Graphene is a carbon structure possessing three single bonds, along with a delocalized electron on its surface, and spreads out in a large, flat, 2D sheet (Figure 3.1b), with the C-C carbon distance being equal to 0.141 nm. This makes it like the other organic $sp^2$ structures, but it does not have any double bonds. Additionally, the graphene is still considered aromatic, but not in the sense of the organic molecules. The electrons are delocalized, but never too much so.[47]

If this all seems confusing, don’t worry, it definitely is. The differences between graphene and large organic molecules are present, but are difficult to elucidate in pure bonding terms. The key aspect of a graphene sheet is that it should be considered infinite, flat, composed only of single bonds, and most importantly, only one layer thick.[48] The one layer thickness is paramount, as even a second layer of carbon atoms will begin to change the electronic and mechanical properties of the sheet. The organic molecules on their part, are often more than one layer thick, typically re-arranging into molecular solids.[49]

Though graphene is the simplest version of the $sp^2$ carbon structure, it was also the hardest to be discovered. In fact, for a long time, the graphene structure was purely theoretical, as it was though that the Van Der Waals forces prevented it from arranging into a flat, and stable structure. Instead, structures where graphene where stacked on top of each other, like graphite, or curled into a cylinder, like carbon nanotubes (CNTs), or into a sphere, as in the case of $C_{60}$, also referred to as fullerenes & buckyballs, were thought to be the only expression of $sp^2$ type materials that were not organic solids.
Figure 3.1: Representation of the various types of $sp^2$ carbon forms. (a) Coronene molecule. These aromatic molecules are more aptly considered molecular solids. (b) Graphene sheet. Various sub-allotropes which can be derived from the graphene sheet, including (c) C$_{60}$ molecules (d) Carbon nanotubes, and (e) graphite. Ref. [1]

There was good reason for such a pervasive thought: monolayer graphene is in fact really difficult to obtain, and needs specialized equipment, or very repetitive processes.[50] Most of the time graphene is mentioned in the literature, it is should be referred to as few-layered graphene, as it does not meet the monolayer quality necessary to earn the distinction of graphene.[51]

Talking in greater details about the sub-allotropes, graphite is the simplest one: it is just several graphene sheets stacked on top of each other (Figure 3.1e). The sheets sheets are separated by empty spaces referred to as galleries, and held together by Van Der Waals interactions. These separate graphite layers are spaced 0.335 nm apart. Furthermore, they are not directly stacked on top of each other, but rather adopt a staggered ABAB arrangement, where the graphene sheets are offset by half a unit cell length at every level.[52] The layered structure, held together solely through Van Der Waals forces is the reason for the "flaky" nature
of graphite. Additionally, it is also the reason why graphite compounds can easily be intercalated through the addition of guest species, as in the case of LIBs.

CNTs are cylindrically rolled parts of a graphene sheet (Figure 3.1d). They can come in many forms including single-walled CNTs (SWCNTs), where they are comprised of just one cylinder and multi-wall CNTs (MWCNTs), where there are many concentric cylinders. Additionally, they can have different diameters, different chiralities, and various overall lengths, all which play a part in the electronic and structural properties of the materials. [53]

Lastly, C60 structures are the spherical form of a graphene sheets (Figure 3.1c). Aside from the structural complexity of the material, these materials do not find much extensive usage for the purpose of NIB anodes. [54]

3.1.3 the sp³ Allotrope

The last type of bond structure to cover is the sp³ type bond. In this bonding configuration, a carbon atom forms four single covalent bonds with the nearest carbon atoms in a tetrahedral arrangement (Figure 3.2). These sp³ type bonds constitute the building blocks for diamond, which is a clear and non-conductive carbon structure. It is important to point out that the diamond structure occurs only when there are sp³ bonds present over a long range order. Just because individual sp³ bonds exist in a carbon structure, does not automatically make it diamond.
3.1.4 Mixed Carbon Structures

Thus far, three different bonding schemes of carbons have been covered, which, all lead to distinctive structure. However, carbon structures do no have to abide to a specific bonding scheme. They can mix and match bonds in any order, and frequency the like. A carbon structure can be comprised of differing intensities of the three characteristic bonds, which leads to a host of other structures.

Some of these structures can be very orderly. A good example is graphidyne, which is a 2D sheet composed of a mixture of $sp$ and $sp^2$ bonds. It resembles a graphene sheet, yet it is arranged with a different bonding scheme.

However, most mixed carbon structures are not nearly as straightforward as graphidyne. The majority of carbon structures, especially those used for NIB purposes, contain a mixture of $sp^2$ and $sp^3$ bonds. Furthermore, the $sp^2$ bonds in question do not always form the characteristic six-membered rings seen in graphene sheet, sometimes forming four, five and seven membered rings. This leads to an atypical structure, which has no real definite label. As a result, carbon structures which
do not abide by a repetitive bonding scheme simply earn the label: amorphous carbon.

3.2 Failure of Graphite as a NIB Anode

One of the main motivations of this PhD was previously explained: unlike their LIB counterparts, NIBs cannot make use of graphite as an anode material. The reason typically give is one of size: Na ions, being in a lower on the periodic table than Li ions, have trouble intercalating graphite due to a size issue. Na ions are 95 pm, while Li ions are only 68 pm. Thus, the larger size causes problems, as it forces a greater expansion of the graphene galleries, which is energetically unfavorable. However, this explanation is short-sighted, and does not address the real causes of the problem.

3.2.1 The Standard Voltage Potential Explanation

One of the primary arguments against the size explanation is that potassium ions, while being larger than Na ions, manage to intercalate graphite forming a KC$_8$ intercalation compound without a problem. This can even be done electrochemically. Intercalation compounds can also be formed with even larger alkali ions, like rubidium and cesium atoms, leaving opened questions about how well size explains the inability to form a GIC.

However, looking at standard voltage reduction potential versus $2\text{H}^+/$H$_2$, yields
more information. Under standard reduction potentials, \( \text{Li}^+/\text{Li} \) is -3.05 V, \( \text{Na}^+/\text{Na} \) is -2.71 V, while \( \text{K}^+/\text{K} \) is -2.92 V. When a plot of lithiation versus voltage is observed, a long plateau appears in the region from 0.2 V to 0.1 V above the lithium plating potential. This long plateau region has been demonstrated to be when the Li ions intercalate the graphite.

Using deduction techniques, it can be argued that an intercalation potential of 0.2 V to 0.1 V above the plating of lithium metal, translates to an intercalation potential of roughly -0.1 V to -0.2 V below the Na plating potential, if sodium metal is used as a reference. Thus, under such conditions, Na metal would plate onto the graphite surface before being able to intercalate it.

Of course, this explanation suffers from a few setbacks. First off, the conditions near the graphite surface change as the voltage nears the plating potential. At such a voltage, metallic interactions between the ions become more prevalent, which changes certain aspects of solvation with the electrolyte, thus lowering the energy barrier for intercalation. Never-the-less, it allows to explain why both lithium and potassium can intercalate graphite, while sodium cannot.

3.2.2 The Density Functional Theory explanation

Another, and more detailed explanation is offered through the theoretical study of alkali ion intercalation into graphitic structure via density functional theory (DFT) calculations.[55] These calculations determined the alkali atom intercalation process to be a function of three separate steps:
1. Removal of the alkali atom from its host metallic structure.

2. Expansion of the gallery as to make the requisite room for the alkali atom

3. Electron transfer from the alkali atom to the surrounding graphene layers.

Under this three step process, the first two steps are both endothermic, thus incurring an energy penalty, while the last step is exothermic, which can make the reaction more favorable. The first two steps show similar trends. Lithium is the hardest to remove from the host metallic structure, while sodium is easier, and potassium is easier still. For the gallery expansion, the expansion for the lithium atom is less energy intensive than for the sodium atom, which itself is less energy intensive than the expansion for the potassium atom. Again, this all makes sense, as the potassium atom causes the greatest gallery expansion of the three.

However, the last step poses a problem. Whereas the first two steps followed similar trends, the last step does not. The electron transfer from the lithium to the graphene is highly exothermic, and well able to compensate for the first two steps. While the electron transfer from the potassium atom is slightly less exothermic than the lithium one, the energy that needs to be overcome is also less. As a result, the total $\Delta E$ of the process is also negative, meaning that intercalation can in fact proceed.

This is not the case for the Na atom. The electron transfer from the sodium atom to the graphene sheet is markedly different from that of the lithium and potassium. If the trend was consistent, the energy released should be somewhere between that of lithium and potassium. Yet, the energy released from the electron transfer is
below that of potassium. As a result, there is not enough energy to overcome the penalties from the first two steps, thus preventing intercalation from favorably occurring.

In short, the DFT explanation for the failure of sodium atoms to intercalate graphite comes a combination of two factors. The first being the energy penalties incurred to make intercalation possible, and the second being the inability of the electron transfer to cancel out the energy penalties.

3.2.3 Solvent Mediated Intercalation

The failure to intercalate graphite with a sodium atom rests on the fact that the atom will intercalate the graphite alone. There will not be any electrolyte present. In the context of a battery, and of DFT calculations, this is a significant. When a sodium atom is removed from its metal host, it does not go into a vacuum, rather it becomes solvated in a electrolyte, which is an exothermic step. If we are to assume that the sodium atom intercalates graphite fully desolvated, then that exothermic gain of the solvation will be entirely canceled out by the desolvation prior to the intercalation. For this reason, in DFT calculations, we do not have to consider the effect of the electrolyte, if we assume that the sodium atom will interact with the carbon substrate without being in the presence of electrolyte.

However, in the event that an atom could be solvated by electrolyte, and intercalated at the same time, a process called co-intercalation, the the solvation of the sodium atom is an exothermic step. This changes the entire dynamics of the
process, and as a result, makes intercalation possible (Figure 3.3).

This process of co-intercalation of graphitic structure by sodium atoms has in fact shown to be possible in several research papers, with the first one being published by Adelhelm et al. in 2014. Using a glyme based electrolyte, the authors were able to demonstrate the reversible intercalation of graphite by a glyme solvated sodium atom. The intercalation, as evidenced by the long flat voltage plateau in the sodiation curve happens at a potential much above 0 V, thus showing the effectiveness of the glyme, in lowering the energy barrier needed for intercalation.

While the co-intercalation of sodium atoms with glymes, among other electrolytes, does introduce the possibility of utilizing a graphite based anodes for NIBs, it also does pose some issues. The glyme electrolytes tend to be unstable in large voltage
windows. While this is not a problem for testing a proof of concept, it quickly becomes one when operating a full battery. The energy density obtained in a full battery is dependent on a large voltage window, and the use of such an electrolyte would cut down upon that. Additionally, the co-intercalation of the solvent causes a large expansion of the graphite gallery, which induces a significant volume change. Large volume changes, while insignificant in small, lab-scale cells, pose more of an issue in larger cells meant to provide capacity at the Ah scale. Thus, while co-intercalation remains an interesting subject, it does bear more consideration when being evaluated as a long-term solution for large scale batteries.

3.2.4 Structure Mediated Intercalation

Looking back at the DFT findings of the failure to intercalate graphite, it becomes evident that the only thing we can control is the energy penalty associated with the expansion of the graphite – we can hardly do anything about the energy need to remove the sodium atom from the metallic host, or the exothermic gain from the electron transfer. However, it is widely assumed that, if the interlayer spacing can be increased, less of an energy penalty will be incurred, and thus render the whole process favorable.

For this reason, a common trend in NIB anode research has been to increase the d-spacing (e.g. interlayer space) of graphite, through the use of oxygen groups (Figure 3.4), to aid intercalation. Some research groups have claimed that they have been successfully able to expand the d-spacing, which has then led to intercalation. Those claims are somewhat dubious, and thus readers are urged to take
Figure 3.4: Expanded graphite as a NIB anode. The graphite is expanded through the hummer’s method, before being partially reduced. Whether or not it can still classify as graphite is a more debatable issue. Ref. [2]

them with grain of salt.[2]

In papers which claim to have done this, the insertion of oxygen atoms into the interlayer spacing was used. However, the synthesis process turned a pristine graphite structure, into a rather disordered one. Whether the claim that the graphite structure remained, but did so as ‘expanded graphite’, is more of an opinion than a proven fact. The expanded graphite structure did not show the same degree of long-range order as typical graphitic structure, long range order being critical in the definition of ‘graphite’.

Additionally, these expanded graphite structures also have heteroatom artifacts present, such as oxygen, in order to keep the structure expanded. As a result, the structure loses the claim of being a pure carbon structure. While it could be claimed to be doped carbon, this brings up another question: at what point are the presence of heteroatoms no longer considered dopants in the carbon structure, but rather part of a carbon composite. Again, something to consider when evaluating
the claim of an expanded graphite structure.

3.3 Amorphous Carbon

When going over the allotropes, based on the hybridized bonding scheme, they have defined structures. There is also the case of mixing $sp$ and $sp^2$ bonds to create graphdiyne,[57] which is an ordered structure, with multiple bonding schemes. However, when a combination of all the bond types are mixed, the resulting structure is amorphous carbon.

3.3.1 Description of Amorphous Carbon Structure

While amorphous carbon is said to be without shape, there are repeating structural motifs that do allow some degree of characterization. Historically, there have been three main models utilized to describe the structure.

The first model was put forth in the 1930’s by Warren, and was based on X-ray diffraction (XRD) data.[58] Using carbon black as the amorphous carbon basis, the structure was described as a collection of disoriented graphite nanocrystals. On the long range, such a structure did not have order, but if the length scale considered was small enough, graphite-like crystals could be observed. As a result, the important quality used to evaluate the structure of an amorphous carbon was the average graphite nanocrystal size, which could be obtained using the Scherrer equation.[59]
The second model, also put forth by XRD measurements, was put forth by Rosalind Franklin, the same one of the DNA fame. Her model, while similar to Warren’s, implied that the graphite nanocrystals were not just arranged in a spatially disoriented manner, but rather, were connected with $sp^3$ linker bonds. These linker bonds were considered to be thermally stable, meaning that the amorphous carbon structure could not re-arrange into planar graphite, even if annealed at high temperatures. Such carbons were then dubbed non-graphitizable carbons. Meanwhile, carbons that can re-arrange into graphitic structures at higher temperatures were called graphitizable carbons. This is where the difference between “hard carbons”, or non-graphitizable carbons, and ”soft carbons”, which are graphitizable ones, stems from (Figure 3.5).

Figure 3.5: The schematic representation of (a) hard carbon (b) soft carbon. The hard carbon fails to graphitize when annealed at higher temperatures.

The early models by Warren and Franklin did an adequate job of providing a framework, which made characterization of amorphous carbons possible. However, their methods reduced a complex structure to something that was simply a deviation of graphite. Structural complexities such as curvature were lost in the translation of the structural data. This became evident as more refined characterization techniques came to gain more accessibility. Transmission electron microscopy (TEM) measurements of amorphous carbon structures make it evident that many of the
Graphite domains have significant amounts of curvature.

Moreover, other studies, both theoretical and from finer TEM measurements showed the presence of defective $sp^2$ type bonds. Whereas typical $sp^2$ type bonds typically are arranged into six-membered rings, many of the $sp^2$ type bonds in amorphous carbon were found to be arranged in four, five and seven membered rings – thus explaining for the curvature seen in the structure.

To incorporate this concept of curvature and defective carbon rings into the amorphous carbon model, Harris et al. introduced a structure that was based on the annealing fragments of $C_{60}$ molecules using molecular dynamics (MD) simulations. This approach, while theoretically based, allowed to reconcile the presence of curvature with the previously graphitic crystal dependent model.[61]

3.3.2 Working Definition of the Amorphous Carbon Structure

The working definition, which was utilized at the beginning of these studies, and is still utilized in much of the literature is the Franklin model. It assumes that amorphous carbon is comprised of spatially disoriented graphitic nanocrystals that are a few layers of graphene thick, though the thickness of the graphene layers can change based on the synthesis conditions, as well as the type of precursor used. The domains are connected to a various degree through $sp^2$ bonds, while the empty space, or voids, between the domains, is the source of porosity in the carbon material. These voids can also be considered to be the pores present in the structure.
The graphite nanocrystals, also referred to as graphene domains, or graphene nanodomains, are not strictly graphitic. They do not strictly follow the 0.335 nm ABAB packing between the various planes, nor do they have long range lateral order along the AB plane. Some domains can have an expanded interlayer spacing due to AA stacking, the presence of in-plane defects, or even curvature. Thus, a key measure of the amorphous carbon is considered to be its average d-spacing, its average crystal size, and the defect concentration present. The other key measure is the porosity of the material – though that is more a characterization of a macroscale property, as opposed to a nanoscale one.

3.4 Characterization Methods of Amorphous Carbon

The analysis of the structure we can have, as well as the structure-property relationships we can garner from that information, is limited by our characterization methods. This section will go over some of the amorphous carbon characterization methods that were used in the course of this project, as well as some of the other methods used in the literature. One thing that is important to remember, is that most of these methods pertain to the characterization of graphite/graphene. As such, the characterization methods utilized for amorphous carbon depend largely on how much of a deviation there exists between the obtained measurements, and the expected measurements if we were dealing with strictly a graphite/graphene structure.
3.4.1 X-ray diffraction

This technique makes use of X-ray radiation, typically from a CuK-α source to bring about information on the crystal structure of the material. The incident radiation is passed through a sample, where it is deflected/transmitted, by various planes in the structure, thus yielding information of the sample. This is observed through the presence of a peak in the XRD spectrum. The distance between the plane of atoms is obtained through Bragg’s law (eq. 3.1)

\[ n\lambda = 2dsin\theta \]  

(3.1)

In the context of carbon materials, the most important peaks present are the 002 peak, which occurs at 26°, and the 100 peak, occurring at 42.5°. The first peak presents the interlayer d-spacing between the graphene sheets which are stacked together to make the graphitic structure, which can be estimated using Bragg’s law. The second peak represents the lateral direction that runs along the graphene plane (Figure 3.6). In the context of amorphous carbon, the 002 peak is often shifted to the left, as the d-spacing is not uniform. There are some domains that have a d-spacing larger than 0.335 nm, while some have a d-spacing close to the ideal value. It is important to point out here that, for amorphous carbon structures, there is not a single d-spacing, rather there is an average.

In cases where broad peaks are seen, and this will happen often with amorphous type carbon materials, the peak position of the 002 peak can be taken to be the average d-spacing. Furthermore, the full-width at half-maximum (FWHM) can be
used to calculate average crystallite size using the Scherrer equation,[59, 62] where $t$ is the average crystallite length, and is obtained by eq. 3.2

$$t = \frac{\kappa \lambda}{B \cos \theta}$$  \hspace{1cm} (3.2)

For the length in the c-axis ($L_c$), represented by the 002 peak, the value of $\kappa$ is of 0.9, while it is of 1.84 for the length of the a-axis ($L_a$). Using the average d-spacing, as well as the parameter of obtained using the Scherrer equation, we can get a rough estimate of the number of layers per graphite nanodomain, which is a powerful way of characterizing amorphous carbons, as well as other nanocarbons.

An additional measurement that can be garnered regarding the ‘order’ of the graphite structure, was proposed by Dahn et al. and simply involves taking the intensity of the 002 peak, labeled as B, and dividing it by the background intensity, labeled as A (Figure 3.7). The lower the B/A ratio is, the more disordered the
structure is.[63]

Figure 3.7: Representation of the empirical R parameter, as obtained through XRD measurements of amorphous carbon.

3.4.2 Raman Spectroscopy

Raman spectroscopy involves using a laser probe to probe the carbon structure. If the incident light does not trigger any lattice vibrations in the structure, also known as phonons, it will be reflected without any energy loss. However, if the laser triggers Raman active vibration modes, the scattered light will have some energy loss to it.[64] Correlating the Raman signals, and their intensity, with known vibration modes allows us to learn more about the nature of the carbon structure. Since the displacement of the phonons occurs in reciprocal space, it is also important to consider the Brillouin zone of graphene as shown in Figure 3.8a.

The main features spotted in the Raman spectrum of a graphene sheet, one of the building blocks for graphite and amorphous carbon, are the D band at 1350 cm\(^{-1}\),
Figure 3.8: (a) Brillouin zone of graphene, with the first phonon Brillouin zone displayed in red. The Dirac cones are also displayed. (b) Typical Raman spectrum, with the labeled bands, of pristine graphene at the top, and defective graphene at the bottom. Also displayed is a six-membered graphene ring undergoing the $A_{1g}$ ring-breathing mode, associated with the D band. (c) Other vibration modes present in graphene/multilayer graphene. Ref. [3]

the G band at 1580 cm$^{-1}$, and the 2D band, also called the G’ band, as 2700 cm$^{-1}$. The G band at 1580 cm$^{-1}$ is one typically seen in $sp^2$ materials, and stems from the optical $E_{2g}$ phonon (Figure 3.8c). The 2D band is a second order feature where momentum is conserved between phonons traveling in opposite directions, and is also typical of $sp^2$ material.[3]

The D band on the other hand, stems from a $A_{1g}$ ring-breathing mode that must
be activated by a defect in the $sp^2$ structure, and thus is not present in pristine materials (Figure 3.8b).[3] As such, a ratio between the D-band and the G-band is typically obtained, as to quantify the defectiveness of the carbon material, which is called the $I_D/I_G$ ratio. This can be done through either the peak intensities, or the integrated intensities of the respective bands.

There exists many other bands present with carbon materials, such as radial breathing mode (RBM) present in the case of CNTs around 180 cm$^{-1}$, and other minor peaks, especially if the broader beaks are deconvoluted into separate peaks.[64] One example of this are the broad D & G peaks present in defective materials. These can be broken down into five peaks when performing analysis, listed by rising wavenumber: The transpolyacetylene (TPA) band, the D band, the A band, the G band and the D’ band. The origin of the TPA band is from edge-like transpolyacetylene, while the D’ is from an intravalley resonance process in reciprocal space. The origin of the A band is still somewhat unclear, but is assumed to be to the defective nature of the carbon material (Figure 3.9).[4]

The same can also be done with the 2D band in the case of few layered graphene materials. However, it is important to remember that in the context of amorphous carbon, the main use of Raman spectroscopy is to get a rough idea of the defect concentration, and deviation away from the pristine structure – measurements which rely primarily on the D, G and 2D bands.

Aside from providing a figure of merit, and identifying defects present within the material, Raman spectroscopy measurements can also be used to calculate average domain length along the lateral axis using eq 3.3 [65]
Figure 3.9: Deconvolution of the traditional D & G bands in defective carbon, to five separate bands, going from low to high wavenumbers: TPA, D, A, G, D’. Ref. [4]

\[ L_a = 2.4 \cdot 10^{-10} \lambda_{nm}^4 \frac{I_D}{I_G} \]  

(3.3)

On a side note, it must be stated that the \( L_a \) obtained from the Raman measurements tends to overestimate the distance, as compared to the Scherrer equation.[66] Furthermore, it should be noted that the \( I_D/I_G \) ratio, is not indicative of \( sp^3 \) bonds, and that Raman spectroscopy only offers limited insight onto their presence, as the Raman cross-section for \( sp^2 \) materials is much greater than for \( sp^3 \) materials, thus potentially drowning out any signals emanating from such bonds.[67]

3.4.3 Total Scattering Measurements

These measurements were made possible in large part through the help of Wesley Surta in Michelle Dolgos’s group at Oregon State University, as they acted as the point of contact with Oak Ridge National Lab. Special thanks to Wesley for helping to edit this section.
Total scattering measurements take into account both bragg scattering to determine long range order, as well as diffuse scattering to determine short range, and medium range order. In a way, it is similar to XRD measurements, as it uses the scattering of incident radiation in order to generate information about the material. However, while XRD measurements are dependent on the presence of long-range order, something which amorphous carbon often lacks, pair correlation measurements do not.[68] Instead, such measurements can be used to uncover short and mid-range order about a structure, and reveal information such as bond coordination, defect concentration, and coherence length.

These measurements, which also take the name pair distribution function (PDF), radial distribution function, pair correlation function, total correlation functions, or differential distribution functions, rely on scattering of high energy radiation, often times from a neutron or synchrotron source, to generate a scattering vector. This PDF is obtained from G(r) which is a result of eq. 3.4 [69]

\[
G(r) = 4\pi r (\rho(r) - \rho_0)
\]  
(3.4)

where \(r\) is the distance separating disparate radial pairs, \(\rho(r)\) is the atomic density at a specific distance of \(r\), and \(\rho_0\) is the average atomic density of the sample. In order to obtain G(r) from physical characterization measurements, in the case being neutron diffraction, the structure factor S(Q) is generated by eq. 3.5 [69]

\[
S(Q) = \frac{I(Q)}{\langle b \rangle^2} - \frac{\langle b^2 \rangle - \langle b \rangle^2}{\langle b \rangle^2}
\]  
(3.5)
Where $I(Q)$ is the intensity of the scattering vector, and $b$ is the neutron scattering length. The equation used to obtain the structure factor using synchotron radiation would be similar, save for the scattering length. The $S(Q)$ can then be inputted into eq. 3.6 [69]

$$G(r) = \int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ \quad (3.6)$$

as to obtain the $G(r)$. In the previous equation $Q$ is the wave vector, and $S(Q)$ is the structure function, $G(r)$ can be obtained. It should be mentioned that any radiation source could potentially obtain $S(Q)$, and thus $G(r)$, however, not all radiation sources can provide a defined enough $S(Q)$, such that the $G(r)$ would be physically relevant. This is why $G(r)$ measurements are obtained from high energy radiation sources, and do not work with traditional Cu-Kα sources.

This results in a ‘probability map’ of the coordination of atoms in space: by looking at a PDF spectra, one can estimate the probability of finding an atom at that distance. When atoms are within a coordinate distance, the $G(r)$ expresses that (Figure 3.10a & b). Furthermore, one can also estimate the coherence length of the material, by looking when the intensity values of the $G(r)$ become negligible (Figure 3.10c). Thus PDF measurements allow to establish the coherence length, as it relates to long-range order, something which XRD measurements could not do.

For the purpose of characterizing amorphous carbon materials, there are three main takeaways that should be kept in mind when analyzing PDF results.
Figure 3.10: (a) Schematic representation of a graphene sheet, with the radius of the concentric circles representing the nearest neighbor coordination lengths. (b) A typical PDF output displaying short-range order for a carbon material, with the corresponding coordination lengths. (c) Long-range order, and loss of coherence length, for an amorphous carbon material.

1. The presence of a shoulder peak at 0.335 nm.

2. The overall peak intensity.

3. The coherence length.

The first item, the presence of a shoulder peak at 0.335 nm, is used to distinguish amorphous carbon from graphite. In a graphitic structure the presence of the ABAB packing will lead to the presence of interlayer C-C distances of 0.335 nm.[70]
This will be reflected in the G(r) plot as a shoulder peak on the fourth peak. Amorphous carbon, which eschews ABAB stacking, and is somewhat dilated will show no evidence of this peak, and neither will single monolayer graphene (Figure 3.11).

Figure 3.11: Comparisons of a graphite PDF plot, versus a monolayer graphene PDF plot. The shoulder peak at 0.335 nm is highlighted.

The second item concerns that of the overall peak intensity. G(r) plots with lower peak intensities imply a greater defect/vacancy concentration than G(r) plots with higher peak intensities. On their own, peak intensities can effectively be used as comparative measurements between two materials observed under the same conditions, but no too much more (Figure 3.12). However, if additional factors such as the packing density, material density, and scattering length are known, the peaks can then be integrated to obtain a physically meaningful coordination number.[68]

Lastly, the coherence length, or lateral order in the AB direction, can also effectively be measured from the G(r) plot. A material that exhibits long range order, such as that of graphite, will not show a decaying peak intensity, even at higher
Figure 3.12: Comparisons of a pristine, and defective carbon material. The defective carbon material has lower peak intensities than the pristine one.

distance. Conversely, a material like amorphous carbon, which does not possess planar lateral order in the AB direction, shows attenuated intensities at relatively early distances – thus implying a shorter coherence length (Figure 3.13). [71]

Figure 3.13: Comparisons graphite with an amorphous carbon material, in order to obtain the coherence length. The graphite shows consistent intensities, even at long distances, while the amorphous carbon does not.

Overall, for amorphous carbon materials, G(r) measurements are particularly useful, as they provide information that is not dependent on long-range structural order. Unfortunately, there is somewhat of an accessibility barrier, as the equip-
ment needed to obtain a sufficient $S(Q)$ is not always readily accessible in academic labs, and thus necessitates a collaboration with national labs, to have access to such equipment.

3.4.4 Porosimetry

Moving away from the characterization of the short-range atomic structure, another characterization technique used is that of porosimetry, which utilizes gas adsorption measurements in order to determine the overall porosity, and surface area of the material.

For carbon materials, this is typically done via gas adsorption measurements, such as $N_2$ or $CO_2$, were the quantity of the gas absorbed it correlated to an overall porosity and surface area. The measurements are often done a cold temperatures, usually 77K, the temperature of liquid nitrogen, as to increase the amount of gas adsorbed by the sample. The main models for obtaining porosity is usually the density functional theory (DFT) model, while that for surface area is the Brunnaeur-Emmett-Teller (BET) model. As such, they are often referred to as DFT pore volume, and BET surface area. They work by correlating the quantity of gas adsorbed, with the pressure they were adsorbed at.

In addition to being able to determine the overall surface areas and pore volumes, these measurements can also distinguish between the types of pores that exist in a material. Pores, defined at the empty spaces in the material are classified under three categories, as defined by the IUAPC: micropores (less than 2 nm), mesopores
(between 2 and 50 nm), and macropores (50 nm or above). The trends seen in the gas adsorption curve symbolic of the porosity type of the material, and have been classified into six types of isotherms (Figure 3.14).[72]

Figure 3.14: IUPAC types of isotherms which include (I) Microporous materials. (II) Non-porous materials with attraction to the gas. (III) Non-porous materials with negligible attraction to the gas. (IV) Mesoporous materials. (V) Porous materials with weak interactions with the gas. (VI) Homogeneous surface materials.

For our purposes, we will go over the three main ones which are typical of carbon materials. Highly microporous materials typically have large volumes of gas absorptions at very low pressures, with little adsorption after that, making them a type I isotherm. Mesoporous materials typically have a hysteresis at higher pressures between the adsorption and desorption curves: the gas escapes the material at a lower pressure than it entered, like the type IV isotherm. Lastly, material that have a uniform porosity are a mixture between a type I and type III isotherm: they
absorb a lot of gas at lower pressures, but continue to absorb more as the pressure rises.

3.4.5 Microscopy Measurements

The microscopy measurements can be divided into two classes: transmission electron microscopy (TEM), which allows to observe the nanostructure on the nm scale, and scanning electron microscopy (SEM), which allows for imaging on the \( \mu \text{m} \) scale. For the atomic properties of amorphous carbon, SEM measurements are not too relevant, as they only allow for an understanding of the macrostructure.

3.4.5.1 TEM

TEM measurements are helpful to look at the atomic features of the carbon structure within the order of a few nm. In the TEM measurement, electrons are sent through a thin layer of sample, before being captured by a receptor. The information captured is then transformed into a visual image.[73]

These measurements allow us to estimate lattice parameters, such as the d-spacing, look at the layer stacking of graphene, and get an overall idea of the disorder and curvature present in the material. However, aside from the lattice parameters, this is more of a qualitative characterization tool than it is a quantitative one. Furthermore, the images seen are highly dependent on the area of the sample selected, thus leading to the risk of a confirmation bias. Thus, TEM measurements
should be used carefully by researcher, who should be ever present of potential biases they might bring in.

3.4.5.2 SEM

As opposed to TEM measurements, where the electrons are sent through the sample, electrons in SEM measurements are reflected off the sample, captured and the processed into an image. As the electrons are reflected off the sample, it only allows a surface characterization, and thus is most helpful to characterize the large scale structural features of the material.

The length scale of typical SEM image is usually on the order of a few \( \mu \text{m} \), though some modern machines can go below that as well. While they are helpful to determine overall structural morphology, such as whether the carbon is present in a sphere, or a wire, one should also be careful in attributing Na-atom storage properties to macro properties seen on an SEM.

3.4.6 Selected Area Electron Diffraction

Selected area electron diffraction (SAED) is a technique complimentary to TEM analysis. As the TEM electrons are passing through a thin sample, the presence of the atoms in the sample act as a sort of diffraction grating, leaving a distinct diffraction pattern from the electrons. Thus SAED can help to reveal information of the structure of the material, which corroborates that observed in the TEM
image. In the case of highly crystalline material, bright individual spots can be observed, while in amorphous materials, such as carbon, broad diffuse rings, corresponding to the planes are observed.

This technique suffers from the same constraints as TEM, as far as user bias is concerned. Since the user can easily choose the area which is to be used for diffraction, patterns can vary widely, even within the same sample.

3.4.7 Electron Dispersive X-ray Analysis

Electron Dispersive X-ray analysis (EDX) is usually associated with SEM measurements, though it can also be done with TEM measurements as well. Unlike the previously described methods, whose aims were to establish the structure of the carbon material, EDX is used to identify the presence of heteroatoms within the sample. The presence of heteroatoms, which will be described later, is largely due to the precursors, or synthetic processes used in making the carbon.

In the operational phase, electrons from an incident source eject inner shell electrons from the atoms that comprise the sample, leaving behind an empty space. This empty space is then filled by an electron that moves from an outer shell, to the now vacated inner shell. In the process of doing so, fluorescent x-rays are released, which differ in energy according to the element which they came from, as well as the energy transition they have undergone.

This technique is useful to get a rough idea of the elemental composition of the sample, as well as the type of impurities/dopants that it may contain. It is possible
to obtain those, both as a function of mass %, as well as atomic %. However, what
the technique is not helpful for, is to determine the type of bonding scheme of the
elements in question, or the definite mass & atomic %’s present in the sample.
There are more appropriate techniques for doing that.

3.4.8 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) works in a fashion similar to EDX, except
for the radiation source, and the measurement method. In XPS, an incident X-ray
is shone onto a material surface, which causes the ejection of an electron. The
ejected electron is then captured and analyzed for kinetic energy. Based on the
energy of the incident X-ray, and the kinetic energy of the captured electron, the
binding energy of the electron can be determined.[74]

From this analysis of the binding energies, several things can be determined. First,
the elemental composition can be obtained. Furthermore, the type of bonding
scheme of the element, can also be obtained, which makes these measurements
very useful to understand to nature of the impurities and dopants present in the
sample, as they allow to determine how the impure atoms are bonded in the sample.
It must also be mentioned, unlike EDX, which probes the whole sample, the X-
rays utilized in this technique only manage to probe a few nm into the surface of
the sample. As such, XPS is mainly a surface measuring tool. For the purposes
of measuring carbon, this can be deceptive at times, as the oxygen content on
the surface of the carbon material can change significantly based on factors of the
storage environment.
3.4.9 Inductively Coupled Plasma Mass Spectrometry

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is another technique to measure the presence of impurities in carbon samples. It has the advantage of being very accurate, as well as representative of the whole sample, which gives it an edge over both EDX and XPS, as far as measuring impurities is concerned. However, despite being able to measure elemental composition, it cannot do so for oxygen and carbon, which are usually the main elements present in a NIB anode. Thus, the usage of this technique is primarily limited to impurities that are not oxygen/nitrogen related.

3.4.10 CHN/CHNO Analysis

CHN/CHNO analysis makes up for the lack of testing for oxygen/nitrogen offered by ICP-MS, as it is a method that can be used to test of oxygen and nitrogen content. The CHN test, which is the simpler and cheaper of the two, consists of combusting a carbon sample, and measuring the carbon/hydrogen/nitrogen content from the effluent oxides that are produced in the reaction. The CHNO method is slightly more involved, as the oxygen content cannot directly be solved for, and thus is slightly more expensive. However, the CHNO test is an efficient way of obtaining an accurate elemental composition of an entire sample, which the previous methods could not do.
3.4.11 Near-Edge X-ray Absorption Fine-Structure

Unlike typical XRD measurements that rely on backscatter radiation, Near-Edge X-ray Absorption Fine-Structure (NEXAFS) provide structural information through the intramolecular resonance that occur near K-shell excitation threshold of low atomic number atoms.[75] As it pertains to carbon materials, use of NEXAFS directly probes the unoccupied electronic states of the chemical bonds, which in this case are either in the sp$^2$ or sp$^3$ state. Using these measurements allows to obtain a ratio between the absorption from the $\pi^*$ orbitals, which are present in double and triple bonds, and the $\sigma^*$ orbitals, which are present in single bonds – though it does get slightly more complicated, as the level of the conjugation bonds can lead to different absorption energies, with some that may overlap with the absorption from the $\sigma^*$ orbitals.[76] Aside from the ratio between the $\pi^*$ orbitals and $\sigma^*$ orbitals, the adsorption of the $\sigma^*$ orbitals also varies according to the type of bond: an sp$^3$ bond will have an absorption of 291 eV, while an sp$^2$ bond will have an absorption of 297 eV, giving an additional method of differentiating between the two types of bonds. Furthermore, like PDF measurements, the use of NEXAFS also does not depend on long-range crystalline order, and is appropriate for use as a local structure probe.[77] Unfortunately, such measurements usually require a synchotron X-ray source, as the wave length needs to be tunable in order to get the resolution needed for such measurements. As such, NEXAFS measurements were not obtained in the course of these studies.
3.5 Synthesis & Structural Properties of Amorphous Carbon Materials

Having described methods of characterizing carbon materials, we will now describe some synthetic methods, as well as some of the resultant structural properties that can be expected.

3.5.1 Hard Carbon

Hard carbon is typically obtained from the pyrolysis of organic matter, with most of the examples in the literature making use of plant matter. Due to this fact, most hard carbon materials are determined to be 'free', as the precursor materials is generally a waste product, such as straw, corn stalks, corn-cobs, and a lot of cellulose based materials that otherwise have little use: cellulose, in its native form, cannot be digested for energy by humans, and contains too low of an energy density to use as an effective fuel source. While it is possible to refine cellulose into biofuels with higher energy densities, such a process is costly, and thus, not economically viable. As a result, these products are most often discarded, which is the reason why their use as a hard carbon precursor seems appealing: pyrolyzing them, and using them as NIB anodes, would provide some added value.

Aside from plant matter, animal based products, though harder to obtain in large quantities, can also be used as the basis for hard carbon. Precursors such as human hair, egg-whites, and horn come to mind. Although these are viable, one must be realistic about the volume and amount that can be collected in order
to meet the demands of amorphous carbon needed by the market. The animal based products, even if effective, would be very hard to collect and pyrolyze in a substantial amount – no matter how many barbershops you visit. The same can also be said for plant matter. Plant matter, while being a ’waste’ product, is not entirely free. It must be collected and processed. This is energy intensive, as the waste must be transported. Thus, when evaluating potential plant products, one should also consider how available it is, and how feasible it will be to collect and process it.

In the pyrolysis process, there are three phases that must be keenly considered: pre-treatment, treatment and post-treatment. All of these impact the final material properties of the carbon structure, and as such deserve further explanation.

3.5.1.1 Pre-treatment

When pyrolyzing a hard carbon precursor, one can chose to do it with no pre-treatment, meaning the sample is just placed in the tube furnace as is, or include some pre-treatment. Usually, a pre-treatment occurs, which has a few aims.

One of the first aims of a pre-treatment is to reduce the water content. Most precursors contain a significant amount of oxygen and hydrogen, which when released as H$_2$O, can significantly etch the carbon sample – as will be described later. To that end, if a low porosity material is desired, it is good practice to pre-treat the material as to remove hydrogen and oxygen content. Failure to remove significant content of hydrogen and oxygen, will lead to a material of greater porosity.
This can be done through a few ways. The first one is by heating the precursor at low temperatures, usually in the 100°C to 200°C range. These temperatures are high enough to release H$_2$O, yet still low enough that they will not result in combustion of the precursor. Another method is to chemically induce the dehydration of the sample. A potential method for that is the addition of a graphene oxide solution to a sample,[78] which leads to its dehydration, even at very low temperatures. Other chemical methods, such as the addition of TEMPO,[79] have also shown to be viable, though such chemical methods have been less explored.

One of the second aims of a pre-treatment, is the removal of metallic impurities from the sample. If the precursor comes from unpurified organic matter, there is a guarantee that the carbon material will have some metallic impurities: metals are vital to life processes, and thus trace amounts are expected to be found in all organic matter. If those metals are not removed prior to the pyrolysis, they could impact the structural properties of the final carbon material. This is because they can either impact the formation of the graphene nanodomains, or because they have the potential of increasing the porosity.

A common way of removing these trace metals is to conduct an acid-wash of the precursor, using some type of concentrated acid, whether that be HCl, H$_2$SO$_4$, H$_3$PO$_4$, or HNO$_3$. Following the acid treatment, the material must then further be washed with H$_2$O, as leftover salts from the acid washing has the potential of causing greater porosity in the material, as is the case with H$_3$PO$_4$, which is known to be an activation agent.

Of course, the pre-treatment step is optional, and not necessary to the formation of the carbon material. Simply pyrolyzing the precursor is sufficient enough. But the
pre-treatment is one of the ways to control the final structure of the hard carbon material, which is important if we are to optimize the property of the material as an NIB anode.

3.5.1.2 Pyrolysis

Following the pre-treatment, the next step becomes annealing the material at high temperatures. In order to obtain hard carbon materials, the precursor is pyrolyzed under inert gas flow, either N$_2$ or Argon, in a tube furnace. Depending on the temperature of the pyrolysis, the final structural properties of the carbon material can be vastly different.

At temperatures below 1000°C, the resulting carbon material does not exhibit very large graphite nanodomains, or high crystallinity. The XRD spectrum will show a very broad 002 peak, while the Raman spectrum will show a low intensity, and broad D band. Furthermore, a high oxygen content is expected, as the low annealing temperatures are not conducive to removing oxygen from the structure. Lastly, the surface area and porosity are expected to be somewhat elevated, and though it varies between samples, it will definitely be higher than 100 m$^2$ g$^{-1}$.

At higher annealing temperatures, ranging from 1000°C to 1400°C, a more crystalline carbon structure is expected. The size of the nanodomains is expected to be larger, while the average d-spacing is expected to be smaller. The XRD will exhibit a sharper 002 peak, and the Raman spectrum will have a narrower D band, even though the intensity will probably be on par with that of the G band. Ad-
ditionally, there might be small evidence of the 2D band, also increasing the more crystalline trend. Lastly, when compared to the low temperature annealed carbon, there is expected to be less of an oxygen content.

At annealing temperatures of greater than 1400°C, the structure becomes to be more and more like that of graphite, though it never fully graphitizes. Glassy carbon, which is often annealed at temperatures greater than 2000 °C, never fully graphitizes, though it does begin to resemble graphite, in terms of d-spacing, very closely. Keeping up with the previously seen trends, the 002 peak becomes narrower, and more shifted to the right, indicating a large domain size, along with a smaller d-spacing. With the Raman spectrum, the D band is narrower and of decreased intensity, while the 2D band becomes apparent. Additionally, oxygen content is also lowered. Regarding data obtained through PDF measurements, low temperature annealed carbon are expected to have lower peak intensities, along with a shorter coherence length, while carbons annealed at higher temperatures are expected to have higher intensities, and a longer coherence length.

Besides the temperature of the annealing process, other aspects, such as the pyrolysis time, and the heating ramp-up rate, measured in °C min⁻¹, can also be controlled. The effect of pyrolyzing materials for longer periods of time has not been comprehensively studied, though it can be assumed that a longer pyrolysis should favor the formation of a more graphitic structure – and even then, that is a guess at best, as the process of going from an organic structure to a carbon structure is still not fully known.

The heat rate also has a subdued impact due to the prospect of self activation reactions. If a high heating rate is used, in conjunction with a low flow rate of inert
gas, their lies the possibility that the effluent gas can engage in self-activation reactions with the carbon material. Using a lower heat rate would give more time to evacuate the volatile gas, and thus lead to a lower incidence of self-activation reactions. However, lowering the heat rate invariably changes the dynamics of the carbonization process, especially if the material undergoes a liquid/semi-liquid transition. As such, there is no clear cut answer of how the heating rate affects the final structure of the material. Like many things, it depends of the nature of the precursor.

3.5.1.3 Post-treatment

Following the pyrolysis of the carbon material, the obtained carbon material can also undergo a post-treatment. This post-treatment can range from acid washing, as to remove metallic impurities, mechanical milling, as to change the microstructure of the carbon material, and activation as to increase the porosity.

The first post-treatment, acid washing, is similar to what is done prior to the pyrolysis. However, when applied as a post-treatment step, a lot less acid is needed, as the volume of the carbon has shrunk greatly from its precursor phase. Furthermore, the amount of H$_2$O that is needed following this treatment is also less, due to the smaller volume. While this seems somewhat insignificant, it is important to remember that if hard carbon is to be produced in large enough quantities to satisfy grid-level storage needs, these washing steps will start to weigh in on the final cost.
Mechanical milling, or ball-milling, can be used to break the carbon material into finer particles. Depending on the length, and intensity, of the milling treatment, this can have an effect of increasing surface area, defect concentration, and reducing the overall crystallinity of the carbon material. Whether or not this is needed, or desired, depends on what is wanted out of the final material.

The last post-treatment option that is available, activation, involves reprocessing the material in order to increase the porosity and surface area. This can be done through either chemical, physical, or self-activation means. These types of activation mechanism will be discussed in greater details later in this thesis, as they deserve further attention.

3.5.2 Soft Carbon

Unlike hard carbon, which does not re-arrange to form graphitic structures upon high temperature annealing, soft carbon does re-arrange to form a graphitic structure when high enough temperatures are applied. A typical trait of most soft carbon precursors, is that they are often aromatic molecules, with a ratio of oxygen/hydrogen to carbon ratio.

As such, many petroleum and coal byproducts, such as petroleum coke, petroleum pitch, coal pitch, and coal tar, as well as aromatic molecules such as PTCDA, NTCDA, and coronene, all make ideal soft carbon precursors. Due to lower incidence of C-O and C-H bonds, these typically carbonize at temperatures much lower than hard carbon precursors. Whereas most hard carbon precursors need
to be pyrolyzed at temperatures of over 1000°C in order to obtain a good carbon material, soft carbon precursor can be effectively pyrolyzed at temperatures less than that, with a 900°C pyrolysis displaying good performance in many cases.

Use of higher temperatures can also be used, however, one must be cautious, as high temperatures usually lead to a material with greater long-range order, as graphite would have. This makes it markedly different from hard carbon, which at higher temperatures also becomes more graphitic in nature, but only on the short range order, therefore still allowing it to keep some of its hard carbon characteristics. This is not seen in soft carbon, and the closer and closer resemblance to graphite leads to decreased performances, hence the shift away from using high temperature annealing for soft carbon material.

An added benefit from using lower temperature during the pyrolysis process is that fact that there is a lesser need for pre-treatments or post-treatments to remove metallic impurities, or at the very least, not to the point that such treatments are necessary for hard carbon precursors. Some of the potential downside to soft carbon precursors include the toxicity and cost associated with some of the aromatic organic molecules. Precursors such as PTCDA and NTCDA need to be synthesized themselves, and are toxic to handles.

As such, while good materials to use for lab scale synthesis of soft carbon, their scalability becomes a concern. Thus, the most realistic option for soft carbon based materials as NIB anodes, are those such as petroleum coke, and pitch, which are already heavily used items in the synthetic graphite production industry.

From a characterization perspective, these soft carbons follow many of the same
trends as the hard carbons. Use of higher annealing temperatures results in a sharper 002 peak and a larger domain size, as measured through XRD measurements, a smaller D band and more prominent 2D band in the case of Raman spectroscopy, and a decreased defect concentration in the case of PDF measurements. One of the different things though, is that the domains can grow much larger and more freely than in hard carbon, which affects the electrochemical mechanism, as most of the defects then become 'in-plane' defects, which are of a different nature than those found in hard carbon. Lastly, it should also be stated that the surface area and porosity of the amorphous carbon is often quite minimal, much like that of graphite is. When annealed at temperatures greater than 1100°C, surface areas of 10 m² g⁻¹ or less are common, with those values becoming even smaller as the temperature is increased.

3.5.3 Graphene Based Materials

Graphene offers more potential synthesis windows than graphite. These routes can be broadly categorized into two categories, the first one being “top-down” synthesis, while the other one is “bottom-up” synthesis.

From a characterization perspective graphene based materials most often have the resemblance of a very disordered, and defective amorphous carbon materials. The synthetic methods used usually lend themselves to creating few-layered graphene domains that are not very large, as evidenced by the broad and dilated 002 peak on the XRD. Furthermore, most exfoliative procedures lead to a significant D band on the Raman spectra, along with attenuated peak intensities on a PDF spectrum.
Lastly the theoretical surface area of graphene, assuming a 0.141 nm bond length is 2600 m$^2$ g$^{-1}$. Most graphene materials have a surface area under the theoretical area, as graphene sheets that stack up into domains end up having a lower surface area. In fact, one of the main challenges of graphene synthesis is to keep the graphene sheets from re-assembling on top of each other, as to keep the surface area higher. However, if enough defects are induced in the material, the surface area of the graphene structure can in fact be higher than 2600 m$^2$ g$^{-1}$. Inducing significant amounts of defects into the structure allows for surface areas of 3000 m$^2$ g$^{-1}$ or greater, as measured by gas adsorption, since gasses have a preferential affinity to defective sites.

### 3.5.3.1 Top-Down Synthesis

Top down synthesis aims to take regular graphite, and exfoliate it through chemical or physical means into individual graphene layers. The most common approach to this is through use of the Hummer’s method,[80] which involves oxidizing the graphite with functional oxygen group, followed by the reduction of such groups to yield reduced graphene oxide (rGO). When the graphite is oxidized, the individual galleries expand. Upon reduction, oxygen groups will be removed, but the graphite will remain exfoliated, thus leading to the formation of graphene. Various Hummer’s methods procedure differentiate themselves based on the chemicals which they use as oxidizing agents, as well as the methods of reduction that is used.[81, 82, 83] Reduction methods can range from chemical reduction, to microwave and thermal reduction,[84] all of which lead to a slightly different rGO
material. When using this method, it is important to make the distinction that the final product obtained is not pure graphene.

As a result of the oxidation process, some oxygen is bound to be left over on the carbon material, lest very high annealing temperatures, of very reducing agents are used. Furthermore, the rGO obtained using this method is hardly defect free. The final product often include a significant concentration of defects and few layered graphene domains. But again, those parameters are highly dependent on the synthetic process, which gives experimentalists a rich amount of possibilities and combinations to test out.

The other ‘top-down’ synthetic approach for electrochemical materials involves mechanical exfoliation through high energy ball milling. Using this technique, the graphite domains are sheered into graphene domains, thus leading to a “pseudo-graphene” structure. Such an approach, while effectively transforming graphite into a more graphene-like carbon, also leads to a carbon with a higher concentration of defects.

The two methods covered above are by no means inclusive of all of the top-down synthetic methods that are used. Other methods include unzipping of carbon nanotubes, use of solvent based exfoliation, and exfoliation of GICs, and electrochemical exfoliation.

No matter what method is used, it is important to keep the end-goal in mind. If the goal is to produce a specific carbon material, or just intellectual curiosity, the choice in synthetic method matters little. However, if the goal is to make graphene based material on a large scale, the cost of reagents, as well as the labor needed
for the formation of the carbon material should be factored in. One of the key selling points for carbon materials as an NIB anode is that it is cheap. As such, an expansive synthetic process will effectively neutralize it. Additionally, the role of chemical additives in the synthetic process should also be considered, as they often leave behind residues in the final product. If those residues negatively affect the electrochemical performance, removing them should be given more consideration, however, if benign, they can be left alone.

3.5.3.2 Bottom-Up Synthesis

While the top-down approach focuses on taking a graphitic material and turning into graphene, the bottom-up approach does the reverse: it focuses on building graphene sheet from simple precursors on an outward scale. Bottom-up synthetic technique include deposition methods, such as chemical vapor deposition (CVD), flash pyrolysis, and magnesiothermic reduction of CO$_2$.

Of these bottom up methods, CVD is the most common, as it allows exquisite control and fine tuning of the graphene structure, along with the relative ease of my large surface area graphene.[91] In CVD, as gas is deposited onto a catalyst, usually a metal one, which causes the decomposition of the hydrocarbon gas, and it subsequent rearrangement into a graphene structure. Some of the key parameters that can be controlled in CVD include the substrate used for the deposition, the size of the catalyst particles, the precursors involved, as well as growth time and temperature.[92] When the rights conditions are met, such a procedure allows for the formation of uniform, monolayer graphene. Following the growth of the
graphene layer, the material can then undergo post-treatment such as ion etching to make unique structures.[93]

As is, CVD based synthetic technique are ideal to make materials used for determining structure-property relationships, or to test the limits of a material. However, one must bear in mind that the amount of graphene that can be economically produced with such a method is orders of magnitude lower than what will be necessary to meet the demand of carbon material for grid level storage purposes. If such techniques are to be used for large scale graphene productions, engineering improvements regarding the scale up process will need to be made. Thus, as with all experiments, one should keep in mind the question: what is the end goal of this material?

Other bottom-up synthetic techniques include flash pyrolysis, and magnesiothermic reaction of CO$_2$. Flash pyrolysis is an abridged version of CVD, whereby a hydrocarbon is incompletely combusted, thereby leaving a graphene residue as a byproduct.[94] Magnesiothermic reduction of CO$_2$ involves flowing CO$_2$ in a heated furnace over Mg powder, with the Mg subsequently reacting with the incident CO$_2$ gas, and forming MgO and pure carbon, which will rearrange into graphene.[95] Both of these aforementioned synthetic methods have the benefit of both lower in material cost, and labor, than CVD methods. However, this cost does come at the expense of quality, as the resulting material will be few layer graphene, with a higher defect concentration. This doesn’t mean that it will be inferior graphene in the context of NIB anode materials, but it does mean that the graphene will be different, which must be taken into consideration.
3.5.4 “Nano” Carbons

The last class of amorphous carbon materials that is routinely discussed in the literature, are the “nano” carbons. These carbons are amorphous in nature, but come with a distinct morphologies, such as nanofibers, spheres, or a controlled porosity, thus giving the sense that their architecture was engineered. This sets them apart from other type of amorphous carbon, where the final morphology, aside from the particle size, and the porosity, is not controlled. It is assumed that, by controlling the carbon architecture, favorable structure property relationships can be extolled, and their performance of the NIB anode can be optimized.

From a structural point of view, most nano carbons contain all the hallmarks of defective, short ordered, and porous carbon. The XRD spectrum often contains a broad 002 peak, the Raman spectrum shows a broad D band, the PDF has a faster peak attenuation that graphitic type materials, and the material is generally of high porosity.

3.5.4.1 Carbon Nanofibers

Carbon Nanofibers (CNFs) are one dimensional fibers, usually greater than 20 nm wide. The one dimensionality of the fiber is somewhat of a misnomer, the CNF is wide enough that it should not be considered to be in a single dimension, yet for all intents and purposes, such an assumption is made. Thus, it is best to claim that, on the macroscale, CNFs are one dimensional, but on the nanoscale, they are not.
The process of making the fibers involves either a vapor deposition process of a polymer, or a spinning process. The vapor deposition process is akin to the methods of making CNTs, whereby polymer growth into a fiber is catalyzed at a reaction site. The spinning technique involves having a polymer solution, and obtaining a fiber via extrusion. This can be done through many different techniques, such as electrospinning, dry-jet spinning, or wet-jet spinning.

For NIB anode purposes, the precursive polymer nanofibers can either be commercially obtained, or synthesized in-house, with the method of choice being electrospinning, considering its lower cost, and ease of setup. When making polymers through electrospinning CNFs is devising the right polymeric precursive solution. Most are composed of polymers such as poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), poly(vinyl pyrrolidone) (PVP), poly(ethylene oxide) (PEO), poly(methyl methacrylate) PMMA, or any combination of such material. It should be noted that this list is by no means extensive, and as such, more polymer solutions are feasible for CNF synthesis.

These polymer solutions, which mostly contain carbon, oxygen, hydrogen, and in a few cases, nitrogen, easily carbonize to carbon, or doped carbon, and thus can directly be used as an anode material. Furthermore, an added benefit is that the cross linked CNFs can effectively function as a self-standing anode, thus limiting the need to add binder to the anode. However, more often alloying and conversion nanoparticles are also included in the CNF solution, leading to fibers that are ‘decorated’ with heterogeneous particles. As a result, the performance of the anode can include electrochemical contributions from the alloying/conversion processes, while mitigating the negative effects associated with the volume expansion, and
the low electrical conductivity.

3.5.4.2 Porous Materials

If refined architectures such as hierarchically porosity, uniform porosity, foam-like structures, core shell structures, and hollow spheres are desired chemical and physical activation techniques will not be enough. Synthesis of such structures is typically done through the use of a templating method, which can either be a hard-template, soft-template, or a combination of both.

In a hard templating method, an inorganic based template, such as SiO$_2$, is impregnated with a carbon precursor, before being pyrolyzed and removing the template through chemical means. This procedure allows for effectively making a carbon material with the “negative” image of the template. Mesoporous carbon, hollow carbon spheres, and hierarchically porous carbons – carbons with interconnected macro, meso and micropores, have all successfully been made in this manner.

Unlike the hard templating method, where the inorganic template needs to be removed following the pyrolysis, the soft templating method involves a direct one step reaction. In this method, a template is made, either using polymers, block-copolymers, naturally occurring polymers, metal-organic framework materials (MOFs), or polyaromatic framework materials (PAFs), and subsequently pyrolyzed. The porosity imbued in the resulting carbon material is similar that the one that was present in the precursive material, but unlike the hard template method, there is not need to etch away the hard template. However, in some cases,
both the hard and soft templating methods have been employed simultaneously, in order to achieve the desired porosity effect.

3.5.5 Doped Carbons

Thus far, the aforementioned carbon materials contain strictly carbon – or at the very least, intend to. There are some that have a higher oxygen content than others, but except in the case of the expanded graphite anode, most of that is not intentional, and is an artifact from the synthetic process. However, strictly limiting the anode material to carbon, though the intent of this thesis, limits the inherent possibilities in the structure property relationships. By including a small amount of heteroatoms into the carbon structure, we can change both the structural and electronic properties of the carbon material, as to bring about different sodium atoms storage properties, and potentially, better performances.

The type of dopants that can be used vary, but they are generally lighter non-metal elements, that can be classified into two types of dopants: $n$-type, and $p$-type. The $n$-type dopants, such as nitrogen, sulfur, and the halogens introduce extra electrons to the carbon structures, thereby lowering the ionic interactions with the positively charge sodium ions during the electrochemical process. The sodium atoms cannot transfer as much of their charge to the carbon sheet, due to the already increased presence of electrons. Though there are decreased interactions, it is important to remember that this is not necessarily a bad thing; the anode material is meant to be reversible, and if the interaction is too strong, there lies the possibility that the reaction will be irreversible.
The \textit{p}-type dopants, such as boron, are the opposite. They withdraw electrons from the carbon structure, and thus can more readily accept electrons from the sodium atoms, being that the sheets are electron deficient. As a result, this leads to increased ionic interactions between the atom and the carbon substrate, leading to a more favorable binding energy. Whether or not this process will be reversible is another question altogether, but at the very least, the initial sodium atom storage will be favorable.

Aside from considering just the electron gain/loss of the doped material, it is important to understand how the dopant material has incorporated itself into the carbon structure, as well as how the dopant affect the overall carbon structure. Dopants like nitrogen can incorporate themselves into a graphene lattice in many different ways, with each one having a slightly different effect on the overall electronic property of the material. With large atoms such as phosphorous and sulfur, it is not immediately clear that the atoms work their way into the graphene lattice as is. More often, they are incorporated into the carbon structure in the form of oxides, which greatly changes their impact on the structural and electronic properties. Thus, for doped carbon materials, XPS is a critical characterization test, as it allows to determine the atomic configuration of the dopant atom, which is necessary in order to fully understand its impact on the structure.

The synthesis of doped carbon materials generally occurs through a pyrolysis process of either, a precursor already containing the dopant atom of choice, or a pyrolysis under an atmosphere that contains the dopant atom. In the case of the most common type of doping, nitrogen doping, the most common synthetic methods relies on pyrolyzing a previously nitrogen containing material at low temperatures,
as to end up with a doped carbon. Other methods include a pyrolysis process with the addition of \( \text{NH}_3 \) gas, or with the addition of \( \text{HNO}_3 \). Similar processes are also used in the case of phosphorous, sulfur, and boron doping, all of which can be done through mixing a precursor with the acid solution, before pyrolyzing it.

However, when using the acid mixing approach, it is important to keep in mind that the acid can act as an activation agent, and as a result lead to greater porosity. If that is the case, there comes to be a conundrum: are the differing electrochemical properties due to the increased porosity of the material, or are they due to the presence of the dopant atom? Thus, when trying to ascertain whether of not the doping of the carbon has tangible effects on the electrochemical performance, it is important to compare carbon materials with similar structural properties, and let the only difference be the presence of the dopant atoms.

3.6 Activation of Carbon Materials

In the prior section, it was mentioned that a key factor in the final structure of a carbon material was its porosity. Furthermore, the porosity is an intriguing factor, as it is a feature of the carbon material that we have more control over in the synthetic process. Unlike the domain size, where our only control is the precursor type, and annealing temperature, porosity can be controlled following the pyrolitic step, using activation processes. These processes enable us to take a low surface area/low porosity material, and transform it into a porous material. The types of activation processes can be classified into three different types: physical activation, chemical activation, and self-activation.
3.6.1 Physical Activation

Physical activation relies on the modification of a pre-existing carbon structure. Such activation relies on gas-solid reactions, which utilizes chemical reactions. Some of the most common physical activation methods involve CO$_2$ activation and steam activation, though other gasses such as NH$_3$ have also shown to work well as activation agents.

3.6.1.1 CO$_2$ Activation

The CO$_2$ activation involves the Boudouard reaction [96] described below (eq. 3.7 & Figure 3.15)

$$ C(s) + CO_2(g) \rightarrow 2CO(g) + C(s) $$  \hspace{1cm} (3.7)

Figure 3.15: Schematic illustration representing the CO$_2$ activation of carbon concept.

This type of activation is done by flowing CO$_2$ gas in a tube furnace at elevated
temperatures with a carbon material inside. Tuning the temperature of the tube furnace, the flow rate of the CO$_2$ gas, as well as the duration time of the activation reaction allows for control of the degree to which the carbon material is activated. Through simple $\Delta G$ calculations, it can be shown that the CO$_2$ activation reaction will become spontaneous at temperatures above 700°C. This leads to a tradeoff when considering the activation parameters. Achieving a high degree of porosity at temperatures close to 700°C can be a lengthy process. This can be sped up if a higher activation temperature is used, as it will favor the formation of CO, thus leading to more activation in a shorter amount of time. However, it was been demonstrated that use of higher temperatures also favors the formation of larger pore sizes, which is counter-productive if one is aiming to increase solely the microporosity.

3.6.1.2 Steam ($H_2O$) activation

Another widely used form of carbon activation is done through steam activation. Steam activation involves mixing $H_2O$ in the gas form with solid carbon in an inert environment at elevated temperatures. This will lead to the following two reactions

\[ C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \]  \hspace{1cm} (3.8)

\[ C(s) + 2H_2O(g) \rightarrow CO_2 + 2H_2(g) \]  \hspace{1cm} (3.9)
We notice that in the following equations 3.8 & 3.9, we obtain CO, CO$_2$ and H$_2$ as products, which can then be re-used in the following reactions causing further activation to happen

\[ C(s) + 2H_2(g) \rightarrow CH_4(g) \]  \hspace{1cm} (3.10)

\[ C(s) + CO_2(g) \rightarrow 2CO(g) \]  \hspace{1cm} (3.11)

Furthermore, the CO, H$_2$ and secondarily produced CH$_4$ can engage in feedback loops leading to the further formation of activation agents through the reactions

\[ CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \]  \hspace{1cm} (3.12)

\[ CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \]  \hspace{1cm} (3.13)

As with the CO$_2$ activation reaction, some parameters that can be controlled to influence this reaction include the furnace temperature of the reaction, the reaction duration time and the flow rate of the steam used in the reaction. As with the CO$_2$ activation method, the thermodynamics of steam activation necessitate a temperature greater than 700°C, with higher temperatures and greater flow rates leading to greater amounts of activation in a shorter time. However, there is still the tradeoff between micropores formed in a longer time at low temperatures and larger pores created in a shorter time at high temperatures.
3.6.1.3 NH\textsubscript{3} Activation

The use of NH\textsubscript{3} as an activation agent was also found to increase the porosity and surface area of carbon materials. Systematic studies by Luo et al. showed that annealing N-doped carbon under a NH\textsubscript{3} flow led to activation through the following reaction: [97]

\[ 4NH_3(g) + 3C(s) \rightarrow 3CH_4(g) + 2N_2(g) \] (3.14)

Such a reaction actually has a dual effect on the resulting carbon materials, as it was found to be an effective way to both increase the porosity as well as dope nitrogen atoms into the carbon structure.[97, 98] However, special precautions must be taken before employing such a method, as the use of ammonia gas at high temperatures has a risk of explosion.

3.6.2 Chemical Activation

Chemical activation is the other major type of activation mechanism. Unlike physical activation, chemical activation is a one-step process, where the pyrolysis of the carbon material, along with the activation process is done simultaneously. In the process, a variety of chemical activation agents are added to the carbon precursor prior to pyrolysis. During the subsequent pyrolysis, the chemical products will alter the decomposition of the carbon precursor and subsequently change to the morphology of the final structure. The chemical agents which have been used
for chemical activation can range from alkali based compounds such as KOH,[5] NaOH,[99] and K$_2$CO$_3$,[100] to acids such as H$_3$PO$_4$[101] and metal salt products such as ZnCl$_2$[102] and FeCl$_3$.[103]

The activation mechanisms for these chemical activations are more complex than those of the physical activations, as there are a lot more possibilities for side reactions. As chemical activation was not a prominent theme of this thesis, only KOH and H$_3$PO$_4$ activation will be discussed in detail.

3.6.2.1 KOH Activation

In the case of KOH activation, the reaction mechanism is broken down in the following manner.[104] First, the alkali hydroxide reacts with the carbon to form an alkali metal, hydrogen gas and a carbonate.

$$6KOH(s) + C(s) \rightarrow 2K(s) + 3H_2(g) + 2K_2CO_3(s) \quad (3.15)$$

From thermodynamic principles, this first reaction can occur at temperatures as low as 570°C. If the temperature of the reaction rises to 700°C and above, the H$_2$ gas will go on to activate the forming carbon material through the same reactions that had been described with physical activation. Following the initial breakdown of the alkali hydroxide, the metal product along with the carbonate begins to impact the activation of the carbon material. The presence of the carbonate as well as the alkali metal were confirmed by XRD measurements at an intermediate
stage during activation. Potassium in this process plays a very unique role as K atoms can intercalate into the gallery of as-formed carbon structures, forming K-carbon intercalation compound. This is directly related to the activation effect of KOH. Lastly, at temperatures greater than 760°C, the carbonate may begin to decompose, leading to the formation of the CO$_2$ activation agent as well as a further activation reaction.

\[
K_2CO_3(s) \rightarrow K_2O(s) + CO_2(g) \quad (3.16)
\]

\[
K_2CO_3(s) + C(s) \rightarrow K_2O(s) + 2CO(g) \quad (3.17)
\]

Additionally, more feedback loops can become involved in the reaction when we consider to presence of the pure metal along with the breakdown of the superoxide. The pure metal, in this case K, can combine with CO$_2$ as such

\[
2K(s) + CO_2 \rightarrow K_2O(s) + CO(g) \quad (3.18)
\]

The superoxide can then also become involved in the activation through the reaction

\[
K_2O(s) + C(s) \rightarrow 2K(s) + CO(g) \quad (3.19)
\]

From the reactions above, the feedback loops can lead to extremely large degrees
of activation. However, these feedback loops as well as the contribution of the K$_2$CO$_3$ in activation can largely be avoided if the reaction temperatures are kept below 750°C. In fact, most literature published on the use of KOH as an activation material typically concluded that an activation temperature of 700°C is the most conducive to forming an optimal microporosity. This may be due to the fact that lower reaction temperatures will not cause pore widening or pore collapse, as would be at higher temperatures. The activation mechanism with NaOH also relies on the formation of a sodium carbonate for the activation mechanism.[105] However, Na metal cannot be intercalated into carbon structure by thermal treatment.

Figure 3.16: Schematic illustrating the pyrolysis and activation of hemp fiber into porous graphene nanosheets. Ref. [5]
3.6.2.2 $\text{H}_3\text{PO}_4$ Activation

In the case of activation using acidic chemical agents, such as $\text{H}_3\text{PO}_4$, the theoretical mechanisms for the activation reactions are not as developed as the ones for the alkali salts: most of the theories accounting for the activation have come from empirical observations such as physisorption measurements of final structures. Undoubtedly, the introduction of the acids changes the pyrolytic process, a process whose mechanism still eludes us, without even considering the addition of acidic additives. Thus, the field has yet to develop a comprehensive carbon activation mechanism for acids though a few ideas have been proposed.

In the case of activation with acidic agents, it is hypothesized that the acid content first causes a breakdown in the organic precursor at very low temperatures, leading to a re-arrangement of the precursor.[106] Additionally, the addition of acids protonates the oxygens of the glycosylic ‘linker’ bonds in the cellulose chains, which affects the hydrolysis of such bonds during pyrolysis.[107] As the pyrolysis temperature increases, the acids begin to break down, forming oxides on the surface of the carbon material. These products eventually along with the rearranged structure lead to different properties obtained in the final materials.

Despite tenuous understanding of the acidic activation process, numerous studies have revealed methods of controlling the degree of activation, as well as the optimal temperatures needed for the reaction. When controlling activation, it was demonstrated that only small amounts of $\text{H}_3\text{PO}_4$ are needed to be added to the precursor to develop the microporosity, and that larger amounts generally cause an increase in larger pore sizes.[107] Most of the literature published on $\text{H}_3\text{PO}_4$...
activation has suggested that a reaction temperature of 450°C to 500°C was best suited for the development of microporosity.\cite{108, 109} The low temperatures used are evidence that this activation method works by affecting the early stages of pyrolytic process. Whereas other activation methods depend on the consumption of carbon by an etchant at higher temperatures, the use of an acidic agent bypasses this, and instead forms an intrinsic porosity. This is extremely useful, as the lower temperatures promote both a higher microporosity as well as a higher yield of the final carbon material.

On the other hand, the use of acidic materials as activation agents also results in different surface properties of the carbon material. In a study that compared activation via H$_3$PO$_4$ activation versus CO$_2$ activation, SEM images of the final carbon products revealed a much rougher surface percolated with cavities in the case of the H$_3$PO$_4$ activation, compared to a much smoother surface in the carbon activated via CO$_2$. The authors of that study concluded that activation using acidic materials had its greatest impact on the surface of the carbon, as opposed to CO$_2$ activation that had a greater impact on the inside structure.

3.6.3 Self-Activation

Self-activation could be characterized as a subset of physical activation. It occurs primarily due to the H$_2$O released during the pyrolysis of organic sources, which ends up etching the very substrate it is making.\cite{110, 111} There is also the possibility that some of the metal compounds present in the organic material could also act as activation agents, thus leading to chemical activation – however, this
being an organic precursor, there likely isn’t a lot of metals present in it to start with, only trace amounts.

The degree of self-activation that will occur in a material depends on two things: how much latent H$_2$O content exists at higher temperatures, as well as how well ventilated the reaction chamber is. If most of the H$_2$O content has been evaporated at lower temperatures, the potential for self activation greatly diminishes, as there will be no activation agent left at higher temperatures. This is the reason why the low temperature dehydration of sucrose using a GO solution, or cellulose with a TEMPO solution was so effective at reducing the surface area: both limited the H$_2$O content that was released at higher temperatures. This also explains why soft carbon precursors, which typically have lower oxygen and hydrogen content do not see as much self-activation as the hard carbon obtained from the organic sources.

The second factor is the ventilation of the reaction chamber. If all the volatiles that are emitted from the organic material are quickly removed, the potential for self activation goes down greatly, as the etchants do not have time to react. As such, self-activation can be controlled by tuning the flow rate used during the pyrolysis.

While the concept of self-activation may not be very relevant on the lab-scale, it is a concept that should garner more attention if the ultimate goal is to scale up the production of amorphous carbon. With large scale pyrolysis, there will be a much greater generation of volatile gasses in the pyrolysis process, which will need to be evacuated in a timely and efficient manner as to prevent the activation of the sample. This will present a considerable engineering challenge, which we should keep in mind when trying to establish which carbon precursor will be the most
ideal to produce amorphous carbon anodes for NIBs.
Chapter 4: Electrochemical Methods

Talk of carbon aside, it is important to remember the driving force of this thesis: batteries. The carbon that we are hypothesizing about, synthesizing, characterizing, is meant to be used as an NIB anode. That being the case, once the material is used to make a battery, the electrochemical parameters need to be tested.

Different electrochemical tests reveal different processes, all giving distinct pieces of information on the carbon material and its electrochemical behavior with sodium atoms. When pieced together, these various bits of information can be combined to give a complete picture of the structure property relationships of the amorphous carbon material.

4.1 Galvanostatic Cycling

This technique stands for fixed current as a function of time, and is aptly named after the Italian scientist who introduced the concept of an electric current: Luigi Galvani. In galvano static cycling, current is outputted at a fixed rate, while other parameters, mainly voltage, and time, are measured. The current rate, while delivered in amperes (A), is usually determined as a function of loading mass, which is the mass of active material on the electrode. As such, current rate is usually measured in units of mA g$^{-1}$, as to normalize the current as a function of
the weight.

Cycling is usually done between two set voltage potential, and when the total capacity, which is obtained by multiplying the current rate with the time it was applied, is measured, it is usually indicated in terms of mAh g\(^{-1}\). This number is usually the one by which we decide whether an anode material is good or not. Anodes with high capacities are desired, while anodes with low ones are not. There are other factors that are important in a battery, but this one is one of the most important.

Expressing capacities in mAh g\(^{-1}\) can be both a good thing, and a bad thing. It is a good thing, as it allows an objective comparison between two different anode materials. If one anode is heavier than another, it can store more sodium atoms, just by virtue of being larger. This leads to a higher overall capacity, but it does little in telling us whether one material is better than the other. Thus, normalizing the capacity by weight allows such comparisons to be made. On the other hand, this is also its greatness weakness. If an anode material performs well, but only at low loading masses, this can be obscured by normalizing the capacities by mass. An anode that performs well as a loading mass of 1 mg cm\(^{-2}\), but cannot do the same at higher loading mass is of little use for grid level energy storage. Thus, when reporting capacity, it is not enough to just report it in mAh g\(^{-1}\), it is also important to give the loading mass, and the net mass as well.

By plotting the galvanostatic charge/discharge cycles as a function of voltage, we can also determine several electrochemical processes occurring with the material. Long plateaus usually mean a fixed electrochemical reaction, while a sloping profile indicates an electrochemical reaction that proceeds in a changing environment.
4.2 Potentiostatic Cycling

As opposed to galvanostatic cycling, where the current is fixed, and the voltage/time vary, potentiostatic cycling changes the voltage as a function of time, while recording the current. In a way, this is like galvanostatic cycling, as the amount of charge that a battery can store is measured, but what used to be the long plateaus in the galvanostatic cycling had been traded for peaks in the potentiostatic cycling.

The potentiostatic cycling, which is often referred to CV for ‘constant voltage’, is good for determining the voltage at which reduction-oxidation reactions occur, as well as measuring the difference between capacitive contributions to currents, and redox active contributions to the current. This is done through use of eq. 4.1

\[ I(V) = k_1 s + k_2 s^{\frac{1}{2}} \]  \hspace{1cm} (4.1)

where \( I(V) \) is the current as a function of voltage in amperes, \( s \) is the sweep-rate in volts sec\(^{-1}\), \( k_1 \) is a constant for the capacitive current contribution, and \( k_2 \) is a constant for the redox current contributions, which are diffusion limited. The use of eq. 4.1 is dependent on running many different sweep rates on the same electrode while re-arranging the equation into a linear \( y=mx+b \) format as seen in eq. 4.2

\[ \frac{I(V)}{s^{\frac{1}{2}}} = k_1 s^{\frac{1}{2}} + k_2 \]  \hspace{1cm} (4.2)
4.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a method of using current pulses in order to uncover electrochemical processes happening in a battery. In EIS, either the voltage, or the current, is varied sinusoidally over a range of frequencies. Since the stresses placed on the system are varied, the system responses do not behave with traditional assumption. A simple example of this is a capacitor. With a DC current, the charge on the capacitor is proportional to the voltage, which itself is proportional to the current and the resistance. However, if an AC current is used, the charge on a capacitor becomes dependent on the frequency of the current, and is not in phase with the voltage. This can get more complicated when additional circuit components are factored in such as electrical double layers, resistors, inductors, and in the context of an electrochemical cell, ionic gradients, diffusion controlled processes and solid electrolyte interphase (SEI) layers. An example of a typical circuit for a sodium half cell battery is displayed in Figure 4.1

![Figure 4.1: Circuit representing the carbon anode interface in a Na half cell. $R_1$ is the electrolyte resistance, $C_1$ & $R_2$ are the double layer capacitance and resistance, $C_2$ & $R_3$ are the surface layers capacitance and resistance, while $W$ is the Warburg element, which is diffusion restricted.](image)

For analysis, once a representative circuit is chosen, a computational program will
‘fit’ data values to the circuit, as to match the output that is recorded during the electrochemical trial. This approach is done numerically, as an analytical solution to the problem would be very difficult to obtain even with just a few circuit components, and exponentially so with each growing component.

By analyzing the response, information such as cell resistance, diffusion coefficients, and the charge interface can be obtained. This leads to a more complete understanding of the environment inside the electrochemical cell, and thus helps with our understanding of the structure property relationships of the carbon material.

4.4 Diffusion Techniques

Through careful electrochemical testing procedures, as well as the repurposing of certain diffusion equations and electrochemical models, coefficients for the diffusion of sodium atoms in carbon electrodes can be obtained. Though I will not derive the diffusion equations here, I will briefly discuss their operational principle, and list their associated equations as to introduce them. Some of the diffusion model, especially the GITT model, will be discussed heavily later in this thesis.

4.4.1 Galvanostatic Intermittent Titration

Galvanostatic intermittent titration (GITT) is a diffusion technique in which a current pulse is applied for a finite period of time, whereby the voltage of the cell increases/decreases.[112] Following the current pulse, the voltage of the cell
will equilibrate to steady state conditions. When the change in voltage between the transient current pulse, and the resting state is taken as a ratio, a diffusion coefficient can then be estimated. This is the resulting equation (4.3) when using a thin-film, one dimensional geometry, for the assumptions being used is

\[
D = \frac{4}{\pi \tau} \left( \frac{m_b V_M}{M_b S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2
\]

(4.3)

When \( D \) is the diffusion coefficient in cm\(^2\) sec\(^{-1}\), \( m_b \) is the mass of the anode, \( V_M \) is the molar volume, \( M_b \) is the molar mass, and \( S \) is the surface area of the anode. In this case, the assumption is made that the surface area is the contact area, and not the specific surface area of the carbon material. For the second term in parentheses, \( \Delta E_s \) is the change in voltage under steady state conditions when compared to the starting voltage, while \( \Delta E_t \) is the change in voltage under transient current conditions, also compared to the starting voltage. It also should be noted that the initial resistance drop, often called the ‘IR’ drop, is not included in the voltage change (Figure 4.2).

If there is a large change in voltage under the transient current, but a negligible one under steady state conditions, it means that the electrical pulse resulted in polarization of the electrode, but no significant changes in composition, as the overall voltage did not change. As a result, this is indicative of a low diffusion coefficient. Conversely, if there is a large change in both the transient current, and the steady state current, it means that there was little polarization of the electrode, and as such, a high rate of diffusion.
4.4.2 Potentiostatic Intermittent Titration

The difference between GITT, and potentiostatic intermitted titration (PITT), is much like the difference between galvnostatic cycling and potentiostatic cycling. In galvanostatic cycling, the current is a fixed quantity, while the voltage, or time, is measured. In potentiostatic cycling, the voltage change is a fixed quantity, while the current response to the voltage change is measured.[113]

In the case of diffusion techniques GITT uses current pulses, while monitoring voltage responses of the on/off time periods. In PITT, a voltage is applied and maintained until the current reaches a steady state condition close to 0 amperes. The diffusion is then estimated by looking at the nature of the current response, and how it decays over time. Briefly, the diffusion time $\tau$, is equal to the diffusion length over the diffusion coefficient (4.4)

Figure 4.2: Schematic illustration the calculation of diffusion using the one dimensional, GITT approximation.
\[ \tau = \frac{l^2}{D} \]  

(4.4)

This diffusion time is related to the amount of charge, \( Q \), inserted into the electrode for a small potential step, as modeled by eq. 4.5 [114]

\[ \tau = \left[ \frac{Q\Delta x}{\pi^{\frac{1}{2}} I t^{\frac{1}{2}}} \right]^2 \quad \tau << l^2 \]  

(4.5)

In the previous equation \( It^{\frac{1}{2}} \) is a Cottrell slope that is constant in the short time domain, and is dependent on potential, while \( \Delta x \) is the concentration coefficient of the inserted species, in this case, sodium. The following model is best suited to evaluate diffusion using small potential time steps, as that minimizes the effects of competing ionic interactions, such as charge screening at the electrode interface, or finite diffusion lengths. More thorough analysis utilizing PITT can be performed, where different regions of the current decay curve are analyzed using different methods, but these will not be reviewed here.

### 4.4.3 Capacity Intermittent Titration

The last type of diffusion technique that will be covered is the use of capacitive intermittent titration (CITT). Such a technique is a mixture of both GITT and PITT. In CITT, a current is applied until a designated voltage is reached. Once the designated voltage is reached, the voltage is held constant while the current rate drops to a negligible value. Once the current rate has dropped to a low
enough value, the capacities obtained during the constant current section of the cycling, and those obtained during the constant voltage section of the cycling are plugged into a diffusion equation, leading to a diffusivity value that is voltage specific.[115, 116]

Qualitatively speaking on the issue, it can be reasoned that obtaining a high capacity during the galvanostatic charging process, while a low capacity in the potentiostatic charging process is sign of a high diffusion coefficient: most of the atoms are able to be stored at a specific voltage, with little polarization. Conversely, obtaining a low capacity during the galvanostatic part of the charge, while obtaining a high capacity in the potentiostatic region of the charge, is sign of a low diffusion coefficient, as the voltage change was clearly occurring due to a polarization of the electrode, as opposed to the insertion of atoms.

4.5 Electrochemical Cells

Having gone over the different types of electrochemical methods used for testing cells, it is also important to go over the type of cell that is used for testing. The type of cell used has a significant impact in the overall result, as different cell setups lead to different environments, all which affect the electrochemical cycling in a distinctive way.
4.5.1 Half cells vs. Full cells

An electrochemical cell is comprised of two working electrodes: a cathode, the positively charged terminal, and an anode, the negatively charged terminal. For fully functional NIBs, the anode is comprised of amorphous carbon, while the cathode is some type of layered material, such a prussian-blue, or prussian white, which is an iron-cyanide type of material. Those are called full cells.

However, for lab-scale testing, it is common to only have one working electrode, and substitute the other one for a piece of sodium metal foil. The rationale behind this is to take away the uncertainty brought on by cycling a cell with two working electrodes. If one is trying to evaluate the performance of an amorphous carbon material, the last thing they should be worried about is the performance of the other working electrode. In a full cell, there are concerns such as load balancing, the availability of sodium atoms in the cell, and the state of both electrode materials. However, by replacing a working electrode with a piece of sodium metals, those concerns are non-existent. Throughout the life of the cell, it can be assured that there will always be a plentiful supply of sodium atoms needed for cycling, as the sodium metal provides the atoms in excess, and there is no need to worry about a loss of electrical conductivity, or contact with the metal.

While being beneficial to limit the factors that can affect cycling by using a half-cell, there is a downside to it: it does not replicate the actual electrochemical process. While one does not have to worry about the finite presence of sodium atoms in a half-cell, that is a real concern in a full cell. Thus, if a material with a very high capacity and a good rate performance in a half-cell, is also beset with
poor efficiencies, it will hardly be an ideal candidate for a full cell, as it will be sure to consume all the available sodium atoms within a matter of cycles.

Additionally, use of a half-cell can also lead to performances that are poorer than expected. It has been shown that the presence of a sodium metal electrode in a half cell leads to the quicker degradation of the electrolyte. As such, the quicker degradation of the electrolyte leads to decreases in capacity and cycling efficiency, thus leading to the conclusions that a material leads to poor electrochemical performances, when really, it was the fault of the sodium metal. Thus, if someone wants to draw conclusion about how a material will fare in a full cell, the testing should be done in a full cell.

4.5.2 Two electrode cells vs. three electrode cells

The other type of issue aside from cell configuration is that of a two electrode cell versus a three electrode cell. In a two electrode cell, the voltage potential is measured between the anode and the cathode. Since both of these electrodes are electrochemically active in the process, there is the potential that the voltage readings are not as accurate as they should be, due to increased polarization of the system. This is somewhat of a problem, considering that most of the electrochemical cycling is based on charging/discharging between certain voltage windows. Thus, if the voltage is inaccurate, this leads to the potential that the electrochemical step can end prematurely: cycling machines cannot evaluate if a full charge has been obtained, they only operate according to the parameters they can measure, which in many cases, is voltage. Stopping the cycle prematurely will lead to
a lower capacity, and thus, might cause some erroneous conclusions – especially when it comes to rate cycling, where a three-electrode cell displays much better capacity.[117]

A way to avoid these problems is through the use of a three-electrode cell, also called a T-cell. In a three-electrode cell, the voltage is determined from the potential difference between the reference electrode, such as a Ag/AgCl, a mercury-based Saturated calomel electrode, and the working electrode, or if a half-cell is being used, a piece of sodium metal (Figure 4.3). Since the reference electrode is not actively participating in the electrochemical reaction, there is a more accurate voltage reading for the cell. As such, when the reaction is determined by a voltage cutoff, it is more likely to go to completion. Thus, using a three-electrode cell allows for a more thorough understanding of the electrochemical processes involved, as there are less worries regarding the experimental parameters, and limitations, of the experiment.
Figure 4.3: Schematic illustration of a three-electrode-cell. Courtesy of Ismael Rodriguez-Perez.
Chapter 5: Computational Methods

One of the main issues with experimentally based research is its validity: replicating a good result over and over again is no small task, as is avoiding the danger of confirmation bias. If one obtains a great result, but cannot replicate it, one of two things can happen. The research can attribute it to luck, or an outlier, and move on to something different. Or, they can try, and try again, until they obtain the original result, tightening & varying experimental parameters at every iteration. This approach mostly depends on what is seen as valuable. If time is valued over results, then the first approach is the most sound, as it will save time, which will hopefully be diverted towards more productive pursuits. The only down side is that if the result was indeed promising, one will never know. If the result is more important, then by all means, one must keep trying. However, this could lead someone into a proverbial ‘rabbit hole’, which might be fruitless, though that also depends on one’s attitude regarding the exploration of rabbit holes.

Yet, there is a middle ground. Advances in modern information technology, also known as computers, have made it much easier to do theoretical research using numerical methods, which has allowed for a different method of research. Unlike experimental research, which lies at the mercy of countless external parameters, computational research is more controlled. Systems with variable parameters can be built from first principles, the variables can then be stressed, and the response of the system can then be measured. The applied ‘stresses’, whether they be
forces, temperatures, or potentials, are in essence mathematical functions, which are applied to the system numerically. With the advance of modern computers, computer processors, and graphics cards, the number of these operations that can be performed per second has increased by orders of magnitude – which has allowed the computations to get ever more complex.

Since these factors being computed are controlled, excluding randomness parameters, by the user, the results are easier to replicate. As such, theoretical research is able to avoid the main difficulties of experimental work, as they are more repeatable – and in the even something is not repeatable, a more concise pathway can be analyzed.

However, there is also a great difficulty in utilizing computational methods for research: there is no guarantee that the results obtained are physically relevant. Computers, for one thing, are great at generating data. Whether that data means anything or not is another story altogether, and thus, the key challenge in performing computational research: obtain physically relevant data from theoretical calculations.

To date, several different ‘categories’ of computational research methods have been developed, with each having their own merits, and being best suited for different types of problems. These computational methods can range from multi-physics model which look at diffusions over large scales, to atomistic simulations which calculate energies from electron densities at the nm scale. Like all the fields of science that have pre-dated it, computational research is far from a universal research
field, but rather, one that contains many fiefs, domains and principalities. Over the course of this research, Density Functional Theory (DFT) was the primary computational method used, along with some molecular dynamics (MD).

5.1 Density Functional Theory

DFT is a computational method that seeks to elucidate the electronic structure of matter. This application has made it of key importance in applications ranging from simulating atoms, molecules, solids, and even fluids. From the calculations, many different physical properties can be estimated, such as material structure, vibrational frequencies, ionization energies, electrical properties, magnetic properties, and reaction reaction pathways, among other things.

When exploring physical processes at the atomics level, the ultimate goal is to solve the Schroedinger equation, as to obtain the energy and wavefunction of the atom/system in question. For a many atom problem, such as those that would be found when evaluating properties of materials, the time independent schroedinger equation would be

\[
\hat{H}\Psi_i(x_1, x_2, ..., x_N, R_1, R_2, ..., R_M) = E_i\Psi_i(x_1, x_2, ..., x_N, R_1, R_2, ..., R_M) \quad (5.1)
\]

For a system consisting of \(N\) electrons and \(M\) nuclei, the Hamiltonian would then be
\[ \hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{1}{2} \sum_{A=1}^{M} \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} Z_A r_{iA} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \]  

(5.2)

Where \( A \& B \) run over the \( M \) nuclei, while \( i \) and \( j \) are the \( N \) electrons in the system. The first two terms are the kinetic energy of the electrons, while the other terms are the electrostatic interactions between the nuclei and electrons, and repulsive electron/electron and nuclei/nuclei interactions.

We can use the Born-Oppenheimer approximation to simplify the Hamiltonian to a ‘Electronic Hamiltonian’ which would be

\[ \hat{H}_{\text{elec}} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} Z_A r_{iA} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} = \hat{T} + \hat{V}_{\text{Ne}} + \hat{V}_{\text{ee}} \]  

(5.3)

Where \( \hat{T} \) is the kinetic energy operator, \( \hat{V}_{\text{Ne}} \) in the potential of the nuclei acting on the electrons, and \( \hat{V}_{\text{ee}} \) is the electron/electron repulsion. The solution to this hamiltonian is expressed by

\[ \hat{H}_{\text{elec}} \Psi_{\text{elec}} = E_{\text{elec}} + \Psi_{\text{elec}} \]  

(5.4)

With these equations, the energy for a system can be approximated with

\[ E(\Psi) = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]  

(5.5)
and thus, it is expected that the ground state energy be obtained by the ground state wavefunction

$$E(\Psi_0) = E_0$$  \hspace{1cm} (5.6)

Instead of solving the Schrödinger equation using wavefunctions, DFT theory makes use of the Hohenberg Kohn theorem, which states that the total energy of a system of electrons in a external potential can be given exactly as a functional of the electron density – a functional being a function of a function.[118] Thus, instead of solving for the wavefunction to get the energy, we can approximate the presence of the electrons as an ‘electron gas’ at to solve for the ground state energy.

Thus we can rewrite eq. 5.3 as

$$E(\rho) = T(\rho) + E_{Ne}(\rho) + E_{ee}(\rho)$$ \hspace{1cm} (5.7)

which can also be written as

$$E(\rho) = T(\rho) + E_{ee}(\rho) + \int \nu_{ext}(r)\rho(r)dr$$ \hspace{1cm} (5.8)

Where $E(\rho)$ is the total electronic energy as a functional of the electron density $\rho$, and $\nu_{ext}$ is the external potential.

In practice, DFT calculations are run by guessing an electron density $\rho_0$, which is then used to build a set of initial wave functions using the equation
\[ \rho(r) = \sum_i^N |\psi_i(r)|^2 \]  

(5.9)

The Kohn-Sham potential based on this density is obtained through the functional derivative of \( E(\rho) \) giving

\[ \nu_{KS}(r) = \nu_{ext}(r) + \int \frac{\rho(r_1)}{|r - r_1|} dr_1 + \nu_{xc}(r) \]  

(5.10)

This result is then plugged into the Kohn-Sham Hamiltonian

\[ \hat{H}_{KS} = -\frac{1}{2}\nabla^2 + \nu_{KS}(r) \]  

(5.11)

Which is then used to solve

\[ \hat{H}_{KS}\psi_i(r) = \epsilon_i + \psi_i(r) \]  

(5.12)

This last equation gives a new set of wavefunctions, which can be used to obtain a new electron density. If the density found at the end of the process is the same one that was guessed at the beginning, the system will be considered converged, and the energy obtained will be the desired one. If not, the process will continue, until it becomes self consistent.[119]
Chapter 6: Effects of Activation on Hard Carbon Anodes

6.1 Abstract

One of the biggest priorities for a viable amorphous carbon anode in an NIB is to have a high gravimetric capacity. Graphite anodes in LIBs have a theoretical gravimetric capacity of 372 mAh g$^{-1}$. By comparison, the upper end of capacity for amorphous carbon NIB anodes is around 300 mAh g$^{-1}$. While this is adequate, a higher capacity would be beneficial, as it would allow more charge to be stored with the same amount of material, and thus greatly cut down on the cost of NIBs for electrochemical energy storage. Not only would it decrease the material costs, but it would also decrease the labor costs, which are quite substantial in the whole process. Herein, an initial project was devised where the porosity of hard carbon materials was to be systematically increased through both CO$_2$ activation, and the use of different annealing temperatures. The rationale for this project relied heavily on Dahn el al. ‘falling card’ model of sodium ion storage in amorphous carbon, which postulates that sodium atoms can be stored in either the graphene nanodomains of hard carbon materials, as well as their micropores.[43] In the end, it was found that increasing porosity and surface area did not benefit the capacity in any meaningful way, and that there existed an inverse relationship between those two factors and reversible capacity.
6.2 Introduction

Under the sodium atoms storage model proposed by Dahn et al., the atoms can be stored in two distinct fashions. The first method is to insert them between the graphene sheets in the graphene nanodomains, while the second method relies on forming quasi-metallic nanoclusters in the pores of the structures.[43] The first phase, intercalative storage between graphene sheets, occurs in the sloping part of the galvanostatic voltage curve, while the second part, the storage in the nanopores, occurs in the low voltage plateau part of the galvanostatic storage curve, as seen in Figure 6.1

![Galvanostatic Charge/Discharge Profile](image)

Figure 6.1: Schematic illustration of the ‘falling card’ model, as postulated by Dahn et al., along with the associated voltage curve of both sodiation, and desodiation.

Using the model as a guiding principle, we then hypothesized that increasing the microporosity of a carbon material through an activation procedure would lead
to more favorable sodium storage features, and correspondingly, a higher capacity. Thus, a systematic study was carried out using CO$_2$ activation as a method to increase the porosity of hard carbon materials, as to gage the effects on the electrochemical performance, which, hopefully, would result in higher gravimetric capacities.

6.3 Experimental

6.3.1 Material Synthesis

The active hard carbon material used in this study is derived from sucrose (Macron Chemicals). Sucrose is dehydrated for 24 hrs under atmospheric conditions at 180°C. Chunks of the resulting material are pyrolyzed under continuous argon gas flow in a tube furnace for 6 hrs. The pyrolysis was done at 800°C, 900°C, 1000°C and 1100°C, with a heating rate of 5°C min$^{-1}$. CO$_2$ activation was performed on samples pyrolyzed at 1000°C at temperatures of 700°C, 800°C and 900°C for durations of 1 hr, 2 hrs, 5 hrs and 10 hrs with a heating rate of 10 °C min$^{-1}$ and a CO$_2$ flow rate of 100 cm$^3$ min$^{-1}$.

6.3.2 Characterization Methods

Following the synthesis of the hard carbon material, it was characterized with XRD using a Rigaku Ultima IV Diffractometer operating at 40 kV and 40 mA using Cu
Kα radiation (λ = 1.5406 Å) and a WITec confocal Raman Spectroscopy with a 514 nm laser. Surface morphology was obtained through a FEI Quanta 600 SEM. Surface area was obtained through the Brunauer-Emmett-Teller model (BET) and pore volume was obtained through Density Functional Theory (DTF) using N₂ sorption with a Micromeritics ASAP 2020 Surface Area Analyzer. CHN elemental analyses were performed on the samples pyrolysed at different temperatures by the Environmental Division of ALS Global.

6.3.3 Electrochemical Measurements

Electrodes were made using a 7:2:1 weight ratio of hard carbon, Super-P carbon black (TimCal) and poly-1,1-difluoroethene (PVDF) binder, respectively. This was mixed in an n-methyl-2-pyrroldinone (NMP) solvent before being doctor-bladed onto copper foil. Once the anodes were prepared they were punched into disks with loading masses typically between 1.5 to 1.8 mg cm⁻² which were then vacuumed and moved into an argon-filled glove box for coin cell assembly. The coin cells were composed of a solid sodium metal counter electrode, a glass-fiber separator (PALL) and a 1.0 M NaClO₄ electrolyte solution dissolved in a 1:1 weight mixture of ethylene carbonate / propylene carbonate (EC/PC).

The batteries were galvanostatically cycled on an Arbin BT2000 system at an initial current rate of 40 mA g⁻¹, which translates into a cycling rate of C/8 as we consider 300 mAh g⁻¹ to be 1 C. Higher rates from 100 mA g⁻¹ to 1 A g⁻¹ were used to investigate the rate capability of the materials. The capacity contribution from the Super-P additive was taken into account, where 20% of the reversible
capacity from the Super-P electrode was calculated for corresponding rates and subtracted from the reversible capacity of hard carbon/super P electrode material – however, this was only a negligible amount. Cyclic voltammetry was performed on a VMP-3 multi-channel workstation at a scanning rate of 0.2 mV s$^{-1}$ at room temperature.

6.4 Results

The XRD (Figure 6.2), and Raman (Figure 6.3) both show profiles of an amorphous hard carbon structure, however, nothing much more can be gathered from the data. The d-spacings, the domain sizes, and the $I_D/I_G$ ratios are almost all the same, giving us very little to go off of as far as differentiating the carbon materials. The only notable difference was the complete amorphicity of the carbon activated at 900$^\circ$C for 10 hours, as it shows the lack of a defined 002 peak. Furthermore, in some cases, the peaks appear to be of different intensity, but that is moreso a factor of the collected background of the XRD profile, rather than the nature of the carbon material itself. This could have been caused by a slightly different alignment of the XRD machine, as the profiles were not collected on the same run, as well as a different packing fraction of the material on the sample holder.

Also, being are aware that it is possible that impurities in pyrolysed carbon can have an impact on the Na$^+$ ion storage. Elemental analyses for the carbons obtained at different pyrolysis temperatures were conducted. All the materials tested have carbon ranging from 93 to 97 mass % and hydrogen from 0.2 to 0.6 mass % with the rest as oxygen (Table 6.1). Thus, the composition of the electrodes is
relatively uniform.

<table>
<thead>
<tr>
<th>Pyrolysis Temperature</th>
<th>Carbon Mass %</th>
<th>Hydrogen Mass %</th>
<th>Oxygen Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C</td>
<td>95.49</td>
<td>0.60</td>
<td>3.91</td>
</tr>
<tr>
<td>900 °C</td>
<td>93.79</td>
<td>0.39</td>
<td>5.82</td>
</tr>
<tr>
<td>1000 °C</td>
<td>96.20</td>
<td>0.21</td>
<td>3.59</td>
</tr>
<tr>
<td>1100 °C</td>
<td>97.44</td>
<td>0.31</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Table 6.1: Elemental analysis of hard carbons obtained at different pyrolysis temperatures.

Figure 6.2: XRD patterns of different samples. a) Samples after CO\textsubscript{2} activation at 900°C for different durations. b) Samples of 700°C-10h and 800°C-10h. The untreated sample in a) and b) is the hard carbon pyrolysed at 1000°C.

Despite any obvious differences between the carbon structures, we pressed on, testing them for electrochemical performance with an initial current rate of 40 mA
Figure 6.3: Raman Spectra shifts for a) 900°C CO$_2$ activation series b) 700°C -10hrs and 800°C-10hrs CO$_2$ activation. c) Different Pyrolysis temperatures. The untreated label refers to the sucrose sample pyrolysed at 1100°C.

g$^{-1}$. cycling performance of carbons pyrolysed at different temperatures.

The unactivated sample has an initial reversible capacity of 290 mAh g$^{-1}$. After activation of 1 hr and 2 hrs, the capacities drop to 239 mAh g$^{-1}$ and 208 mAh g$^{-1}$, respectively. The samples that were activated for 5 hrs and 10 hrs exhibit even lower reversible capacities of 120 mAh g$^{-1}$ and 49 mAh g$^{-1}$, respectively. It is evident that CO$_2$ activation at 900°C decreases reversible capacity, with longer activation durations yielding progressively worse results. We hoped that milder activation temperatures of 700°C and 800°C would be more conducive to forming the desired nanopores, and offer an improvement over those obtained at 900°C. However, these lower temperatures also caused a decrease in reversible capacity.
Interestingly, longer activation durations at lower temperatures do not necessarily lead to lower capacities. Contrary to what had been observed at 900°C, the 700°C-2 hrs activated carbon shows an initial reversible capacity of 206 mAh g\(^{-1}\), the lowest of the 700°C series, while the 700°C-5 hrs has the highest reversible capacity at 264 mAh g\(^{-1}\). All in all, there is no clear beneficial trend offered from looking at the activation, as can be seen in Figure 6.4 a-c. The only clear trend that can be seen is that activation at 900°C (Figure 6.4a), only leads to decreases in performances. So there is that. But aside from that, there is not much else.

On the other hand, DFT pore volume and BET surface area, calculated through \(\text{N}_2\) sorption measurements, show dramatic changes following \(\text{CO}_2\) activation. All activated samples exhibit greater measurable pore volume and surface area than the untreated control. The increased surface porosity is evident from the SEM images (Figure 6.5). Higher \(\text{CO}_2\) activation temperatures and/or longer reaction times give rise to larger pore volume and surface area. For example, the 900°C-10 hrs sample yields a surface area of 1410.3 m\(^2\) g\(^{-1}\) and a pore volume of 0.91 cm\(^3\) g\(^{-1}\), comparing to a pore volume of 0.042 cm\(^3\) g\(^{-1}\) and a surface area of 58.7 m\(^2\) g\(^{-1}\) for the unactivated material (Table 6.2).

We then plotted the first reversible capacity of all the samples as a function of their measurable specific pore volume and surface area. When a linear regression analysis was performed, the data yields coefficient of determination values (R\(^2\)) of 0.889 for the pore volume plot and of 0.879 for the surface area plot, however such values were heavily influenced by outlying ‘anchor’ points.

To minimize the bias from the outlying data points from 900°C-5hrs and 900°C-10hrs, while spreading out the clustered ones, we plotted them on a log10 scale
Figure 6.4: Initial cycling performance at 40 mA g$^{-1}$ for carbons activated a) 900°C b) 800°C c) 700°C for different durations and d) Initial cycling performance of carbons pyrolyzed at different temperatures

of the pore volume and surface area values. The consequent R$^2$ values obtained are 0.793 and 0.810 for the pore volume and surface area plots, respectively. Both models demonstrate that reversible capacity is inversely proportional to DFT pore volume and surface area.

Following the CO$_2$ activation, we tried to gauge the effect that different sucrose pyrolysis temperatures would have on the active material. For this, we utilized temperatures of 800°C, 900°C and 1100°C compared to the 1000°C used for our original material.
Figure 6.5: SEM images showing surface macropores (greater than 50nm) of sucrose-derived carbon a) pyrolysed at 1000°C, unactivated, b) pyrolysed at 1000°C and activated under CO₂ at 900°C for 10 hrs. mesopores (2nm-50nm) and micropores (less than 2nm) are not observable at such low magnification.

Once again, the reversible capacities are closely related to porosity values. The material obtained at 1100°C has the lowest measurable pore volume and surface area, 0.015 cm³ g⁻¹ and 24.8 m² g⁻¹, of the all samples obtained. It yields an initial reversible capacity of 335 mAh g⁻¹ with the contribution of super-P carbon taken out. Conversely, the sample pyrolysed at 800°C has the highest pore volume and surface area of the series at 0.199 cm³ g⁻¹ and 265.8 m² g⁻¹, respectively, and only achieved a reversible capacity of 200 mAh g⁻¹ (Table 6.3).

When the data points from the different pyrolysis temperatures were added to the plots, the R² values stay relatively constant: 0.862 for the DFT Pore Volume model and 0.844 for the Surface Area model. The R² for the ln transformed models is also unchanged, standing at 0.786 for the ln DFT Pore Volume model and 0.816 for the ln Surface Area model (Figure 6.6). Looking at the results of the regression analyses performed, all of the p-values obtained, with 30 degrees of freedom (DF), are below 1.5·10⁻¹¹. A p-value is the probability of obtaining a test statistic (e.g.
$R^2$ equal to or greater than one obtained at random. A p-value of less than 0.05 is considered statistically significant. This proves that there is very strong evidence linking reversible capacity to DFT Pore Volume and Surface Area.

![Figure 6.6: Linear regression, plotted on a log10 scale of a) Specific capacity vs. BET surface area. b) Specific capacity vs. DFT pore volume.](image)

Considering that $N_2$ can only be adsorbed in pores approximately equal to or larger than 0.4 nm,[120] we can infer from the models that Na$^+$-ion storage in hard carbon is highly dependent on the absence of such open pores. This leads us to classify the carbon atoms that contribute to the surface area and porosity as ‘exposed carbon atoms’. The percentage of ‘exposed carbon atoms’ is available through the equation

$$\frac{MM \cdot A_t}{2\pi r_2 \cdot N_A}$$  \hspace{1cm} (6.1)

We assume an exposed Carbon atom contributes to measurable surface area with
a single hemisphere, whose area is equal to $2\pi r^2$ with $r$ equal to 0.73 Å, the half the bond length of adjacent carbon atoms in the graphene sheet. Using this estimation along with $A_t$, the measured BET surface area in m$^2$ g$^{-1}$, we can estimate the number of exposed Carbon atoms in 1g of sample. Dividing the estimated number of exposed carbon atoms in 1g of sample by the theoretical number of atoms in 1g of carbon, we are able to solve for the percentage of exposed carbon atoms. The factors MM and NA, being the Molar Mass and Avogadro’s number allow us to do just that.

We then used this to solve for the percentage of unexposed carbon atoms by using the equation

$$Unexposed\ carbon\ atoms = 1 - \%\ exposed\ carbon\ atoms \tag{6.2}$$

Using this metric it was found that the material exhibiting the lowest reversible capacity had only 8.7% of unexposed carbon atoms, while the best performing material had 98.4% unexposed carbon atoms. Plotting the values of reversible capacity vs. Logit transform (eq. 6.3)

$$Logit = ln\frac{\%}{1 - \%} \tag{6.3}$$

of the percentage of the unexposed carbon atoms yields an $R^2$ value of 0.89 with a p-value of $6.3 \cdot 10^{-16}$ on 30 DF (Figure 6.7). This suggests that, unlike unexposed atoms, exposed carbon atoms have inferior contributions towards Na atom storage. This may be due to the fact that the exposed carbon atoms tend to act as nucleation
sites for solid electrolyte interphase (SEI), a passivation layer that stems from the decomposition of the electrolyte solvents or salts. This passivation layer may disable the Na atom storage on the electrode surface due to its electronically-insulating nature and block the access of Na atoms to the enclosed voids inside the carbon structure.

Figure 6.7: Linear regression of the reversible capacity versus the logit of the unexposed atoms %.

Evidence of the greater SEI formation on high surface area material can be seen through a comparison of EIS measurements. These were taken at various voltages in the course of the initial discharge. The low-surface-area carbon (24 m² g⁻¹), referred to as lowSAC, has the larger initial semi-circle, indicating a higher resistivity for interface charge transfer. However, once the batteries have been fully discharged at 0.01 V, the high surface area carbon (1410 m² g⁻¹), referred to as high SAC, exhibits a much larger semi-circle than the low SAC (Figure 6.8). The discrepancy seen at the on the initial EIS run is due to the fact that the battery had not been cycled yet. The first cycle often changes some of the battery conditions in the half-cell, and as such, EIS spectras before cycling can vary greatly,
irrespective of the anode material.

![Nyquist plot comparison](image)

**Figure 6.8:** A comparison of Nyquist plots of electrochemical impedance spectroscopy results of high (1410 m$^2$ g$^{-1}$) and low (24 m$^2$ g$^{-1}$) surface area carbon materials as electrodes. The measurements were taken ex-situ at various stages during the first discharge. The plots at the same voltages from high-surface-area and low-surface-area electrodes have been superimposed for clarity.

It is also well known that SEI formation causes irreversible capacity during the first cycle and is proportional to the measurable surface area of carbon materials.[121] To confirm this, we plotted the percentage of irreversible capacity over the discharge capacity in the first cycle vs. the ln transformed pore volume and surface area for all the samples. A linear regression analysis yields reasonable R$^2$ values. Both corresponding p-values, obtained with 30 DF, are below 7·10$^{-9}$, thereby implying that there is strong evidence linking irreversible capacity with DFT Pore Volume and Surface Area (Figure 6.9).

We further investigated the electrochemical properties of the two materials. The charge/discharge profiles differ greatly between lowSAC and highSAC. The former displays two distinct features during desodiation. The first is a relatively flat
plateau that runs from 0.05 to 0.2 V. This is followed by a sloping curve to 2.0 V. The flat plateau of the desodiation curve can be attributed to the de-insertion of the sodium ions from voids between graphite nanodomains. The sloping curve stems from the sodium-ion de-intercalation out of graphite nanocrystals. The latter eschews these characteristics. Instead it exhibits a capacitor-like behavior where the voltage rises almost linearly from 0.01 V to 2.0 V during the same desodiation process (Figure 6.10).

The lower reversible capacity for high surface area materials is clearly associated with the loss of capacity obtained below 0.2 V. This portion of capacity can be attributed to the de-insertion of sodium ions from voids inside the closed hard carbon structure according to the hypothesis by Dahn et al. With higher porosity generated, such closed hard carbon structure has been destroyed, which is responsible for the observed loss of capacity at low voltage, e.g. below 0.2 V. The capacity
Figure 6.10: a) Galvanostatic charge-discharge profiles of lowSAC, carbon pyrolysed at 1100°C, unactivated, b) charge-discharge profiles of highSAC, carbon pyrolysed at 1000°C and activated at 900°C for 10 hrs.

obtained at higher than 0.2 V may be from either the de-intercalation of ions from graphitic structures or electrical double layer capacitance. In order to quantify the loss of capacity at low voltages, a ratio of the reversible capacity under 0.2 V over the total reversible capacity was calculated (Table 6.4).

When comparing these ratios to the respective measurable specific surface areas, we discovered that low surface area materials typically obtain around 50% of their reversible capacity below 0.2 V. On the other hand, higher surface area materials, notably the 900°C-5hrs and 900°C-10hrs samples, obtain only 10% of their reversible capacity under 0.2 V. The aforementioned ratio vs. surface area was plotted and fitted with a linear regression model that yields an R² value of 0.831 and a p-value of $4.2 \times 10^{-13}$ (Figure 6.11). When increasing open porosity of hard carbon, the volume of the closed hard carbon structure conducive for sodium storage is certainly diminished. This is why the capacity is inversely proportional to the specific pore volume/surface area.
Figure 6.11: The ratio of capacity obtained below 0.2 V over the total reversible capacity as a function of measurable specific surface area

6.5 Conclusion

From this experiment, we have proven that there exists an inverse relationship between porosity/surface area values of a carbon material, and its reversible capacity. Moreover, this proved two things: first, CO$_2$ activation, to any extent, will not result in any capacity increase of the material. Additionally, higher annealing temperature, which induce a lower porosity, result in higher capacity values.

There are two explanations to the inverse capacity vs. porosity relationship. The first one is that greater porosity is often obtained through an increase in larger pore sizes. As such, the larger pores come at the extent of the smaller ones, and thus take away their ability of storing sodium atoms. Conversely, low porosity values preserve the high concentration of very small micropores, which are effective in storing sodium atoms. According to the Dahn model, this would be sensible, as
micropores are associated with sodium storage on the low voltage plateau. The highly porous materials do not have a very significant low voltage plateau, as they do not have as many micropores. This would explain for the lower capacity. The opposite would hold true for the high capacity, low porosity material.

However, there is somewhat of an issue with this previous explanation. Despite having a larger macroporosity, the highly porous carbon materials also have a much larger microporosity – so it cannot be said with absolute certainty that the disappearance of micropores is strictly to blame for the lower capacity. In fact, since the lowest porosity materials had the best capacity, it could be suggested that sorption techniques are insufficient in determining how good a material will be, instead, it can only point out the bad ones. These are some issues that will be addressed in the next chapter.

Additionally, we also showed that there was somewhat of a relationship between porosity values and coulombic efficiency, though it was not as strong as the other relationship that was uncovered. This relationship was previously known for LIB anode materials, but yet to be elucidated for NIBs. Though it was expected, it also reinforces the fact that porosity values for anode materials should be kept at a minimum, as to avoid SEI formation that would be detrimental to the cycling of a full cell.

6.6 Supplementary Tables
Table 6.2: Measurable pore volume/surface area data and capacities for samples obtained through CO\(_2\) activation.

<table>
<thead>
<tr>
<th>CO(_2) Activation Temperature/Time</th>
<th>DFT Pore Volume (cm(^3) g(^{-1}))</th>
<th>BET Surface Area (m(^2) g(^{-1}))</th>
<th>1st cycle Reversible Capacity (mAh g(^{-1}))</th>
<th>Irreversible Capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>0.042</td>
<td>58.7</td>
<td>282.9</td>
<td>28.6%</td>
</tr>
<tr>
<td>untreated</td>
<td>0.042</td>
<td>58.7</td>
<td>290.4</td>
<td>21.0%</td>
</tr>
<tr>
<td>900 °C-1hr</td>
<td>0.177</td>
<td>219.6</td>
<td>239.3</td>
<td>33.5%</td>
</tr>
<tr>
<td>900 °C-1hr</td>
<td>0.177</td>
<td>219.6</td>
<td>214.9</td>
<td>22.2%</td>
</tr>
<tr>
<td>900 °C-2hrs</td>
<td>0.265</td>
<td>340.6</td>
<td>208</td>
<td>45.0%</td>
</tr>
<tr>
<td>900 °C-2hrs</td>
<td>0.265</td>
<td>340.6</td>
<td>186.5</td>
<td>54.9%</td>
</tr>
<tr>
<td>900 °C-5hrs</td>
<td>0.607</td>
<td>832.5</td>
<td>107.1</td>
<td>71.9%</td>
</tr>
<tr>
<td>900 °C-5hrs</td>
<td>0.607</td>
<td>832.5</td>
<td>120.7</td>
<td>75.7%</td>
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<tr>
<td>900 °C-10hrs</td>
<td>0.908</td>
<td>1410.3</td>
<td>49.3</td>
<td>80.8%</td>
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<td>1410.3</td>
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<td>800 °C-1hr</td>
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<td>102.6</td>
<td>257.4</td>
<td>29.1%</td>
</tr>
<tr>
<td>800 °C-1hr</td>
<td>0.082</td>
<td>102.6</td>
<td>229.6</td>
<td>32.9%</td>
</tr>
<tr>
<td>800 °C-2hrs</td>
<td>0.126</td>
<td>154.4</td>
<td>240.6</td>
<td>31.2%</td>
</tr>
<tr>
<td>800 °C-2hrs</td>
<td>0.126</td>
<td>154.4</td>
<td>236.6</td>
<td>32.0</td>
</tr>
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<td>800 °C-5hrs</td>
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</tr>
<tr>
<td>800 °C-10hrs</td>
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<td>256.9</td>
<td>228.9</td>
<td>37.0%</td>
</tr>
<tr>
<td>700 °C-1hr</td>
<td>0.122</td>
<td>152.1</td>
<td>232.5</td>
<td>25.6%</td>
</tr>
<tr>
<td>700 °C-1hr</td>
<td>0.122</td>
<td>152.1</td>
<td>225.3</td>
<td>34.3%</td>
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<td>126.4</td>
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<td>700 °C-5hrs</td>
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<td>141.9</td>
<td>263.5</td>
<td>21.4%</td>
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<tr>
<td>700 °C-5hrs</td>
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<tr>
<td>700 °C-10hrs</td>
<td>0.140</td>
<td>196.5</td>
<td>241.5</td>
<td>25.3%</td>
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</table>
Table 6.3: Measurable pore volume/surface area data and capacities for samples obtained varying the annealing temperatures.

<table>
<thead>
<tr>
<th>Pyrolysis Temperature</th>
<th>DFT Pore Volume (cm$^3$ g$^{-1}$)</th>
<th>BET Surface Area (m$^2$ g$^{-1}$)</th>
<th>1$^{st}$ cycle Reversible Capacity (mAh g$^{-1}$)</th>
<th>Irreversible Capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C</td>
<td>0.199</td>
<td>265.8</td>
<td>199.8</td>
<td>34.0%</td>
</tr>
<tr>
<td>800 °C</td>
<td>0.199</td>
<td>265.8</td>
<td>221.4</td>
<td>23.4%</td>
</tr>
<tr>
<td>900 °C</td>
<td>0.069</td>
<td>92.8</td>
<td>260.9</td>
<td>24.0%</td>
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<td>900 °C</td>
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<td>92.8</td>
<td>248.2</td>
<td>14.3%</td>
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<td>1000 °C</td>
<td>0.042</td>
<td>58.7</td>
<td>282.9</td>
<td>28.6%</td>
</tr>
<tr>
<td>1000 °C</td>
<td>0.042</td>
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<td>21.0%</td>
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<tr>
<td>1100 °C</td>
<td>0.015</td>
<td>24.8</td>
<td>335.0</td>
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<td>1100 °C</td>
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<td>24.8</td>
<td>299.0</td>
<td>20.3%</td>
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Table 6.4: Ratio of capacities obtained under 0.2 V over the total reversible capacity obtained. The ratios are expressed in % values. The best and worst results for the same materials are shown here.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reversible Capacity (mAh g(^{-1}))</th>
<th>Capacity Under 0.2 V (mAh g(^{-1}))</th>
<th>Capacity % under 0.2 V</th>
</tr>
</thead>
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<tr>
<td>900 °C-1hr</td>
<td>239.3</td>
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<td>51.2%</td>
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<td>214.9</td>
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<td>208.0</td>
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<td>120.7</td>
<td>20.5</td>
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<td>900 °C-10hrs</td>
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<td>6.7</td>
<td>13.6%</td>
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<tr>
<td>900 °C-10hrs</td>
<td>43.6</td>
<td>4.5</td>
<td>10.4%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Reversible Capacity (mAh g(^{-1}))</th>
<th>Capacity Under 0.2 V (mAh g(^{-1}))</th>
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<td>800 °C-1hr</td>
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</tr>
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<td>800 °C-1hr</td>
<td>229.6</td>
<td>124.5</td>
<td>54.2%</td>
</tr>
<tr>
<td>800 °C-2hrs</td>
<td>240.6</td>
<td>140.3</td>
<td>58.3%</td>
</tr>
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<td>236.6</td>
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<td>228.9</td>
<td>126.2</td>
<td>55.1%</td>
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<tr>
<th>Material</th>
<th>Reversible Capacity (mAh g(^{-1}))</th>
<th>Capacity Under 0.2 V (mAh g(^{-1}))</th>
<th>Capacity % under 0.2 V</th>
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<th>Capacity Under 0.2 V (mAh g(^{-1}))</th>
<th>Capacity % under 0.2 V</th>
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<tr>
<td>1100 °C</td>
<td>299.0</td>
<td>173.8</td>
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Chapter 7: New Insights Onto the Na-ion Storage Mechanism in Non-Graphitizable Carbon

7.1 Abstract

The somewhat perplexing results in the previous chapter, with the inverse relationship between porosity and capacity, left some open-ended questions. If sodium atoms are preferentially stored in at low voltages, thus leading to a low voltage plateau in the galvanostatic charge profile, why did increasing the porosity lead to the disappearance of such a plateau? Why did minimizing the porosity lead to the longest plateau? What do these results imply about the Dahn model of sodium atom storage in hard carbon? What would happen if even lower porosity materials are used as NIB anodes? Would we see an even greater capacity? All of those questions spurred us to investigate further, which was done in two ways: first, a carbon of exclusive microporosity, synthesized from the pyrolysis a metal-organic-framework (MOF) material was investigated, and showed that the low-voltage plateau was not directly linked to microporosity. The second investigation synthesized a series of progressively lower porosity carbon, as to investigate if the relationship uncovered earlier was steadfast, and what it said about the sodium atom storage mechanism.
7.2 Exclusively Microporous Carbons

7.2.1 Experimental Details

7.2.1.1 Material Synthesis

The MOF precursor was obtained from a collaborator, Dr. Ma, at the University of South Florida in the spring of 2014. It was pyrolyzed at 1100°C under inert gas flow at OSU, before being characterized and tested as a battery material.

7.2.1.2 Material Characterization & Electrochemical Testing

The resulting carbon material was characterized for porosity using BET surface area, and DFT pore volume approximations, using N\textsubscript{2} sorption with a Micromeritics ASAP 2020 Surface Area Analyzer. More detailed material characterization was not performed due to short-sightedness: of the little carbon material that was obtained, it was used to make anodes prior to a full battery of material characterization. Further contacts with Dr. Ma’s lab at USF went unanswered, and thus, not enough material was left to be fully characterized, which should serve as a lesson: characterize the material fully before making batteries.

Electrochemical testing was done in a half-cell, using 1M NaPF\textsubscript{6} electrolyte in EC:DEC solvent, and cycled in a Maccor 4000 machine, at various current rates. CV cycling and EIS testing were obtained in Bio-logic EC lab VMP-3.
7.2.2 Results

From the results of the porosimetry, we can see that the MOF derived carbon is exclusively microporous, as it displays a large adsorption at low pressures, and almost none as higher pressure. It displays the same trend as the isotherm for the low surface area carbon – just with a lot more adsorption. The same can be said with the pore size distribution, where the profiles between the low porosity carbon, and the microporous carbons are similar, with a greater amount of pores for the microporous carbon (Figure 7.1).

![Figure 7.1: a) N₂ adsorption/desorption isotherm for the low porosity material, and the MOF derived microporous carbon. b) Pore size distribution plot.](image)

That being equal, we then evaluated the capacity at a low current rate, as to check if the exclusively microporous material, despite its higher surface area/porosity, was able to match the low voltage plateau of the low porosity material. However, this was not observed. Despite having a much higher microporosity value, the low voltage plateau still encompasses less capacity than the low porosity material, as
seen in Figure 7.2. This is in direct opposition to the Dahn model, which with the higher microporosity, would be expected to have a long low voltage plateau due to the higher incidence of low voltage deposition of sodium atoms into the micropores. Furthermore, unlike the study done in the previous chapter, where the loss of the low voltage plateau was attributed due to the mere fact that CO$_2$ activation increased the porosity at the expense of the micropores, the same argument cannot be made here.

![Graphs](image)

Figure 7.2: Galvanostatic sodiation/desodiation profiles at a current rate of 40 mA g$^{-1}$ for a) Low porosity/surface area carbon. b) MOF derived microporous carbon.

While these results do cast some doubt on the Dahn model, and suggest a potential abrogation, there is something else that should first be considered. When comparing the microporous carbon, of higher surface area, with a CO$_2$ activated carbon of a similar surface area, and the low surface area carbon, no clear pattern emerges. The CO$_2$ activated carbon, which has a similar surface area but a higher porosity value has a lower capacity than the microporous carbon, while lacking a low voltage plateau. This despite having a higher volume of micropores. The
microporous carbon has an intermediate capacity, and somewhat of a low voltage plateau. The low porosity carbon, in this case sucrose annealed at 1100°C has the highest capacity, and the lowest amount of micropores.

Figure 7.3: a) N\textsubscript{2} adsorption/desorption curves for CO\textsubscript{2} activated carbon, microporous carbon, and low porosity carbon. The CO\textsubscript{2} activated carbon, and the microporous carbon have similar surface areas. b) Reversible capacities for said carbons

7.2.3 Conclusion

At first glance, the results obtained appear to muddle the whole mechanism picture. Exclusively microporous carbon, which was expected to have a large low-voltage plateau under the Dahn model does not. It has an intermediate one. A carbon material with a smaller volume of micropores has a much longer low voltage plateau. Furthermore a CO\textsubscript{2} activated with similar surface area as the microporous carbon, but a greater overall porosity, including microporosity, has the smallest capacity and no low voltage plateau.
Beyond a reasonable doubt, we have shown that microporosity is not directly correlated to the presence of the low voltage plateau. We have also shown that it is possible to have a low voltage plateau with a high degree of porosity. What seems to really matter for the low voltage plateau, is the absence of a highly porous carbon, with all types of porosity, such as one obtained with CO$_2$ activation. Beyond that, more investigation is needed.

7.3 New Mechanistic Insights from Low Porosity Carbons

7.3.1 Experimental Details

7.3.1.1 Material Synthesis

Sucrose derived hard carbons where obtained by pyrolyzing sucrose (Macron Chemicals) under constant Ar gas flow at various annealing temperature for 6h. Prior to being annealed, the sucrose was de-watered by heating it at 180$^\circ$C for 24 h. The glassy carbon was commercially obtained from Sigma Aldrich.

7.3.1.2 Material Characterization

Brunauer-Emmett-Teller (BET) surface area and Density Functional Theory (DFT) pore volume calculations are based on N$_2$ sorption measurements on a Micromeritics TriStar II 3020 analyzer. XRD patterns are obtained by a Rigaku Ultima IV
Diffractometer using Cu Kα radiation \((\lambda=1.5406 \text{ Å})\) and fitted with the PDXL software. Raman spectra are collected using a HR 800 LabRam HORIBA JOBIN YVON system with a 532.02 nm laser source.

Neutron total scattering data were collected at the Nanoscale Ordered Materials Diffractometer (NOMAD), Spallation Neutron Source, at Oak Ridge National Laboratory. Samples were loaded into kapton capillaries to perform analysis. These data were reduced such that the integral of the structure function \((S(Q))\) as \((Q \rightarrow \infty)\), \(S(Q) = 1\); allowing the pair distribution function, derived from taking the Fourier transform of \(S(Q)\), of various materials to be related to one another.

7.3.1.3 Electrochemical Testing

The electrodes are prepared by mixing 80wt% active material, 10wt% carbon black, C-45 (TimCal) and 10wt% poly-1,1-difluoroethene (PVDF) binder in n-methyl-2-pyrroldilinone (NMP). The resulting paste transferred onto a copper current collector and dried at 80°C in a vacuum oven. The active mass loading of the electrodes is 1.5-2 mg cm\(^{-2}\).

Half-cells are assembled in 2032 coin cells containing a 1M NaPF\(_6\) (Alfa Aesar) in a one to one solvent of Ethyl Carbonate (EC) Diethyl carbonate (DEC). Sodium foil is used as a counter electrode, and a glass fiber separates the positive and negative sides. All cell assemblies were done inside an Ar filled glovebox

Galvanostatic cycling is conducted on a Maccor 3000 at 25°C at a current rates ranging from 40 mA g\(^{-1}\) to of 5 A g\(^{-1}\). Long cycling is conducted at a current rate
of 200 mA g⁻¹. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectra (EIS) are obtained on a Bio-logic EC Lab VMP-3 under ambient conditions.

GITT testing was done with a half-cell of the s⁻¹100 subjected to 5 cycles of sodiation/desodiation at a current rate of 40 mA g⁻¹ before being subject to GITT testing. During GITT testing, a current pulse of 20 mA g⁻¹ lasting for 30 min was applied before the battery was allowed to rest for a continuous 2 hours. The current pulses were continued until the cutoff potential of 0.01V vs. Na/Na⁺ was reached.

7.3.1.4 Ex-situ XRD Analysis

Ex-situ XRD analysis was performed by running half cells of the s⁻¹100 material for 5 cycles at 40 mA g⁻¹ before running a final time to the desired cutoff voltage. Once desired cutoff voltage was reached the cells were then immediately removed and disassembled in an Ar filled glove box. The anode material was then removed from the cell, cleaned and put onto a glass slide and covered with a layer of Kapton film. The edges of the Kapton film were then sealed with a thin layer of Vaseline as to ensure no contact with the air was made (Figure 7.4). The anode materials were then tested with XRD.
7.3.2 Results

In this study, we tuned the atomic structure of a model hard carbon in order to confirm the electrochemical structure-property relationships given in the card-house model. We hypothesized that annealing sucrose-derived hard carbon at progressively increasing temperatures would yield the desired ‘tunable’ hard carbon structures by controlling the domain dimensions of the all-important turbostratic nanodomains (TNs) along the axial axis, $L_c$, and along the ab planes, $L_a$. Sucrose-derived carbons were compared to a commercial glassy carbon (Aldrich) that is essentially the ‘hardest’ available hard carbon, as it is typically obtained through pyrolysis at temperatures of over 2000°C. However as our results will later show, we found some experimental discrepancies that could not be reconciled with the card-house model. This leads us to propose an alternate perspective on the storage of Na-ions in hard carbon materials.

In the XRD patterns, we observed the (002) peaks, indicative of the d-spacing between the graphene sheets in the TNs, to be contracting from 0.375 nm for pyrolyzed sucrose annealed at 1100°C($s^{-1}100$), to 0.371 nm for $s^{-1}400$, 0.370 nm
for \(s^{-1}600\) and 0.352 nm for glassy carbon (Figure 7.5a). Average \(L_c\) and \(L_a\) values were estimated through the PDXL software by use of the Scherrer equation on (002) and (100) peaks, respectively.24 The results reveal that the \(s^{-1}100\) is likely to have the smallest TN dimensions with \(L_c\) and \(L_a\) values of 1.15 and 2.54 nm, respectively, while these values increase to 1.17 and 3.18 nm for \(s^{-1}400\), 1.19 and 3.50 nm for \(s^{-1}600\) and 1.25 and 6.13 nm for the glassy carbon (Figure 7.5a-b & Table 7.1).

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<tr>
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<th>(L_c) (nm)</th>
<th>Average number of graphene layers</th>
<th>(L_a) from XRD (nm)</th>
<th>(L_a) from Raman Spectroscopy (nm)</th>
<th>(I_d/I_0) ratio</th>
<th>Reversible Capacity (mAh g(^{-1}))</th>
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<tr>
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<td>3.50</td>
<td>13.3</td>
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<tr>
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<td>3.53</td>
<td>6.13</td>
<td>19.4</td>
<td>0.99</td>
<td>214</td>
</tr>
</tbody>
</table>

Table 7.1: Characterization results of carbon samples through X-ray diffraction, Raman spectroscopy, and electrochemical performance.

While the X-ray trend is difficult to unambiguously distinguish between the different sucrose carbons, Raman spectroscopy was used as a local probe for more reliable measurements of amorphous materials. The increase in \(L_a\) is also observed through Raman spectroscopy by using equation 3.3.

Results of the Raman spectra show a similar trend as the XRD results, with \(L_a\) values of 9.2 nm, 10.5 nm, 13.3 nm and 19.4 nm for \(s^{-1}100\), \(s^{-1}400\), \(s^{-1}600\) and glassy carbon, respectively (Table 7.1). The scale discrepancy between the XRD
and Raman $L_a$ values has been noted before, as Raman measurements tend to overestimate the $L_a$ values. However, when performing a linear regression of the Raman $L_a$ values vs. the XRD $L_a$ values, we find an $R^2$ of 0.95, thus confirming the increasing trend in $L_a$ in the carbon materials (Figure 7.6). Additional information from the Raman data includes an $I_D/I_G$ ratio, which can be used to quantify the concentration of defects along the graphene sheets.27, 28 These ratios
indicate that the s\textsuperscript{-1}100 material has the greatest concentration of defects, while the glassy carbon contains the smallest concentration.

![Linear regression plot of Raman spectra L\textsubscript{a} values vs. XRD L\textsubscript{a} values. The R\textsuperscript{2} value for the regression plot is 0.95.](image.png)

While these traditional measurements are insightful, they fall short of revealing local atomic structures. Thus, to probe the short and mid-range order of the carbon materials, we performed total neutron scattering measurements and the associated PDF analysis. The peaks up to 5 Å represent the short-range correlations of the C-C bonds of one hexagon unit within a sheet of graphene (Figure 7.5c). Regardless of the annealing temperatures, all the peaks are well aligned, and are consistent with the graphene lattice.29

There is an absence of a C-C correlation at 3.35-3.45 Å, which is found in highly ordered, graphitic carbon. This lack ordering between the graphene sheets supports the existence of turbostratic disorder. The size of the graphene nanodomains can be estimated in the mid/long range where well-resolved peaks vanish at certain r values. The s\textsuperscript{-1}100 has notable peak features until 15-17 Å, the s\textsuperscript{-1}400 exhibits
features diminishing around 18-21 Å, while the glassy carbon has features that persist past 30 Å (Figure 7.7). These data are consistent with XRD and Raman results, as the glassy carbon exhibits the largest domains, while the s\(^{-1}\)100 has the smallest.

![Figure 7.7: Zoomed in PDF plots for a) Short range order. b) Mid range order. c) Long range order.](image)

In addition to the size of the graphene sheets in TNs, neutron PDF results also provide information on the sp\(^2\) defect concentration present in the TNs. Importantly, we note that the intensity of the PDF peaks differs from sample to sample. In PDF patterns, the area underneath a peak is proportional to the coordination number of that pair correlation.\(^{30, 31}\) At 1.42 Å the intensity of s\(^{-1}\)400 and glassy carbon is virtually identical and only s\(^{-1}\)100 has a slightly lower intensity. However, as r increases, the difference in peak intensity becomes readily apparent. In particular, the first three peaks in the s\(^{-1}\)100 pattern have lower intensities, meaning that it possesses a significant number of non-hexagonal carbon rings. These defects likely result in a bending of the graphene sheets, which diminishes the long range ordering and therefore the size of the domains.\(^{32}\) The PDF data show s\(^{-1}\)100 has the greatest defect concentration, the glassy carbon has the least while
s^{-1}400 is somewhere in the middle. The trend regarding the defect concentration corroborates the Raman spectrum results.

Using several techniques, we have demonstrated that TN sizes increase upon annealing and are the largest for glassy carbon. According to the card-house model, capacity obtained in the sloping region, defined as the region above 0.115 V vs. \( \text{Na}^+/\text{Na} \) of the potentiogram curve, is due to intercalation of sodium ions in the TNs. With larger TN sizes, the card-house model predicts increasing sloping capacity from \( s^{-1}100 \) to \( s^{-1}600 \). However, the sloping capacity decreases from 120 mAh g\(^{-1}\) to 102 mAh g\(^{-1}\) and to 92 mAh g\(^{-1}\) for \( s^{-1}100 \), \( s^{-1}400 \) and \( s^{-1}600 \), respectively (Figure 7.8a). One may be concerned about whether it is the decreased d-spacing from \( s^{-1}100 \) to \( s^{-1}600 \) that causes the lower capacity. As estimated from the XRD patterns, we notice that the d-spacings are only different by 0.005 nm between \( s^{-1}100 \) and \( s^{-1}600 \). We are aware that this average d-spacing difference is beyond relevant meaning in physics.

Instead of being dependent on the size of TNs, the capacity in the sloping region seems to be directly correlated to the defect concentration present. When plotting the slope capacity versus defect concentration in the carbon samples, as expressed by the integrated ID/IG ratio, we observe a linear relationship with an \( R^2 \) value of 0.90 (Figure 7.8b). This leads to our hypothesis that the defected carbon sites in hard carbon rather than the TNs are responsible for the capacity in the sloping region. The obtained PDF data also supports this hypothesis as it shows that the \( s^{-1}100 \) material has the greatest defect concentration and the largest sloping capacity while the glassy carbon has the lowest defect concentration and the smallest sloping capacity. Prior computational studies also support this hypothesis.
Figure 7.8: a) Sodiation potentiograms for different carbons. b) Plot of the sloping capacity vs. the ID/IG ratio from Raman spectra. c) GITT profile and diffusivity as a function of states of charge (inset). d) dQ/dV plot from 0.12 V to 0.01 V with corresponding diffusivity values.

as they show that binding energy between Na-ion and carbon is highest at graphene defect sites and vacancy sites, which corresponds to the high sodiation potentials in the sloping region.[122, 123, 124, 125]

Furthermore, the ‘sloping’ nature of this region can be attributed to the fact that there is no clear-cut definition of defect sites in amorphous carbon. They range from dangling bonds at the edge of TNs, to mono-vacancies, divacancies, stone-wales defects and extreme curvature in graphene sheets; along with the presence
of the sp³ ‘linking’ carbons that connect the neighboring TNs. The plethora of different morphological defects indicates that each type may have its own respective sodiation voltage, thereby giving the sodiation of defects a slope-like shape on the potentiogram curve. Furthermore, considering the delocalized nature of electrons of graphene, binding of a sodium ion at defect sites is more energetically favorable, as the defect sites have low energy unfilled molecular orbitals that can effectively store extra electrons. This increases the binding energy with sodium, and thus allows the sodiation to happen at higher voltages vs. Na⁺/Na.

We further investigated the sodiation mechanism through the evaluation of kinetic properties using GITT. The Na-ion diffusivity in hard carbon calculated as a function of potential (Figure 7.8c) shows that diffusion associated with the sloping potentials is much faster than that with the plateau. This suggests that initial sodiation happens on easily accessible sites in the carbon structure.

It is reasonable to say that the surface sites of TNs are more accessible than the interlayer space in the TNs. As these sites are progressively sodiated, Na-ions should then diffuse inside the TNs. However, in order to do so, the Na-ions have to overcome a repulsive charge gradient from the previously bound Na-ions on defect sites in order to diffuse inside the TNs. This explains the steep drop in diffusivity in the plateau region of the potentiogram.

These kinetic results not only support our hypothesis that the sloping capacity is due to defect sites on the TN surfaces but also give further insights into the sodiation mechanism of the plateau region of the potentiogram curve. This has the subject of ambiguity, as recently published experimental results have suggested that the plateau region is due to Na insertion into TNs as opposed to the pore
filling mechanism suggested by the card-house model.[126, 127, 128] Similarly, we also observed reversible expansion and contraction of d-spacing due to sodiation and desodiation at the plateau region, i.e., from 0.2 V to 0.01 V, while conducting ex-situ XRD. This suggests that intercalation occurs at lower voltages (Figure 7.9a-b).

![Figure 7.9](image)

Figure 7.9: a) Ex-situ XRD profiles at various stage of sodiation (S) and desodiation (D) with the (002) peak indicated. b) Corresponding d-spacing plots. c) Potentiogram of sodiation until Na-metal plating is induced. d) Potentiogram and schematic of proposed Na-ion three part storage mechanism. Please note that the figure is meant as a schematic representing the three different types of binding sites as opposed to an accurate representation of the hard carbon structure.

Despite our hypothesis that the plateau region could be attributed to intercalation of sodium ions in TNs, the newly obtained diffusion results, combined with the rest of our experimental data suggest that the plateau region is in fact a function
of both intercalation into TNs as well as pore-filling suggested by the card house model. When observing the values at low voltages, we can observe that diffusion values reach a minimum at 0.05V—the same voltage where dQ/dV values reach a maximum. From 0.05V to the cutoff voltage, the diffusion values gradually increases while dQ/dV values decrease (Figure 7.8d). This observation begs the question: if intercalation is the one and only mechanism in the plateau region, why do diffusivity values begin to rise at the very end, displaying an almost U-turn like reversal? If intercalation were the only mechanism, diffusivity values should become progressively lower and lower, as the diffusion length to storage sites keeps increasing. However, the continuous drop in diffusivity values is not observed.

This suggests that the sodiation mechanism is changing in the voltage range right before reaching the cutoff potential. At such low voltages, storage sites can be characterized by a weak binding energy. Furthermore, the increasing diffusivity values suggest a more facile diffusion than intercalation. Considering the weak binding energy and facile diffusion, we postulate that storage at low voltages is due to the Na-atom adsorption on the sp$^2$ configured pore surfaces. First off, a sp$^2$ graphene surface has been shown in computational studies to be the least energetically favorable binding site for sodium ions.

Thus it is logical that storage of sodium ions on pore surfaces should only occur at low voltages close to that of sodium plating. Additionally, unlike intercalation, storage of on pore surface does not require the expansion of two adjacent graphene layers to make insertion possible, which may account for its faster diffusivity.

To test the above hypothesis, it is critical to determine whether such adsorption is of the same potential as the Na plating. When running a half-cell to voltages below
0.0 \text{ V vs. } \text{Na}^+/\text{Na}, \text{ we found that the onset of Na-metal plating actually occurs at -0.02 V before reaching a steady value of -0.015 V (Figure 7.9c). When looking at the potentiogram near 0.0 V, we notice that the slope becomes much steeper starting at 0.04 \pm 0.01 V and stays linear until plating begins. We hypothesize that this is a result of continuous deposition of sodium atoms on the pore surfaces until a critical point is reached, and the sodium atoms begin to agglomerate into metallic clusters. Therefore, considering the increase in diffusivity values at the very end of the sodiation process, we find it reasonable to propose that the last storage mechanism that occurs during the sodiation of hard carbon is the deposition of sodium atoms on pore surfaces (Figure 7.8d).

This hypothesis of storage on pore surfaces is in good agreement with the original one made by the card-house model, and is also supported by the computational results; which show that the binding energy between planar graphene sheets and Na is much smaller than binding on defect sites or in a graphene bilayer. This is a logical claim, as a sodium ion between two graphene sheets is more coordinated than an electron interacting with only a single graphene sheet.

7.4 Conclusion

Prior to this study, sodium storage in hard carbon material was assumed to proceed by the Dahn model: at higher voltages, sodium atoms would intercalate graphene nanodomains, while at lower voltages, sodium atoms would be deposited into micropores. There were some discrepancies with that in our earlier work, as it was shown that increasing the microporosity did not lead to higher capacities, along-
side the disappearance of the low voltage plateau. With the new investigations, we have shown that the presence of micropores does not guarantee a large low voltage capacity, and that the two are not directly related. Furthermore, we are able to demonstrate that unlike the Dahn model, the capacity obtained in the sloping region of the galvanostatic voltage curve, does not arise from the intercalation of graphene nanodomains. Instead, our studies suggest that storage in the sloping region of the voltage curve is dependent of the interaction between sodium atoms and defect sites in the carbon structure, the initial part of the low voltage plateau is due to intercalation in graphene nanodomains, while the latter part of the plateau, at voltages close to 0 V vs. Na$^+$/Na, is due to deposition in pores, and on graphene surfaces.

This newly proposed model accounts for the observations we have seen thus far in our studies. In the case of carbon materials annealed at high temperatures, the sloping region is diminished as there are less defect sites by which we can bind sodium atoms to. In the case of highly activated materials, the destruction of the graphene nanodomains by the higher porosity takes away the structural features associated with the storage of sodium atoms at low voltages. Lastly, highly microporous carbon materials, can still have a low voltage capacity plateau, as the micropores favor deposition of atoms into the micropores, which structurally, can be defined as graphene surfaces.
Chapter 8: Computational Insight on the Na-ion Storage Mechanism

8.1 Abstract

In our subsequent investigation using a multitude of Na/carbon configurations, we reveal that there are two methods to Na-ion storage on carbon materials. The first method is through ionic storage, where electrons are transferred from the Na atom to the carbon substrate, leading to an ionic interaction between the two. The second storage mechanism is through the stabilization of the system from Na/Na interactions. If the concentration of Na atoms passes a certain point, or if multiple Na atoms are introduced into a single system, pseudometallic interactions between the Na atoms can stabilize the system leading to favorable conditions for Na-ion storage.

Herein these results furthers our understanding of Na-ion storage onto carbon materials, in a DFT context, in four significant ways: (1) it allows us demonstrate that there are two routes to Na-ion storage in carbon materials, ionic storage and pseudo-metallic storage (2) it provides compelling support towards an earlier experimentally derived Na ion storage for carbon materials (3) it makes it possible to suggest a sodiation onset potential on pure carbon, which should give a rough estimate of a theoretical capacity limit of carbon materials (4) it shows the im-
portance of boundary conditions, symmetry conditions and symmetry breaking in DFT simulations, something which is applicable to simulations much beyond that of this work.

8.2 Introduction

In the previous chapter, an experimentally determined model was postulated. However, this is a situation where we must be careful of a confirmation bias. Much of the characterization evidence, as well as assumptions made, we circumstantial. The ex-situ XRD results, and the GITT testing are prime examples of this. The ex-situ XRD result claimed a shift in the 002 peak. However, those peaks were noticeably broad, and the margin of error can easily outweigh any meaning we ascribe to the shift of the peaks. Furthermore, with the GITT testing, we are operating under the assumption that an intercalative process is of slower diffusion than a surface process. This might be logical, but that is the problem: logic and facts shouldn’t be conflated.

Thus, we went further in our investigation of the sodium ion storage mechanism, and decided to investigate it computationally using a DFT approach. The aim of this was were two fold. The first is to determine if the proposed mechanism is supported by theoretical evidence. The second is to see if a theoretical limit, such as the one elucidated for graphite and lithium atoms, can be found. Both of these would have large implications for the NIB anode field.

Currently, pending uncertainties on the performance of the amorphous carbon
anodes for NIBs have catalyzed a high-throughput testing approach of amorphous carbon materials, with the hope of synthesizing the ideal, high capacity, high efficiency and stable cycling anode material. This has included testing of carbon materials derived from a host of different precursors ranging from organics plant material, to different types of polymers. Additionally, nanostructures such as graphene and CNT composites have also been experimented with. That said, most of these structures have a capacity ranging from around 200 mAh g\(^{-1}\) to 300 mAh g\(^{-1}\), with some high performance outlying carbons being moreso on the order of 350-400 mAh g\(^{-1}\). While all these reports laud the carbons as highly promising NIB anodes, most do not broach the theoretical questions: what are the features which enable Na-ion storage in amorphous carbon materials, and how effective can such features be? Are we up against a theoretical limit of sorts?

In order to further probe these questions, a detailed understanding of the Na-atom carbon interactions at the atomic level is critical. This makes this problem ideal for density functional theory (DFT) first principles calculations. Such an approach allows to compute binding energies in light of certain parameters such as NaC\(_x\) concentration, which can also be expressed as capacity in mAh g\(^{-1}\) equivalent, structural topology, defect concentration and electronic doping. The correct use of DFT techniques have the potential of providing validation and foresight to experimentalist, as optimize research efforts.

Herein, we explore the energetics of Na ion binding on various carbon substrates and at various concentrations using perdew-burke-ernzerhof (PBE) generalized gradient approximation (GGA) semicore pseudopotentials with a DFT-D3 Grimme correction for Van der Waal forces. These calculations are used to form the basis
of our fundamental understanding of Na atom/carbon interactions at the atomic level.

8.3 Binding of Na on Graphene

In the present work, our utilization of DFT calculations revolves around a simple premise: is the energy change between the final Na/C configuration and the original individual components enough to overcome the energy of removing a Na atom from a bulk BCC configured metal host? This concept is illustrated in (Figure 8.1) which shows the overall energy path of the Na atom and carbon structure from their original configurations into the final state.

![Figure 8.1: Energy path of the an individual Na atom, and bare graphene sheet, into the final Na/C configuration.](image)

The cohesive energy of a Na atom in a bulk BCC metal was measured to be -1.31 eV, which is similar to what was found in earlier DFT studies by Shenoy.
et al. [129] As such, moving the Na atom to a vacuum state will incur an energy penalty of 1.31 eV. However in the context of our calculations, the Na atom is not in a vacuum state. It is in a unit cell with periodic boundary conditions, which can lead to cross-boundary interactions if the unit cell is not large enough. As such, the energy need to move the Na from the BCC lattice to a unit cell of predetermined size, is not dependent on the vacuum energy, and the change in energy can be written as

$$\Delta E_{Na} = \frac{E_{Na \ Unit \ Cell} - E_{xNa \ BCC}}{x} \quad (8.1)$$

Following the transfer of the a Na atom from the bulk BCC metal to its individual unit cell, we then combine the Na unit cell with the carbon structure unit cell—both being of the same size—so gauge the interactions between the two, with the energy change being equivalent to the binding energy between the Na atom and its carbon substrate. This gives us the equation:

$$\Delta E_{Binding} = \frac{E_{Graphene+Na} - (E_{Graphene} + E_{Na \ Unit \ Cell})}{x} \quad (8.2)$$

This first equation to determine the strength of the binding interaction between the Na and the carbon substrate was theoretically validated by gradually “lifting” the Na atom off of the carbon substrate. This results in an energy well, whose depth is approximately $\Delta E_{Binding}$ obtained using the equation. By combining the first 2 equations, we can get an expression which relates the final change in energy to the cohesive energy of a Na atom in a BCC structure, which gives us the equation:

$$\Delta E = \frac{E_{Graphene+Na} - (E_{Graphene} + E_{xNa \ BCC})}{x} \quad (8.3)$$
Considering that Eq. 8.3 is using metallic Na as its reference, it is equivalent to the voltage obtained in an Na/C half-cell, which also uses metallic Na as a reference state. Thus, we can estimated voltage from the DFT calculations by using the equation

\[ \text{Voltage} = -\left[ \frac{E_{\text{Graphene}+\text{Na}} - (E_{\text{Graphene}} + E_{\text{Na BCC}})}{x} \right] \]  \hspace{1cm} (8.4)

If the voltage obtained using Eq. 8.4 is negative, it implies that the binding of the Na atom to the carbon substrate, as illustrated in Fig. 8.1, will be unfavorable. The Na metal will plate onto the substrate before a favorable interaction can be obtained. The first simulation conducted explores the interaction between a Na atom and a pristine graphene sheet, while varying the NaC\(_x\) concentration, by changing the size of the graphene patch, and as such, the size of the unit cell. The unit cells used are herein designated as 2 by \(x\), 3 by \(x\), and \(x\) by \(x\) as demonstrated in the schematic in Fig. 8.2a. Such a method allowed us to probe the dependency, if any, of the Na atom interactions with graphene sheets based on the cell geometry.

From the initial results seen in Fig. 8.2b, we can see that no amount Na atom interactions with a graphene substrate are never favorable, no matter the Na concentration. However, there is an interesting trend which arises. At low concentrations of Na, the voltage is close to -0.25V. As the concentration increases, the voltage decreases, with values close to -0.6V at its lowest point. However, after a certain point, the trend reverses itself. Concentration goes up, as does voltage. This is most evident with the voltage obtained from the 2x2 unit cell, an equivalent sodiation of NaC\(_8\). At such a concentration, the voltage is close to -0.1V. This is considerably higher than what it was at extremely lower NaC\(_x\) ratios, which suggests a changing storage mechanism as the concentration increases.
While the voltage vs. capacity chart shows little dependence on cell morphology, this narrative changes when looking at the binding energy vs. capacity. As seen in Fig. 8.2c, the trend between binding energy and capacity is affected by two factors: Na concentration and cell geometry. The former is expected. As the concentration
of Na on the substrate increases, the ionic interactions are attenuated, as there are more electrons to store per unit area on the graphene surface. However, we also see that the binding energy is strongly dependent on the geometry. Whereas some of the $2 \times x$, $3 \times x$, and $x \times x$ substrates have the same concentration, they have very different binding energies. This is most likely due to the Na/Na metal interactions across the periodic boundary conditions. Such interactions are stronger in a $2 \times x$ cell than they would be in a $3 \times x$ or $x \times x$ cell, as the distance between Na atoms is reduced in the lateral direction. This is confirmed by looking at the energies of the individual Na$_{Unit\,Cell}$ as shown in Fig.8.2d, as well as the charge distribution plots in Fig.8.2f-i. As we can see in the charge distribution plots, the Na atom in the $2\times2$ and the $2\times7$ cell shares its charge with the neighboring unit cell. This happens to a slightly lesser extent in the $3\times3$ cell, and does not happen at all in the $6\times6$ cell.

This difference between the sharing of charge between Na atoms due to proximity, as opposed to confinement of the charge to the graphene sheet, gives us a good insight to the changing storage mechanism as a function of Na concentration on the graphene sheet. At high concentration, or close proximity due to cell geometry, Na/Na interactions will factor heavily into the binding energy. At low concentrations, ionic interactions will be the main source of binding energy. This is concisely summed up in Fig.8.2e. Looking at the voltage as a function of electron transfer to carbon, we see that a high voltage can be obtained without a high degree of electron transfer. Low amounts of electron transfer happen in high-concentration cells, were Na/Na interactions are prevalent. Likewise high voltages can also be obtained with high degrees of electron transfer, which lead to strong ionic interactions. As such, we see that in the case of graphene sheets, there are two methods of
Na ion storage. Either strong ionic interactions between the Na and the substrate, or stabilizing Na interactions between neighboring Na atoms. However, being in the middle of those two, leads to the weakest interactions. These systems are seemingly caught in a proverbial ‘no man’s land’, with the unit cell being too large for stabilizing Na-Na interactions, but the degree of charge transfer too small for strong ionic interactions between the Na and the graphene sheet.

8.4 Binding of Sodium on Defected Graphene

In the previous section, we were able to demonstrate that as Na concentration increases, the mode of binding goes from ionic to metallic. However, in the case of graphene, no simulation was ever found to have a positive voltage, which make the whole excercise non-sequitur – at least when trying to make a functional battery material.

Fortunately for the prospect of using amorphous carbon as a NIB anode, most carbons are not pure graphene. They contain defects and sheets of graphene stacked into nanodomains. Thus, the next goal focused on the investigation of Na atoms interaction with defected sites. For this task, we chose to simulate the interaction between Na and representative defect sites found in graphene sheets: monovacancy, divacancy, and stone-wales defects utilizing unit cells ranging from 2x2 to 6x6. Additionally, ”edge” or ”pore” like defects were simulated by hollowing out different degrees (Fig.8.3a).

Unlike the pristine graphene sheets, the associated voltage most of the defected
Figure 8.3: (a) Different types of graphene defects, from left to right: stone-wales defect, monovacancy, divacancy, edge, and pore defect. (b) Measured voltage vs. capacity plot obtained using Eq. 8.4. (c) Binding Energy vs. capacity plot obtained using Eq. 8.3. (d) Binding energy vs. electron transfer to the carbon substrate. Charge distribution maps showing the negative charge regions of (e) stone-wales (f) divacancy (g) monovacancy (h) edge-like (i) pore-like defects.

Graphene sheets is positive, and shows little dependence on NaC_x concentration. The only exceptions are some of the stone-wales defect on the larger 5x5 and 6x6 sheets where the voltages are slightly below 0V. Other than the two exceptions with the stone-wales defects, the strength of interactions between the defected
carbon substrate ranks, from highest to lowest as a function of the defect, edge, pore, monovacancy, divacancy, and stone-wales defect Fig.8.3b. Before going any further, it must be state that the difference between an “edge” and a ”pore” is a hard one to pin down, and as such it is more appropriate to label the two as ”edge-like” defects. That being said those two defects account for the most energetically favorable Na atom storage. The difference in voltage between the monovacancy and divacancy defects is more subdued, with the monovacancies being slightly more favorable. Meanwhile the stone-wales defect, which possess no vacancy, are still defective enough to favor the storage of Na-atom, though they can only do so with the aid of Na/Na interactions, as only the higher concentrations of the 3x3 and 2x2 graphene sheets offer a positive voltage. With the defects, it can be observed that the principle factor behind binding is due ionic interactions with the carbon substrate. The binding energy vs. capacity plot Fig8.3c is very closely aligned with the voltage vs. capacity plot (albeit the signs are flipped). Additionally, like the case of the Na on the pristine graphene sheet, we do see an increase of Na/Na interactions for higher concentration, especially in the case of the 2x2 graphene sheet with the monovacancy and the stone-wales defect. However, the 2x2 defected substrates show a considerably greater electron transfer than the pristine 2x2 graphene. Whereas the electron transfer to the 2x2 sheet is only of 0.21, the transfer for the 2x2 sw sheet is of 0.48, while it is 0.71 for the 2x2 monovacancy sheet (Fig8.3d).

Further exploring the relationship between binding energy and electron transfer to the graphene sheet, it can also be seen that binding energy is not directly correlated to the degree of electron transfer. For most of the defective substrates, the electron transfer from the Na atom ranges from 0.8 to 0.9, yet the binding energies vary
greatly. While this seems unexpected at first, observing plots of the negative charge surfaces offers a plausible explanation (Fig. 8.3e). Looking at the negative charge surfaces for a host of different defects, with similar electron transfers, it can be seen that the concentration of negative charge varies greatly. For the sw and divacancy defect, the negative charge is spread through a more diffuse region, around a 7 member-carbon right for the sw defect and a 8 member ring for the divacancy defect. However, in the case of the monovacancy and "edge-like" defects, the negative charge is gathered at local points in the carbon structure. As such this suggest that the strength of the ionic interaction is not dependent solely on the amount of electron transfer, but also on its distribution on the substrate. Furthermore this also suggests, much like an elementary concept in electrostatics, that charge prefers to gather at "sharp" points, which are typical in monovacancy and edge-like defects.

8.5 Binding of Na in Bilayers

Having established the binding characteristics of Na atom binding to pristine graphene sheets and defected graphene sheets, we then explored the last type of binding environment present in the hard carbon structure: bilayers. Under the experimental model, an expansion in the average interlayer d-spacing was observed at low voltages, and as such, the storage mechanism associated with the first part of the low voltage plateau region was deemed to be the result of the intercalation of the few layered graphene nanodomains. The bilayers evaluated ranged from 2x2x2 to 5x5x2 bilayers, with both AB and AA arrangement. Utilizing static calcula-
tions, the most energetically favorable d-spacing was found to be close to 0.335 nm for the AB arrangement, and close to 0.365 nm for the AA arrangement. In these simulations, the voltage was obtained using two different conditions: dilated and relaxed. It was seen over the course of the ionic relaxation that the individual graphene sheets forming the bilayer experienced a 'buckling' at the position of the Na atom. As such, the dilated $E_{\text{Carbon}}$ term takes into account the curvature induced by the buckling, while the relaxed $E_{\text{Carbon}}$ term considers the energy of the flat bilayer, which has no curvature Fig.8.4a-b. The binding energy was obtained using solely the dilated bilayer as the $E_{\text{Carbon}}$ term.

The reason for the inclusion of both the dilated and relaxed reference state is as follows: it has already been proven in the literature that Na cannot intercalate a graphitic structure. As such, we don’t expect the voltage obtained using the relaxed reference state of the bilayer to be positive, and looking at the results, it is negative Fig.8.4c. This was to be expected. However, in the event that such a structure could exist, irrespective of the formation energy barrier, would it have a positive voltage? The results obtained certainly suggest so. If in the case of the 2x2, 4x4 and 5x5 bilayer, if such a theoretical structure could be conceived in actuality, it would be stable. If we were considering graphite as an anode material, these results would be meaningless: graphite is present in the 'relaxed' state. However, the case is different for amorphous carbon. While amorphous carbon also possesses graphitic nanodomains, they lack the order which graphite has. Some of the domains have a dilated d-spacing, some of the domains have curvature, and some of the domains are defective – all of which could give an energy reminiscent of that which we find with the ‘dilated’ reference state.
Figure 8.4: (a) Schematic and 2D color relief plot showing the buckling in the graphene sheet induced by the insertion of the Na atom. (b) Schematic showing the reference states of $E_{\text{Carbon}}$ in both the relaxed reference state, and the dilated reference state. (c) Voltage vs. capacity plot obtained using Eq.8.4. Both the dilated and relaxed reference states are included. (d) Binding energy vs. capacity using Eq.8.3. (e) Voltage versus d-spacing plot. (f) Voltages of 4x4 AB and AA graphene-Na bilayers with expanded d-spacings under static conditions.

Looking at the equivalent voltages obtained using the dilated reference state we see that, with the exception of the 5x5-AA bilayer, all are below 0.2V. Furthermore, the difference in voltage as a function of Na concentration is very low. The voltage
for a NaC$_{16}$ AB-bilayer is of 0.05V, while that for a NaC$_{100}$ bilayer is of 0.15 V. This implies that the intercalation of the bilayers takes place in a very narrow low voltage window, irrespective of NaC$_x$ concentration. There also exists an oddity in the data, which was previously seen in other graphene system. All bilayers besides the 3x3 bilayer show a positive voltage. As in the other simulations the 3x3 bilayer lands in the unstable region where the combination of ionic binding to the carbon and Na/Na intercations are not strong enough to render the binding favorable. This is seen in Fig.8.4d as we see that, despite having a very low binding energy, the voltage is still positive. This means that it must be a function of the Na/Na interactions occurring stemming from the high Na concentration. Meanwhile, the 3x3 bilayer does not have the benefit of having either the Na/Na interactions, or a high enough binding energy.

At this juncture, the question "well how dilated does the bilayer need to be?" usually arises. Given that one of the most common ways to characterizing amorphous carbon is by estimating the d-spacing using X-ray diffraction (XRD), the question seems most appropriate. However a universal, let alone correct, answer is more nebulous. As is demonstrated in Fig.8.4e, there is no relationship between d-spacing and voltage. A larger d-spacing does not lead to a more favorable energy. A more appropriate question would be, how dilated does the unintercalated bilayer need to be for the insertion to be favorable. Yet this is also a question which lacks a clear answer. If the graphene sheets are very dilated at the beginning, there will be little penalty for inserting Na in the bilayer. However the interaction of the Na with the graphene once in the bilayer will be weak. The case would be different if once in the bilayer, the graphene sheets would converge on the Na to an ideal d-spacing. However, if the sheets are allowed to converge on the Na once in the
bilayer, they would most likely have converged beforehand, leading to a smaller d-spacing.

Hence we performed static-calculations of a dilated bilayer (Fig. 8.4f). The calculations entailed taking the relaxed 4x4 bilayers, artificially dilating the z-coordinate of the atom positions in the POSCAR file, and placing a Na atom in the middle. As a result of these calculations, we see that in the 4x4-AB bilayer, the ideal d-spacing is of 0.51 nm, while the ideal spacing for the AA bilayer is of 0.47 nm. This is in sharp contrast to the obtained d-spacing of 4.13 nm and 4.06 nm for the dynamic 4x4-AB and 4x4-AA bilayers, respectively.

It is important to make the distinction that in these simulations, all atoms were held static. In simulations were the atoms were allowed to ionically relaxed to their low energy configurations, the energies converged the d-spacings and energies that were obtained using the original 0.335 and 0.370 d-spacing as the starting configuration. Furthermore, we see that the voltage as a function of d-spacing in the relaxed 4x4 bilayer, lies outside the curve. This is where we have to make a distinction between local d-spacing and average d-spacing. When the atoms are allowed to move, the Na atom creates a local pocket of increased d-spacing. However, the rest of the graphene bilayer resists this expansion, as it is most favorable for the carbon atoms to be spaced closer together. Thus, the average d-spacing will be much smaller than the local d-spacing where the Na atom is located. The average d-spacing mentioned here is analogous to the one obtained in XRD measurements. Thus in a simulation where the atoms are allowed to move, there is
1. A higher (e.g. more favorable) $E_{\text{Carbon}}$ from the increased curvature of the graphene layers.

2. A difference in $E_{\text{Carbon}}$ from the increased d-spacing.

3. A difference in the binding energy of the Na atom, due to its different intercalation with the graphene "pocket" as opposed to flat graphene surfaces.

It is unclear whether the second item on the list will prove to be a favorable or unfavorable difference in energy. The local d-spacing in the area of the graphene pocket is of higher energy, which makes it more favorable for Na atom storage. On the other hand, outlying parts of the bilayer may be spaced closer together, leading to a lower $E_{\text{Carbon}}$ which is less conducive to a favorable Na atom binding. The third item, with regards to the binding energy, can only be evaluated once the first two item are quantitatively evaluated.

As such, performing individual simulations on decoupled systems, we can effectively compute the expansion penalty of a bilayer in both a dynamic and static state. For the dynamic state, energies of 4x4-AB top and bottom graphene layers were evaluated individually. The sum of these two energies was found to be $-596.21$ eV. The sum of the top and bottom relaxed 4x4-AB bilayer was found to be $-596.40$ eV, meaning that the $E_{\text{Distortion}}$ in the individual graphene sheets was 0.19 eV. This is not too far from the amount calculated by Safran el al. [130], who calculated the strain to be 0.13 eV per intercalant atom – assuming lithium as the intercalation. Na for its part, is larger. The amount of energy needed to dilate the bilayer was then computed using the equation
\[ \Delta E_{\text{Expansion}} = E_{\text{Dilated Bilayer}} - (E_{\text{Relaxed Bilayer}} + E_{\text{Distortion}}) \quad (8.5) \]

Using this equation, we find that the \( E_{\text{Expansion}} \) for the 4x4-AB bilayer was of 0.46 eV. Meanwhile, the expansion energy needed for the static-dilated bilayer with the same 4.13 nm d-spacing yielded an expansion energy of 0.47 eV. Furthermore, since the top and bottom layers were identical to that of the relaxed bilayer, the \( E_{\text{Distortion}} \) was 0. The expansion penalties being roughly similar, and the distortion energy of the buckled bilayer being of 0.19 eV, the increase in voltage due to more favorable \( E_{\text{Carbon}} \) term should only be of 0.2 V. Yet the voltage for the buckled sheet is more than 0.6 V greater than the dilated, but unbuckled sheet. As such, we can estimate that the presence of curvature in the graphene bilayer is responsible for a 0.4 eV increase in binding energy. Thus, a universal answer to the question: what is the ideal d-spacing? has some complexity to it. While a wider d-spacing, such as one great than 0.45 nm is useful, a narrower d-spacing does not make intercalation totally unfeasible. If the graphene bilayers can relax and create a ”pocket” to accommodate the Na atom, its storage can be favorable while keeping the d-spacing relatively low. As such, we postulate that intercalation in more likely favored to be favored in lower density amorphous carbon materials with few layered graphene domains. The combination of the lower density and the few layered graphene domains give the structure more room to expand and create the Na "pockets" necessary for intercalation to happen at a lower d-spacing.

It must also be said that the expansion seen in the graphene sheets was in a bilayer. This then brings up the question, what would the results look like if the intercalation did not occur in a bilayer, but a multi-layer. For this purpose, a
four graphene layer AB stack was intercalated with a sodium atom. Following relaxation, it was found that the layers directly by the sodium atom experience a similar type of buckling as was seen in the bilayers, with the d-spacing being similar to the previous expansion. The second level of graphene layers also experienced some slight buckling and expansion of d-spacing, but only up to 0.35 nm. It is still unclear whether this expansion was due to the buckling effects from the initial sheet, or the switch to an AA stacking pattern, which would naturally cause the d-spacing to expand (Figure 8.5).

Figure 8.5: Schematic representation of the bottom half of a four-stack graphene layer following intercalation with a sodium atom. The graphene sheets become tilted with respect to the z-axis during the simulation, and a vector method was used to estimate the d-spacing. The position of the two sheets with respect to each other is not to scale.
8.6 Simulations with Multi-Atoms

Thus far we have established the storage of Na-ions with in respect to three different carbon structures: pristine graphene sheets, defective graphene sheets and graphene bilayers. In those simulations, we gaged the effects of NaC\(_x\) concentrations, albeit such concentrations came with a caveat: only a single Na atom was used, which limits our understanding of the behavior of multiple Na atoms in the same system. When using a single Na atom, it cannot break symmetry conditions, as all unit cells are periodic across their boundary conditions. However, with this all changes when two atoms are placed in the same unit cell, as their interactions do not necessarily have to be symmetric. Thus, with freedom of movement within the unit cell, Na/Na interactions energy will invariably be different. Furthermore, this leads to the question of whether or not the Na atoms will cluster together, and if so, how it will happen.

These calculations were started off with a 5x5 graphene sheet with 2 Na atoms located at various places on the graphene sheet. The choice of a 5x5 graphene sheet was used, as to minimize the effect of periodic boundary conditions. Three of the four trials led to the clustering of the Na atoms, which ended up with a separation distance of roughly 0.35 nm (Fig.8.6). The clustering effect happened both as a ”clustering-in” process, whereby the Na atoms decreased their separartions (Fig.8.6a&b), as well as a ”clustering-out” event, where the Na atoms increased their separation from the starting configuration (Fig.8.6c). With the short distance between the two atoms, the Na/Na interaction was increased, which served to increase the voltage, even though the end voltage was still negative. This Na/Na interaction can be seen through the charge density plot, where the clustered Na
Figure 8.6: Simulation of two Na atoms on a 5x5 pristine graphene sheet for a-d, and a 5x5 divacancy defected sheet for e-i, distances before and after are (a) 0.488 nm to 0.350 nm (b) 0.423 nm to 0.347 nm (c) 0.244 nm to 0.348 nm (d) 0.646 nm to 0.652 nm (e) 0.532 nm to 0.550 nm (f) 0.323 nm to 0.374 nm (g) 0.366 nm to 0.384 nm (h) 0.244 nm to 0.351 nm. The charge density plot is shown in the relaxed cell. Isosurface values are all plotted to the same scale.

atoms share charges with each other. The one exception where the Na atoms did not move closer together was in fact due to the boundary conditions, where the original placement of the atoms led to an energetically stable symmetry condition, which was unfavorable to break (Fig.8.6d).

However, unlike the pristine graphene, the case for the clustering of atoms on a defected graphene sheet is different. As we can see in Fig.8.6e-h, the cluster-
ing phenomenon does not happen. No starting configuration leads to the closer spacing of Na atoms. Atoms which start off at intermediate and large separation distances become a little more separated, while atoms which start off very close together become a lot more separated. Furthermore, the charge density is not shared between the Na atoms. This holds true even if the distance between the Na atoms is on the order of the Na atoms on the pristine graphene sheet, as is the case for Fig.8.6h. This refusal to cluster together must be due to the ionic nature of Na atom storage at defect sites. The large degree of electron transfer to the defect creates a positively charge Na species, which effectively repels the other Na atom. As such, we can deduce that defect sites, while very adept at storing individual Na atoms, are not well suited for clustering due to ionic repulsions early on in the process.

While we just established that two Na atoms will cluster on a pristine graphene sheet, but not on a defected one, this leads to further questions. If more the number of Na atoms on the sheet becomes greater than two, the question then becomes: how will the clustering proceed? Will the Na atoms spread out on the surface of the graphene sheet, or will they build on top of each other to form a 3D cluster? To investigate, simulations involving multi-atoms on a 3x3 and 5x5 graphene sheet were carried out, with both a 2D and 3D arrangement being tested (Fig.8.7).

From the plots on Fig.8.7a&b we can see that the voltage, though never positive, rises as the NaC<sub>x</sub> concentration increases. The increase in voltage with concentration is due to the greater amount of Na/Na interactions: as more and more Na atoms are placed on the graphene sheet, the system begins resemble Na-metal
moreso than a carbon-na compound. This switch to a more metallic type bonding is seen in Fig.8.7c&d whereby the average energy per Na atom decreases to values close to those seen in the Na\textsubscript{BCC} structure. The switch to metallic interactions also explains the slight dip in around 100 mAh g\textsuperscript{-1} in the 5x5 graphene sheet. Such a capacity is equivalent to the presence of 2 Na atoms on the graphene sheet. In that case, the Na atoms begin to have interactions, however they do so at the cost of giving up the somewhat stable ionic interactions with the sheet. This again becomes a case of weak ionic binding coupled with only moderate Na/Na
interactions, which leads to the most unfavorable type of voltage.

Aside from the increasing metallic interactions, it is also seen that the clustering process on the graphene sheet starts off as a 2D process. When adding multiple Na atoms to the graphene sheet, a planar configuration in preferable to a 3D one. The planar configuration of the Na atom enhances the Na/Na interactions and thus leads to a higher voltage. While there is greater electron transfer to the graphene sheet in the case of the 3D arrangement, as seen in Fig. 8.7e-h, the interactions between the first and second layer of the Na atoms in the 3D case is prohibitive. Since the first layer of Na atoms is involved in stronger ionic binding, this leads a loss of Na/Na interaction with the second layer. This decrease in Na/Na interaction cannot be overcome through the increase in ionic binding energy between the first layer of Na atoms and the carbon substrate. As such, it is likely that the Na atoms with be spread thin on the graphene surface before forming Na-metal clusters.

8.7 Conclusion

To summarize the work presented in this paper, we have found that Na atoms storage on an idealized carbon substrate occurs most favorably at defective sites, followed by the intercalation of bilayers, and lastly on pristine graphene surfaces. These results are very similar that what was experimentally elucidated, and thus serve to give additional credence to the proposed three-tiered storage mechanism.

The voltage associated storage at defective sites was found to be a function of the defect morphology, as opposed to the Na concentration. This means that
the sodiation of the defective site is expected to take place over a wide voltage window, much like is seen in the sloping nature of the first part of a sodiation voltage profile. Furthermore, this work also shows that a highly defective carbon can be expected to obtain a large amount of capacity at a high voltage, as sodiation is concentration independent. That being said, the favorable binding at defective sites does not necessarily mean that the sodiation of such sites is fully reversible. In fact such sites could be sodiated so strongly, that they could be irreversible, and of not much use to a rechargeable battery. Additionally, it was also found that these defective sites do not induced clustering between Na atoms, as the strong ionic interaction between the site and the Na atom will repel subsequent Na atoms.

At somewhat voltages under 0.2V, it was also shown that intercalation of graphene bilayers is possible, as was predicted in the experimental mechanism. However, a distinction must be made about intercalation. Theoretically, it is not possible to intercalate a relaxed carbon bilayer. However, if the bilayer is dilated/defective, and is is allowed to relax to accommodate the Na atom, intercalation is possible. When a Na atom is intercalated in a bilayer, the compound is rendered more stable is the graphene sheets are allowed to buckle, and form a conformal pocket storing the Na atom. The formation of such a pocket leads to a greater binding energy, which stabilizes the compound and makes it thermodynamically possible. Additionally, high NaC\textsubscript{x} concentrations are possible in bilayers due to stabilizing Na/Na interactions, which explain why the low voltage plateau can extend to higher capacities.

Lastly, at extremely low voltages and high NaC\textsubscript{x} concentration, deposition of Na atoms on graphene surfaces is shown to be possible. Graphene sheets and Na atoms
do not have the requisite ionic interactions needed for stable storage. However, if the concentration of NaC$_x$ is raised to a high enough level, the voltage climbs to values close to 0. While no outright positive values were obtained by increase the Na concentration on a graphene surface we assume that a slightly defective graphene sheet, such as a slightly curved one, combined with a high concentration would result in a favorable voltage. Additionally, it was shown it is more favorable for the Na atoms to assemble in a 2D fashion, forming a film of Na atoms on the surface of the graphene. Once a base graphene layer is established, the Na atoms can begin the deposition process by forming 3D clusters. The refusal of Na atoms to initially cluster is a plausible explanation for why the voltage of a Na-half cell battery drops below 0 V vs. Na$^+$/Na before jumping back up to 0 V once the plating process begins: the atoms spread over the graphene surfaces until they reach a critical concentration point. Once that point is reached and the clustering begins, Na atoms which were only weakly held on the graphene surface leave it to participate in the plating process which occurs close to 0 V.
Chapter 9: SEI formation and Long Term Cycling: an Electrolyte Story

9.1 Abstract

Capacity fading in Na/C half-cells has long been attributed to the continuous formation of the solid electrolyte interphase (SEI). The SEI is often assumed to grow thicker during on the anode during cycling, eventually rendering it electrochemically inactive. However, our findings shed new light on this assumption. We show that SEI has an inward progression into the anode material, not an outward one. Additionally, we also report that the Na metal counter electrode is hardly an inactive component in the Na/C half-cell. Contrarily, it is a primary source of electrolyte degradation. We then show that the combination of SEI formation, along with electrolyte degradation leads to severe kinetic problems at the electrolyte/anode interface resulting in poor electrochemical performances. However, we also demonstrate that such negative effects in a Na/C half-cell are easily reversible. By either drastically reducing the current rate, or pairing it with new electrolyte and Na-metal counter electrode a carbon material with a 70% capacity loss can recover its original performances. These conclusions bring forth valuable insight. This shows that in a Na/C half-cell setting, long term fading is not due to the carbon material, but caused by electrolyte degradation stemming from interface phenomenon.
9.2 Introduction

The majority of the current literature on NIB carbon anodes center around three metrics: capacity, power performance and long-term cycling. It also uses a Na/C half-cell setup for electrochemical testing. To those ends, high performance has been published in the literature. While this is encouraging, there are still a few outstanding issues that need to be addressed to accelerate progress, mainly the issues of mass loading and first cycle coulombic efficiency (CE@1st). Most reported materials typically use mass loadings of 1.0 to 1.5 mg cm$^{-2}$. While this is acceptable on the lab scale, commercial batteries will require mass loadings greater than ca. 5.0 mg cm$^{-2}$, which is a very conservative estimation for the needed mass loading of commercial devices. We have opened commercial Li-ion batteries for brand name cell phones and measured the mass loading of graphite anode and found the loading is ca. 10 mg cm$^{-2}$. Additionally, commercial batteries will also require CE@1st to be at least greater than 80%. There can be little compromise on these two factors if NIBs are ever to be a viable EES technology. However, high mass loading anodes in Na/C half-cells typically exhibit poor performances with regards to CE1st and long term cycling. However, research and insights into these problems have been limited. Unfortunately, there is little incentive to study and analyze poor results.

Herein, we take on the issues of high mass loading and poor long term cycling head on. We study the root causes of capacity fading of hard carbon anode with a high active mass loading in a Na/C half-cell. The “high mass loading” referred to here is defined that an areal capacity can be above 1 mAh cm$^{-2}$, an internal arbitrary standard. If the specific capacity is 200 mAh g$^{-1}$, it would require a mass loading above 5 mg cm$^{-2}$. The mass loading of the self-standing cloth was above that with
a loading of 7 mg cm$^{-2}$. We then probe several crucial questions: is a high-mass loading carbon anode intrinsically poor at long term cycling? Or, are external factors, such as electrolyte/carbon surface interactions, i.e., SEI formation, or the presence of a Na-metal counter electrode to blame? This will allow the field to gain highly valuable insight on its current scientific approach, as well as the viability of hard carbon as long cycling NIB anode material.

To minimize external, non-carbon influencing factors, we select an additive-and-binder-free self-standing hard carbon cloth as the electrode, derived by pyrolyzing “Lyocell” cloth. Using this self-standing carbon anode, we discover that electrolyte degradation is the primary cause for the capacity fading during long cycling in a Na/C half-cell. The electrolyte degradation mechanism manifests itself in SEI formation, which surprisingly does not grow outward from the carbon interface, but rather inward. We also demonstrate that a severe capacity loss can be recovered in its entirety by either drastically lowering the current rate or paring it with new a Na-metal counter electrode and new electrolyte. This latter method also leads to the complete recovery of original rate performance and diffusivity values. Furthermore, we find that in a half-cell setting, the presence of the Na-metal significantly impacts the long cycling life by degrading the electrolyte. Lastly, the self-standing carbon anode offers the CE1st close to 90%, where we identify that the CE1st is lowered by the addition of binder and high surface area carbon additives. It is important to remember that such insights on the fading mechanism/capacity recovery are most applicable to Na/C half-cells with a heavy carbon anode. Speculative application of these findings beyond this system is left up to the individual reader, as is further research, which is highly encouraged. It is likely that there are some significant parallels in the degradation mechanism with Li/C and K/C
half-cells, and with that of full cells—though full cells also have to contend with
delamination of the electrode from the current collector as another degradation
mechanism.[131]

9.3 Experimental

9.3.1 Material synthesis

The Lyocell was a commercially obtained Tencel-C fiber. It was pyrolyzed for 2
hours under high-purity argon gas at a temperature of 1600°C. The heating rate
was of $5^\circ \text{C min}^{-1}$. After annealing, the carbon cloth was washed in a dilute HCl
bath, after which it was fully rinsed with de-ionized water and dried. The areal
density of the carbon cloth was found to be 7 mg cm$^{-2}$.

9.3.2 Electrochemical preparation

Na/C half-cells were composed of a L-1600 carbon cloth working electrode and
a Na-metal counter/reference electrode. The cloth was cut into squares weighing
from 3-4 mg a piece, before being placed in a 2032 coin cell. The Na-metal and the
carbon cloth were separated by two stacking separators: a polypropylene separator
(Celgard) and a glass fiber separator (Aldrich). The electrolyte used was a 1M
NaPF$_6$ (Alfa Aesar) solution in a 1:1 ethylene carbonate/diethylene carbonate
(EC/DEC) solvent. The solvent was obtained pre-mixed from BASF. The Na-
metal was placed onto the glass fiber separator to one side, while the other side was covered with a stainless steel spacer. A stainless steel spring was further added onto the spacer before placing the top half of the 2032 coin cells, and crimping the cells shut.

9.3.3 Switching of Cell Components

9.3.3.1 Changing the Electrolyte

When the electrolyte was changed, the coin cell was fully desodiated and opened in an Ar filled glovebox using a set of pliers to cut the sides of the coin cell. Following the opening of the coin cell, the carbon/separators/Na-metal/spacer/spring stack was rinsed multiple times with fresh electrolyte without ever being separated. The stack was then placed into a new coin cell case where new electrolyte was again added and the cell was crimped shut.

9.3.3.2 Replacing the Na-metal Counter Electrode, Separators and Electrolyte

When the Na-metal counter electrode was changed, the cell was again fully desodiated and opened in an Ar filled glovebox. Once opened, the carbon cloth was taken from the cell and rinsed with electrolyte, it was then placed in a new cell, where new cell components, such as the separators and the Na-metal were added.
The spacer and spring used were the same, as to keep test conditions as close to the original as possible.

9.3.3.3 Long Term ‘Soaking’ of the Na-metal Inside Electrolyte

An electrolyte solution was prepared in a vial and fresh Na metal was put in it, before it was shut, with the cap wrapped in parafilm to keep glovebox impurities out. It was kept in the glovebox for 3 months, being periodically shaken by hand every a few days.

9.3.4 Materials Characterization

SEM/EDX was recorded through a FEI Quanta 600 SEM. The SEM lift out was obtained through a focused ion beam (FIB) using a FEI QUANTA 3D dual beam SEM/FIB. Prior to the lift-out, the carbon anode was fully desodiated, opened in a glovebox and cleaned. The carbon material was then removed from the glovebox and was briefly rinsed in ethanol before being vacuum dried. Immediately following this, it was placed into the SEM chamber, where the selected fiber was sputtering coated with platinum as to protect the surface from the FIB. Once the lift-out was obtained, it was then welded with platinum to a TEM grid before being imaged on a FEI Titan 80-300 TEM.

Transmission Electron Microscopy (TEM) images are collected with a FEI Titan 80-300 TEM at Center for Advanced Materials Characterization in Oregon (CAM-
COR) in Eugene, OR. Image analysis/filtering was performed using a series of high frequency and low frequency filters, followed by a gray scale averaging in a program written by the first author. This was done using the MATLAB R2015a program. Details about the program/a full version of the script are available upon request.

TGA measurements were obtained using a TA Instruments Q600 thermogravimetric analyzer under air atmosphere at 100 mL min$^{-1}$ and a heating rate of 10°C min$^{-1}$.

Surface area and porosity measurements were obtained utilizing a Tristar II series surface area and porosity analyzer from micromeritics, using N2 gas adsorption/desorption. Specific surface area was obtained using the Brunauer-Emmett-Teller (BET) method, while the porosity was obtained through the density function theory (DFT) method.

XRD patterns were obtained on a Rigaku Ultima IV Diffractometer using Cu Kα radiation ($\lambda=1.5406$ Å) and fitted with the PDXL software.

Raman spectra were collected using a HR 800 LabRam HORIBA JOBIN YVON™ system with a 532.02 nm laser source. Peaks were deconvoluted using the voigt function. Fitting of peaks was done using Lorentzian fitting parameters using the LabSpec 6 Spectroscopy Software Suite and OriginPro 8. Raman spectra of electrolytes were obtained through cutting a piece of the glass fiber separator from the cycled half-cell, or soaking a separator with a new electrolyte.

XPS measurements are conducted on a Physical Electrons Quantera ESCA Microprobe with a focused Al Kα X-ray (1486.6 eV) source for excitation. The X-ray
beam is a 25 W, 100 µm X-ray beam spot at the sample. The ion gun used is a standard Quantera ion gun, and the sputtered depth profiles are acquired using a 1 KeV argon-ion beam rastered over a 3 mm x 3 mm area; and the binding energy scale is calibrated using the Cu 2p2/3 feature at 932.62 (+/-) 0.05 eV and Au 4f at 83.96 (+/-) 0.05 eV.

FTIR spectra were collected in attenuated reflectence mode (ATR) using a Nicolet™ iS™ 10 spectrometer. Electrolytes were tested in the same manner by the Raman spectroscopy.

### 9.3.5 Electrochemical characterization

Galvanostatic cycling is conducted on a Maccor 3000 at 25°C. The C-rate was set to be 200 mA g⁻¹.

Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) are obtained on a Bio-logic EC Lab VMP-3 under ambient conditions. The Z-fit® lab software from Bio-logic was used for the circuit fitting of the impedance.

Galvanostatic Intermittent Titration Technique (GITT) testing was performed using a current pulse of 10 mA g⁻¹ with duration of 1 hour, followed by a 4-hour rest period.
9.4 Results

9.4.1 Material Synthesis & Characterization

The carbon materials studied are obtained through pyrolysis of commercially available Lyocell cloth. Lyocell fibers are regenerated cellulose filaments, formed from cellulose dissolution in organic solvents, such as N-methylmorpholine N-oxide (NMNO), followed by extrusion through a narrow opening and re-crystallization in a coagulation bath.[132] In this study, we pyrolyzed light gauge waffle cloth weave Tencel-C, which is a cloth composed of Lyocell fibers of roughly 5 μm diameter threaded into strands close to 100 μm in diameter (Figure 9.1).

The cloth is pyrolyzed at 1600°C under Ar gas for 2h, yielding a self-standing and flexible carbon-fiber cloth. Due to the uneven arrangement of the carbonized threads, a precise thickness was difficult to obtain, however when cut in discs with a radius of 1 cm, the carbon cloth is found to have an areal density of 7 mg cm$^{-2}$ (Figure 9.2)a. This cloth material will be referred to as L-1600 hereafter. Closer inspection of pyrolyzed cloth under scanning electron microscopy (SEM) shows that most individual fibers have retained their morphology as their original ‘bundles’.

N$_2$ sorption measurement reveals hard carbon cloth of low surface area and low porosity with a Brunauer-Emmett-Teller (BET) surface area of 1.96 m$^2$ g$^{-1}$ and a density functional theory (DFT) total pore volume of 0.007 cm$^3$ g$^{-1}$. TEM imaging along with its noise-filtered-frequency-transformed image shows an amorphous carbon structure consisting of few-layered turbostratic nanodomains and amorphous
Figure 9.1: a) A digital image of Lyocell cloth prior to pyrolysis, where an alumina crucible is used for the pyrolysis. b) A SEM image of the Lyocell cloth prior to pyrolysis. c) Lyocell carbon cloth cut into squares following the pyrolysis at 1600°C. d) Demonstration of hydrophobicity of the carbon cloth. e, f) SEM imaging of the L-1600 cloth. g, h) SEM imaging of L-1600 ground into powder form. i) Cross sectional imaging of a L-1600 individual carbon fiber, where large internal pores can be seen.

regions (Figure 9.2b-c).

The Raman spectrum confirms a typical amorphous carbon structure, expressing D-band at 1350 cm\(^{-1}\) and G-band at 1580 cm\(^{-1}\). The D-band is ascribed to phonons scattering at the K-point edge of the Brillouin zone, which stem from the A1g breathing mode of six-carbon rings. Defects must be present in the carbon rings for phonon scattering from this mode to occur. The G-band arises from high-
Figure 9.2: a) A representative SEM image of L-1600 carbon cloth, showing the individual carbon fibers arranged into the bulk strands. The inset shows the flexibility of the cloth. b) A representative high-resolution TEM image of L-1600. c) The same TEM image that has undergone a 2D Fourier transform and subsequent frequency filtering in order to better show the contrast between the graphene domains and amorphous regions of the material. d) Raman spectrum (top) and XRD pattern (bottom) of L-1600. The index of the TiO hongquite phase is shown. e) A representative high angle angular dark field (HAADF) TEM image of a carbon fiber cross-section. f) An image of the enlarged area marked in the box in (e) on one of the particulates/pores in the carbon fiber cross-section and corresponding energy dispersive x-ray (EDX) elemental mappings of titanium, oxygen and carbon.

frequency $E_{2g}$ phonons emanating at the $\Gamma$ point, the center of Brillouin zone. Its intensity is proportional to the number of sp$^2$-bonded carbon, which does not require the presence of six-member rings. There is also the presence of a D band overtone—the 2D band at 2700 cm$^{-1}$, a double resonance frequency made possible
by the absence of defects.[19] The presence of 2D peak indicates that this material has a good degree of graphenic order due to the high annealing temperature during pyrolysis. In addition to the non-graphitic carbon, the spectrum also reveals the existence of TiO$_x$ impurity by the peaks around 150 cm$^{-1}$, 400 cm$^{-1}$ and 600 cm$^{-1}$, which are similar signals found in other TiO$_x$ carbon materials (Figure 9.2d). TiO$_2$ is often added to Lyocell fibers as to increase ultraviolet protection or enhance self-cleaning properties.[133] Surprisingly, the XPS analysis did not reveal any signals of Ti, but it did show faint traces of Ca, most likely a leftover artifact from the synthetic process. The failure of XPS to display Ti signals is most likely due to the presence of the TiO particles on the inside of the carbon fibers, where they are too far from the surface to be probed by XPS radiation. Thermogravimetric analysis (TGA) under air to 900°C reveals an ash mass of 3%, which is attributed to the TiO$_x$ compound along with the trace Ca. Energy dispersive X-ray spectroscopy (EDX) revealed a similar mass percentage of TiO$_x$.

X-ray diffraction (XRD) patterns confirm the non-graphitic carbon structure along with the presence of titanium-containing impurity. The broad peaks around 24° and 43° represent the (002) and (100) crystallographic planes, respectively, where the (002) d-spacing of 0.366 nm is typical for hard carbon (Figure 9.2d). Using the Scherrer equation, L$_a$ and L$_c$, the coherence lengths along the ab plane and c-axis in the turbostratic nanodomains, are estimated to be 3.97 nm and 1.10 nm, respectively. Combining the (002) d-spacing with L$_c$ values, we can estimate that the average turbostratic nanodomains are of 3-graphene-layers thick. These results may appear different from the TEM image; however, it is important to remember that the values provided by the Scherrer equation serve to give the average length: while there are 5-layered domains, and there are also regions that have no order
and thus lower the average. The same can be said for the \( L_x \) dimensions.

The additional XRD peaks at 36°, 42°, 61°, 73° and 77° can be indexed to TiO in the hongquite phase (Figure 9.2d).[134] XRD pattern of the unpyrolyzed cloth fails to show significant crystalline phases; however, Raman spectrum of the unpyrolyzed cloth shows peaks at low wavenumbers consistent with TiO\(_2\). It is likely that the titanium species were reduced from Ti(IV) to Ti(II) during the high temperature annealing under high purity argon gas.[22] Looking at the cross section of a carbon fiber, we can spot the presence of several particulates inside of a fiber, which happen to be high in Titanium and Oxygen content (Figure 9.2e-f). The presence of the TiO on the inside of the cloth would explain why the L-1600 sample failed to show any presence of titanium during the XPS analysis. Unlike the other characterization techniques, such as Raman, XRD, EDX and TGA that give a ‘whole’ characterization of the sample, XPS radiation in only helpful in probing the first few nanometers of a material surface. The location of the TiO particles are well beneath the surface of the carbon fiber, as seen in the SEM lift-out, would explain why the presence of Ti is not present on the XPS but present in all the other tests.

9.4.2 Electromchemical Results

To test electrochemical performance, L-1600 cloth was cut into squares weighing around 3-4 mg per square as the working electrode in Na/C half-cells, where Na foil serves as both counter and reference electrode. For electrochemical testing, the C-rate was set to be 200 mA g\(^{-1}\). At a current rate of 20 mA g\(^{-1}\) (C/10),
L-1600 exhibits a reversible desodiation capacity of 210 mAh g\(^{-1}\) and a CE@1st of 89.4% (Figure 9.3a). This is one of the highest CE@1st values in literature for hard carbon anodes.[23] The combination of the desodiation capacity along with the high CE@1st is important when considering anode materials for a full cell: a full cell is in its charged state when the carbon anode is fully sodiated. Thus the capacity available in a reversible battery is dependent on the amount of ions that can be reversibly desodiated from the anode material. Furthermore, a high efficiency of sodiation is critical. It is also important to remember that a full cell only possesses a finite amount of Na-ions in the cathode, which makes the high CE@1st doubly important.

Some of the cloth was ground into powder and processed into traditional electrodes using polyvinylidene fluoride (PVdF) binder and C-45 conducting carbon additive. However, these cells exhibited a lower CE@1st, with the L-1600-91 (90 wt% carbon, 10wt% PVdF binder) having an efficiency of 81.9% with a loading mass of 2.4 mg cm\(^{-2}\) on an aluminum disc with a diameter of 1 cm. The L-1600-811 (80 wt% carbon, 10 wt% PVdF binder, 10 wt% C-45) had a CE@1st of 82.1% with a loading mass of 2.1 mg cm\(^{-2}\) on a similar aluminum disc. These results hereby show that PVdF and high surface area C-45 are responsible for the lower CE@1st, which is reduced by close to 10%.

The potentiogram profiles are typical for a hard carbon material: a steep sloping region followed by a long low-voltage plateau. The sloping region is attributed to the binding of Na-ions at defect sites in the carbon, while the plateau region is assigned to Na-ion intercalation between graphene layers and atomic layer deposition in the pores. The potentiogram profiles also reveal the lack of significant contri-
Figure 9.3: a) The 1st cycle potentiograms of the L-1600. b) Long-term cycling of the L-1600, total capacity (black), capacity contribution over 0.1 V vs Na\(^+\)/Na (red), capacity contribution under 0.1 V vs Na\(^+\)/Na (blue) and coulombic efficiency (gray). The initial climb in capacity from 210 mAh g\(^{-1}\) to 235 mAh g\(^{-1}\) in the initial cycles is most likely due to a prolonged ‘wetting’ period. c) Linear regression of the total capacity vs the capacity under 0.1 V vs Na\(^+\)/Na for 350 cycles. d) Potentiograms at current rates of 1 mA g\(^{-1}\) and 20 mA g\(^{-1}\) after 350 cycles. e) Impedance spectra conducted after the 1st cycle and after the 350th cycle. Inset shows the equivalent circuit. f) A zoomed in view of the semi-circle comparing the anode materials. The inset shows the difference in ESRs.

Distribution of capacity from TiO, as such a contribution would be manifested in the presence of a much shorter low voltage plateau and longer and more pronounced sloping region from 0.15 V to the cutoff voltage.

Long cycling tests are conducted at a current rate of 20 mA g\(^{-1}\) (C/10). In 350 cycles, the observed capacity decreased from the maximum of 235 mAh g\(^{-1}\) to 70 mAh g\(^{-1}\)—a retention rate of only 30% (Figure 9.3b). While such poor cycling
results are not desirable, it is a great opportunity to investigate the causes of capacity fading in these half-cells.

We notice that the overall capacity fading is primarily due to the capacity loss from the low-voltage plateau region below 0.1 V vs Na\(^+/\)Na. The capacity retention is only 15% for the low-voltage plateau, but 80% for the sloping region. After 350 cycles, negligible capacity contribution is from the low voltage plateau (Figure 9.3b). This is further supported by a linear regression comparing the total capacity versus that obtained under 0.1 V, which yields an $R^2$ value of 0.998 (Figure 9.3c).

Intriguingly, when the current rate is lowered to 1 mA g\(^{-1}\) (C/200) after 350 cycles, the capacity rises to 260 mAh g\(^{-1}\)—even higher than the original capacity at 20 mA g\(^{-1}\) (C/10) (Figure 9.3d). Furthermore, the entire low voltage plateau re-appears. This shows that capacity fading is not due to a structural breakdown of carbon anode, but rather due to kinetic limitations.

To study the kinetic limitation, we first compare electrochemical impedance spectra (EIS) between the 1st and the 350th cycle, along with the fitted circuit (Figure 9.3e). From the Nyquist plot, equivalent series resistance (ESR), the x-axis intercept, increases from 7.42 Ω to 95.02 Ω (Figure 9.3f). The semi-circle is due to the resistance of the solid electrolyte interphase (SEI) and the charge transfer resistance, which should be attributed to both carbon and Na metal electrodes.[25] The sum of the two resistive elements that makes up the semicircle, $R_{SEI} + R_{CT}$, rises from 243 Ω for the 1st cycle to 754 Ω for the 350th cycle. This confirms the presence of severe kinetic problems developing in the cell in the course of long cycling.
Having established the presence of a kinetic problem, the next challenge is to reveal its root causes: whether it is due to the intrinsic properties of the carbon material, or other factors in the Na/C cells.

9.4.3 Visual Analysis of SEI

Our first thought was that increased SEI formation on the surface of the individual carbon fibers is the cause for kinetic problems. Thus, we analyzed two representative L-1600 electrodes at two different cycling life stages in capacity retention: one that has had a 75% capacity retention after 150 cycles and the other that has 35% capacity retention after 250 cycles. To visualize SEI layer, we used a focused ion beam (FIB) to carve cross-sectional slices of carbon fibers. We collected oxygen EDX elemental mappings to profile the extent of SEI formation as a function of oxygen concentration (Figure 9.4a & c). The images are displayed on an enhanced color scale to sharpen the contrast between oxygen signals and the background, where the dark blue represents no oxygen signal. We also plot both profile and 3D pixel intensity maps to better identify concentration gradients (Figure 9.4b, d, e, f), where the pixel values are plotted on the vertical axis, with a high value corresponds to a high oxygen concentration, and thus a high presence of SEI.

It must be pointed out that in our visualization of the SEI, we do not characterize and identify individual SEI components. Rather we look at the SEI as a broad-based entity quantified through the presence of oxygen, as our ultimate goal is to elucidate the relationship between the scale of SEI formation and long term cycling
Figure 9.4: Cross-sectional EDX oxygen mappings of cycled L-1600 carbon, a) An electrode after 150 cycles with 75% capacity retention, c) An electrode after 250 cycles with 35% capacity retention. b, d) Corresponding plots of the pixel values from a profile view. e,f) Corresponding 3D pixel intensity plots of the L-1600-75% and L-1600-35% carbon fibers, respectively. The labelled axis is the z-axis, where the pixel values are plotted on a scale of 0 to 200. The basis for the pixel plots is the sheered images of (a) and (c).

performance. Since we could not control the formation of the SEI, we consider it would be best to treat it as a single entity that could be quantified and imaged by the amount of oxygen content. Prior to the cross-sections being cut with the FIB, the electrodes were removed from the Na/C half-cells in an Ar filled glovebox, and washed and briefly sonicated in ethanol before being vacuumed dried. The intent of the washing and sonication was to rid the electrodes of remaining liquid electrolyte. Thus, with such a preparation, the only oxygen signals present in the characterization should emanate from the remaining SEI deposits. It is likely that the washing affected the concentration of the oxygen content. However, it is
important to mention that both samples were subject to the same preparation, yet both yielded vastly different distributions of oxygen signals.

Comparing L-1600-75% to L-1600-35% reveals a surprising phenomenon: the SEI growth on hard carbon has not been an outward growth as one would expect, but an inward growth. L-1600-75% shows a high oxygen concentration near the surface, which tapers off when moving towards the fiber center. L-1600-35% displays a nearly uniform oxygen concentration through the entire cross section of carbon fiber. This is significant as it shows that the SEI is not the traditional “interphase” as is the case with graphite anodes in LIBs. The unique inward growing Na-SEI in hard carbon may have to do with the innate “microporous” structure of hard carbon despite its low BET surface area measured by N\textsubscript{2} sorption.

9.4.4 Effects of Replacing Battery Components

To investigate whether such inwardly grown SEI would cause slower diffusion of Na-ions inside hard carbon, we measured the diffusivity values using GITT. After 350 cycles, the diffusivity values of half-cells are three orders of magnitude lower in the low-voltage plateau region than the freshly-made cells with the same carbon cloth electrode material (Figure 9.5a). However, it seems likely that the lowered diffusivity values can be related to other components in the Na/C cells than the hard carbon anode. When opening a cycles cell, we notice the yellow tint of the separator indicating the degradation of the electrolyte over cycling.

Therefore, we conducted GITT tests on the same carbon cloth anode at four se-
Sequential stages: (1) as a pristine anode, (2) after 300 cycles (3) after replacement of cycled electrolyte with new electrolyte and (4) after replacing all cycled cell components with new ones, including electrolyte, separator and Na counter electrode except for the cycled hard carbon electrode (Figure 9.6). This 4-tiered diffusivity/rate cycling studies allow us to track the changing electrochemical behavior of hard carbon anodes, electrolyte and Na electrode.

We discover that the diffusivity values of a new cell drop precipitously after 300 cycles, recover slightly when new electrolyte is added, and recovers to nearly its full extent when the electrolyte, the Na metal counter electrode and the separator are replaced with new ones (Figure 9.5b). The capacity values display a similar trend. After long cycling, the capacity at a current rate of 20 mA g\(^{-1}\) (C/10) is 44% of the original; replacement of the electrolyte increases the capacity to 74% of the original value, while the replacement of the electrolyte, separator, and Na metal counter-electrode yields a capacity close to 95% that of the original (Figure
9.5c). The results show a surprising fact: the capacity fading of hard carbon has nothing to do with hard carbon even kinetically, as a poorly performing electrode can easily be rejuvenated into its former self. This shows that the negative effects of SEI formation on a carbon anode are easily reversible. This leaves there be two causes to the fading of Na/C half-cells: degradation of the electrolyte and passivation of the Na-metal counter-electrode.

9.4.5 Electrolyte Analysis

To understand the relationship between the degradation of electrolyte and the role that Na counter electrode plays, we conducted experiments to reveal the reactivity of Na-metal with the electrolyte. We also investigated the chemical composition of electrolyte trapped in the glass fiber separator of a cycled Na/C half-cell.

After being soaked in the electrolyte for three months, Na foil is covered by a
passivation layer, while the electrolyte turns slightly yellowish (Figure 9.7a-b). When exposed to air, the passivation layer on Na foil prevents its surface from being oxidized to sodium oxide, as the soaked Na foil does not turn white as a fresh piece of Na-metal rapidly does (Figure 9.8).

Figure 9.7: a) Digital image of Na-metal disc being soaked in a 1M NaPF$_6$ EC:DEC electrolyte for 3 months in an argon glovebox. b) Close-up image of the Na-metal disc. c,d) FTIR and Raman spectra of new electrolyte in glass fiber separator, cycled electrolyte in glass fiber separator, which has undergone 350 cycles at 20 mA g$^{-1}$ and Na-metal surface soaked in 1M NaPF$_6$ EC:DEC electrolyte for 3 months. e) Magnification of Raman EC ring bending mode at 720 cm$^{-1}$ and PF6- stretching mode close to 750 cm$^{-1}$. f) Magnification of Raman EC ring-breathing mode close to 900 cm$^{-1}$. g) Overpotential versus cycle number over 350 cycles at 20 mA g$^{-1}$. The outlying points correspond to the values obtained during the first 20 cycles where the anode has not been properly wetted. h) Net current on a log scale vs. voltage jump at the beginning of desodiation, leading to a Tafel-like plot. The dashed lines were used to analyze exchange currents.

The Fourier-transform infrared (FTIR) spectra of the soaked Na foil and the cycled electrolyte (350 cycles) in the separator are very similar, much different from the new electrolyte (Figure 9.7c). The measurements of the cycled electrolyte
are obtained by cutting a piece of the yellow tinted separator, which acted as “electrolyte sponge”. Thus we take the measurements from the separator to be representative of the state of the electrolyte in the Na/C half-cells. Measurements of the new electrolyte are also done by using a separator as 'electrolyte sponge', which was then characterized. The background of the glass fiber separator as well as the sodium metal factor little in the measurements (Figure 9.9).

Figure 9.9: FTIR spectra. a) The background of a new glass fiber separator. b) The pure sodium metal exposed to air, versus the sodium metal that has been soaked in 1M NaPF6 EC:DEC electrolyte for 3 months.
The adsorption bands at 1640 cm$^{-1}$ and 1320 cm$^{-1}$ correspond to the asymmetric ($\nu$ AS) and symmetric ($\nu$ S) C=O stretches, respectively, of CH$_3$CH$_2$OCOONa, also referred to as ROCO$_2$Na, which is known to be a main breakdown product in ethylene carbonate (EC)-containing electrolytes due to the ring opening of EC.[135, 136] The peak near 1400 cm$^{-1}$ is due to the formation of a carbonate compound, though it has also been ascribed to the CH$_2$ bending mode ($\gamma$ CH$_2$) of the carbon chain in the ROCO$_2$Na breakdown product.[137] Specifics aside, it is yet another sign of electrolyte breakdown.

The FTIR results show that the passivation layer on the soaked Na metal has the same fingerprint as the SEI electrolyte breakdown species that are found in the cycled electrolyte. This indicates that such breakdown products do not adhere the Na-metal surface well and could leach throughout the cell. Similar results were reported by Ponrouch et al. who explored the surface of Na-metal electrodes after conducting CV cycling in a symmetric cell.[138] However, for the soaked Na metal, the SEI is formed without electrochemical cycling, showing the inherent instability of the Na metal with conventional carbonate electrolytes.

To further understand the electrolyte degradation, we also collected Raman spectra of the cycled electrolyte (350 cycles) and compared them to a fresh, uncycled electrolyte. The spectrum peak intensity was normalized using the peak at 1224 cm$^{-1}$, as this peak represents the C-H bonding mode of EC, which is not affected by the addition of electrolyte salts.[139] We specifically focus on the peaks around 720 cm$^{-1}$ and 900 cm$^{-1}$. The peak at 720 cm$^{-1}$ is assigned to the ring deformation mode of EC, which reflects the cation-solvent interaction.[140, 141] For this peak, firstly, the peak intensity is much smaller for the cycled electrolyte, meaning
that the EC molecules have been consumed in the SEI build up (Figure 9.7d). Secondly, there is a blueshift to a higher wavenumber, meaning that the ratio of coordinating EC molecules in EC-Na$^+$ over free EC molecules has increased (Figure 9.7e). The peak near 740 cm$^{-1}$, ascribed to the stretching vibration of PF$_6^-$ anions,[142] is nearly unchanged. Lastly, the peak at 900 cm$^{-1}$ is due to the ring breathing mode of EC, which blueshifts when there are cation interactions, i.e., forming EC-Na$^+$. [139] Again, the cycled electrolyte exhibits an attenuated peak along with a blueshift when comparing to the new electrolyte (Figure 9.7f). The lower peak intensity indicates the electrolyte degradation along with the blueshift, shows that the concentration of ionic species has increased after cycling.

Comparison between the Raman spectra of the cycled electrolyte and the surface of the electrolyte-soaked Na-metal reveals similar profiles—as is the case with FTIR (Figure 9.10). The insights that cycling increases ionic concentration via electrolyte degradation from Raman results were verified through a controlled trial by taking Raman readings of EC:DEC electrolyte solutions with molarities of 0.5M, 1M, 2M and 4M of NaPF$_6$ (Figure 9.11).

9.4.6 Effects of Electrolyte Degradation

The increase in salt concentration causes greater ion pairing between the Na$^+$ and PF$_6^-$ ions, thus making it more difficult for the Na-ions to be desolvated from the electrolyte before insertion into hard carbon. This could slow down the reaction kinetics, especially in the case of Na-ion intercalation between graphene layers in hard carbon. It has been shown experimentally and computationally that
Figure 9.10: a) Raman spectra comparing a new electrolyte, a cycled electrolyte and the electrolyte soaked Na-metal surface. b) Focus of the EC/EC-Na$^+$ ring deformation mode near 720 cm$^{-1}$ and the PF$_6^-$ stretching mode near 750 cm$^{-1}$. c) Focus near the EC/EC-Na$^+$ ring-breathing mode near 900 cm$^{-1}$.

Figure 9.11: a) Raman spectra of controlled electrolyte solutions of 0.5M, 1M, 2M and 4M NaPF$_6$ in EC:DEC. b) Focus of the EC/EC-Na$^+$ ring deformation mode near 720 cm$^{-1}$ and the PF$_6^-$ stretching mode near 750 cm$^{-1}$. c) Focus near the EC/EC-Na$^+$ ring-breathing mode near 900 cm$^{-1}$. In the higher concentration electrolytes we can see evidence of blue shifting in the 720 cm$^{-1}$ and 900 cm$^{-1}$ peaks, indicating the greater presence of EC-Na$^+$. desolvation is a rate-limiting step as partially-solvated ions diffuse much faster into graphitic domains than naked ions.[143, 144]
This explains why the diffusivity values of the cycled Na/C half-cells obtained via GITT drop so precipitously. If there is a greater energy penalty for an ion to desolvate from the electrolyte, a greater voltage must be applied during GITT to move the same number of ions into the carbon structure in a unit time. This results in a greater polarization. However, this greater polarization causes the battery tester to hit the cut-off potential prematurely, which subsequently switches it into a desodiation mode, before a full sodiation can be obtained. This explains the disappearance of the low voltage plateau after long cycling, along with its recovery if low current rates are used, or the degraded electrolyte is replaced.

The degradation of electrolyte also causes an increase in overpotentials during the desodiation sweeps. When the Na-ions are removed from the carbon anode, they need to be resolvated by EC molecules. If the concentration of free EC molecules is low, there will be greater polarization on the carbon surface—this is much like the concept of overpotential ($\eta$) in Butler-Volmer reaction kinetics.

As further proof of this, we plot the voltage “jump” (Figure 9.7g inset) that occurs when the battery switches from sodiation to desodiation mode. Looking at Figure 9.7g, we see that aside from the initial cycles this voltage jump increases steadily along with cycling, and is well correlated with the desodiation capacity during cycling—when the voltage jump is higher the capacity is lower. The initial voltage jump decreases most likely due to the electrolyte/carbon anode wetting process.

Initially, we took this voltage jump to be a sign of an increasing equivalent series resistance (ESR). However, when running a rate-cycling test at current rates ranging from 1 mA g$^{-1}$ (C/100) to 1500 mA g$^{-1}$ (7.5C), we failed to see a linear
trend of the voltage jump, especially at low current rates, thereby showing that this voltage jump is not entirely a function of ESR (Figure 9.7h). This was the case in multiple cycled cells.

Thus, we postulate this voltage jump to be a pseudo-overpotential: an activation overpotential is needed to desodiate the hard carbon, where upon a higher current rate, a greater overpotential is necessary to sustain the desodiation process. When plotting these overpotential values versus a logarithm-scaled version of their current rates, we see that the resulting plot shares many similar characteristics with a typical Tafel plot, thereby indicating that the onset of desodiation has a Tafel-like behavior (Figure 9.7h). When taking this into the context of the electrolyte solution, a clear picture begins to emerge. When Na-ions become desodiated from the carbon material, they must be coordinated by EC molecules. If the ratio of free EC molecules over EC-Na\(^+\) coordinating EC molecules is small, the frequency of newly released Na-ions pairing up with EC molecules will be diminished, which will cause the system to become more polarized, thereby leading to a higher initial voltage jump.

We model the behavior in Figure 9.7h by the Tafel equation (9.1)

\[
\eta = a + b \log(i) \tag{9.1}
\]

where \(\eta\) is overpotential, \(i\) is the applied constant current (the current density can be referred to as \(j\)), \(a\) is the y-intercept of the \(\eta\) versus \(\log(i)\) plot and \(b\) is the Tafel slope (9.2), which equals to
\[-\frac{\alpha F}{2.3RT}\]

where \(\alpha\) term represents the transfer coefficient, \(F\) is Faraday constant while \(R\) is a thermodynamic parameter and \(T\) is temperature in Kelvin.

Here, we plot \(\log(i)\) as a function of \(\eta\), where the slope is found to be extremely similar in both cases, thereby showing that the overall nature of the electrochemical reaction has not changed. However the y-intercept that expresses \(\log(i_0)\) is vastly different with \(i_0\) representing the exchange current when \(\eta\) is zero. Under Butler-Volmer kinetics, this is the current at which both the cathodic and anodic reactions proceed at the same rate. A smaller \(i_0\) implies more sluggish reaction kinetics, and as a result, a higher activation overpotential is needed to drive the reaction. Extending this to the Na/C cell, a smaller \(i_0\) means that it is slower to transport the Na-ions to sodiate/desodiate the carbon anode, especially in the region near the cutoff potential (\(\tilde{0.01}\) V vs. Na\(^+\)/Na).

When comparing the cycled anode (350 cycles) with old electrolyte/old Na-metal versus the same cycled anode paired with new electrolyte and new Na metal, the measured \(i_0\) is much greater for the new electrolyte/new Na cell. This proves that the degradation in electrolyte and passivation of Na-metal lead to much slower kinetics, which adversely affects the performance. This in turn shows that the capacity fading during long cycling is primarily a function of the electrolyte and Na-metal counter electrode. Furthermore, the improved kinetics can lead to much-improved capacities, especially at current rates between 10 mA g\(^{-1}\) (C/20) and 100 mA g\(^{-1}\) (0.5C) (Figure 9.12).
Figure 9.12: Comparison of capacities at current rates ranging from 1 mA g$^{-1}$ to 1500 mA g$^{-1}$ of the same carbon material after it has undergone 350 cycles at 20 mA g$^{-1}$, and the same carbon material once the electrolyte and Na-metal counter-electrode have been replaced with new ones.

It is important to note that our intent of the electrochemical analysis is not a direct analysis of a Tafel-slope, overpotential $\eta$, exchange current $i_0$ and exchange coefficient $\alpha$. Rather, we are trying to show how our current systems follows behaviors highlighted in basic electrochemical principals, and that such comparisons help to show that degrading electrolyte causes severe kinetic problems, which lead to poor battery performances.

9.5 Conclusion

We have demonstrated five findings in this study: (1) Hard carbon materials can obtain CE@1st close to 90%, but that such high CEs are negatively affected by the addition of PVdF and conducting carbon additive; (2) We reveal that SEI slowly
permeates into the hard carbon electrode, and is not confined to the surface. This underscores the importance of developing a proper surface coating for the electrode; (3) More importantly, we discover that even extreme capacity losses during long cycling can be recovered through very slow current rates or replacing Na/C cell components. This shows that the fading during long cycling is caused by kinetic problems and not the degradation of the carbon material. Furthermore, it also shows that the negative effects of SEI formation are reversible. (4) We analytically prove that degradation of the electrolyte, along with the passivation of the Na-metal is the cause for capacity fading of Na/C cells. The degradation greatly affects the sodiation and desodiation processes, causing increased cell polarization, decreased diffusivity values and decreased capacity, especially in the low voltage plateau region; (5) We found that electrolyte degradation readily happens at the Na metal surface—even with the absence of electrochemical cycling, where the same type of breakdown products were also found in the cycled electrolyte and on the soaked Na metal surface, meaning that these SEI products do not stay confined to the surface of the Na-metal and can leach throughout the cell. It is less likely that it is due to the uniqueness of electrolyte we used in this study that causes the observed electrolyte degradation, as the EC/DEC combination is quite representative among carbonate-based electrolytes employed in LIBs and NIBs. Furthermore, it is quite reasonable to believe that the reactivity of the Na-metal damages the electrolytes, which may not be observed in a full cell setup where Na-ion containing minerals are used as the cathode.
Chapter 10: Pyrolysis, Flow-Rate, and the Self-Activation of Carbon Materials

10.1 Abstract

Current synthetic methods of biomass-derived activated carbon call for a high temperature pyrolysis followed by either a chemical or physical activation process. Herein, we report a simple one-step annealing synthesis yielding a high surface area cellulose-derived activated carbon. We discover that simply varying the flow rate of Argon during pyrolysis enables ‘self-activation’ reactions that can tune the specific surface areas of the resulting carbon, ranging from 98 m$^2$ g$^{-1}$ to values as high as 2600 m$^2$ g$^{-1}$. Furthermore, we, for the first time, observe a direct evolution of H2 from the pyrolysis, which gives strong evidence towards an in situ self-activation mechanism. Surprisingly, the obtained activated carbon is a crumbled graphene nanostructure composed of interconnected sheets, making it ideal for use in an electrochemical capacitor. The cellulose-derived nanoporous carbon, was of too high a porosity and surface area to make an effective NIB anode material, but did perform admirably as a capacitor material: it exhibited a capacitance of 132 F g$^{-1}$ at 1 A g$^{-1}$, a performance comparable to the state-of-the art activated carbons.

This work presents a fundamentally new way to look at the synthesis of activated carbon, and highlights the importance of a controlled inert gas flow rate during synthesis in general, as its contributions can have a very large impact on the final
material properties.

10.2 Introduction

Annually around 50 million tons of forestry residues are produced as ‘waste’ in the U.S. alone [1]. This causes severe environmental concerns, such as a greater risk of forest fires and greenhouse gas emission.[145] While the biomass residues can be processed into valuable products, e.g., biofuels, high overhead costs, such as transportation from forest to processing sites, greatly decrease its economic viability.[146, 147] Thus, it is of high urgency to discover scalable and affordable chemical methods that can convert biomass into valuable materials of even higher values. Along this line, activated carbon (AC) is one of the most promising materials that can be synthesized from biomass. With desirable properties, such as high surface area, chemical inertness, and good electrical conductivity, AC is a critical component for a plethora of applications, including energy storage,[148], catalysis,[149] water/air purification,[150] and gas storage.[151] Currently, there are primarily two routes to synthesize ACs from biomass: “physical” activation and chemical activation. Physical activation requires two steps, where the first is pyrolysis and the following step is activation through gaseous etchants, e.g., CO₂ or H₂O steam. In chemical activation, a mixture of biomass and activation reagents, such as KOH, B(OH)₃, H₃PO₄, NaOH, or ZnCl₂ is pyrolyzed before washing of the resulting carbon following activation. Both physical and chemical activation methods lead to environmental consequences, and they involve multiple steps to obtain the final products, which drives the cost high. Thus, fundamentally more
efficient methods are highly desirable.

The question instead is whether AC can be prepared through a simple control of the pyrolysis parameters of biomass, instead consuming either chemical or physical activation reagents. The influence of pyrolysis parameters such as flow rate of inert gas, pyrolysis temperature and reaction duration on the synthesis of biochar, was investigated Lua et al. [152, 153] who were able to optimize the surface area up to 778 m$^2$ g$^{-1}$; though it should be noted that those reactions consumed CO$_2$ gas—a physical activation agent. Similar looking at the effect of pyrolysis parameters on final properties obtained surface areas of 519 m$^2$ g$^{-1}$ and 707 m$^2$ g$^{-1}$ [154, 155]; but again the former study utilized a steam activation, while the latter study did not change the flow rate. While these early studies demonstrate that the high surface area, porous biochar can be made through control of the pyrolysis parameters, they still were not able to demonstrate a one-step reagent free synthesis producing a surface area comparable to traditional ACs.

Herein, we report that one-step pyrolysis of cellulose results in carbon surface area as high as 2600 m$^2$ g$^{-1}$. Furthermore, we attribute the high surface area to the reaction between H$_2$O released during carbonization and the derived carbon. We identify that the flow rate of the inert gas determines the H$_2$O residence time and subsequently the levels of self-activation: a high flow rate prevents the self-activation due to a low residence time, while a low flow rate enhances the self-activation.
10.3 Experimental Details

Filter paper (Whatman™ Type 1) comprising pure cellulose as the hard carbon precursor. The pyrolysis is conducted under Argon at 1100°C for 2 h in the middle of a tube furnace with the inner diameter of 4.45 cm. The furnace is purged under a high flow rate of Argon for 30 min, before being switched to a desired flow rate. Flow rates of 10, 25, 50, 100 and 200 cm$^3$ min$^{-1}$ (CCM) are used. We refer to the samples according to respective flow rates, e.g., C-200 for the sample obtained under 200 CCM of Argon.

BET surface area and DFT pore volume calculations are based on N$_2$ sorption measurements on a Micromeritics TriStar II 3020 analyzer.

XRD patterns are obtained by a Rigaku Ultima IV Diffractometer using Cu Kα radiation ($\lambda$=1.5406 Å). Raman spectra are collected using a HR 800 LabRam HORIBA JOBIN YVON system with a 532.02 nm laser source. SEM images are recorded through a FEI Quanta 600 SEM. TEM images are collected with a FEI Titan 80-300 TEM.

X-ray photoelectron spectroscopy (XPS) measurements are conducted on a Physical Electronics Quantera ESCA Microprobe with a focused Al Kα X-ray (1486.6 eV) source for excitation. The X-ray beam is a 25 W, 100 μm X-ray beam spot at the sample. The ion gun used is a standard Quantera ion gun, and the sputtered depth profiles are acquired using a 1 KeV argon-ion beam rastered over a 3 mm x 3 mm area; and the binding energy scale is calibrated using the Cu 2p2/3 feature at 932.62 (+/-) 0.05 eV and Au 4f at 83.96 (+/-) 0.05 eV.
Elemental analysis is conducted by a commercial company, Elemental Analysis Inc. Thermogravimetric Analysis (TGA) is conducted on a TA Instruments SDT-Q600 thermal analyzer. During TGA, the samples are heated in a 70-µl alumina crucible under ultra-high pure Argon (50 CCM) from room temperature to 1100 °C at a ramp rate of 5 °C min⁻¹. The SDT-Q600 is also equipped with a mass spectrometer (MS) for detecting evolved gaseous species. Selected gaseous species, including H₂, H₂O, CO, and CO₂, are monitored during cellulose pyrolysis.

The electrodes are prepared by mixing 80wt% activated carbon, 10wt% carbon black, C-45 (TimCal) and 10wt% poly-1,1-difluoroethene (PVDF) binder in n-methyl-2-pyrroldinone (NMP). The resulting paste is painted onto a current collector of stainless steel mesh and dried at 60°C in a vacuum oven. The active mass loading of the electrodes is 1 mg cm⁻². Two-electrode capacitors are assembled in 2032 coin cells containing an aqueous electrolyte of 6 M KOH. Galvanostatic cycling is conducted on a Maccor 3000 at 25°C at a current rate of 1 A g⁻¹. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectra (EIS) are obtained on a Bio-logic EC Lab VMP-3 under ambient conditions. Specific capacitance is obtained from data obtained during galvanostatic cycling using equations (10.1)

$$C_s = \frac{4I \cdot \Delta t}{m \cdot \Delta t} \quad (10.1)$$

where $I$ is the current rate used and $m$ is the mass of the both electrodes. The equivalent series resistance (ESR) is obtained through equation (10.2)
whereby $V_{\text{drop}}$ is the voltage drop at the onset of discharge and $I$ is the current rate used. Lastly electrochemical impedance spectra (EIS) of the symmetric ECs were conducted from 200 kHz to 10 mHz.

10.4 Results

The impact of Argon flow rate is evident from the N2 sorption measurements of the resulting nanoporous carbon (Table 10.1 & 10.1). As the flow rate decreases, the N$_2$ absorption volume steadily increases. Using a low flow rate of 10 CCM results in a specific surface area of as high as 2,600 m$^2$ g$^{-1}$ as opposed to only 98 m$^2$ g$^{-1}$ when a high rate of 200 CCM is used. Performing a linear regression analysis of specific surface area and pore volume as a function of Argon flow rate yields an $R^2$ of 0.961 and 0.965, respectively, revealing a strong inverse correlation (Figure 10.2). Both linear regressions are performed on logarithm-transformed scales of flow rates. The high surface area and a short reaction time here are in sharp contrast to the CO$_2$ activation of carbon that requires long reaction time, e.g., more than 15 hours, in order to yield a surface area of 2,400 m$^2$ g$^{-1}$.

The pore size distributions show that the greatest volume is attributed to pores between 2 nm and 50 nm (mesopores) in width make up most of the pore volume, followed by pores greater than 50 nm (macropores), and pores of less than 2 nm (micropores) making up the least fraction of the volume (Table 10.1). Observing
Table 10.1: Results of BET surface area and DFT pore volume, as well as XRD and Raman results of the carbon materials obtained at different flow rates.

<table>
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<th>Argon Flow Rate (CCM)</th>
<th>BET Surface Area (m² g⁻¹)</th>
<th>DFT Pore Volume (cm³ g⁻¹)</th>
<th>Pore Size Distribution volume (cm³ g⁻¹)</th>
<th>Thickness in (002) direction</th>
<th>Empirical R Value</th>
<th>l₀/l₅ Value</th>
<th>% Yield</th>
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<td></td>
<td></td>
<td></td>
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<td>0.001</td>
<td>3.57</td>
<td>1.82</td>
</tr>
</tbody>
</table>

the pore size distribution plot (Figure 10.1c) we see that the carbon treated at flow rates of 100 and 200 CCM have a higher relative amount of micropores than the carbon materials treated at lower flow rates. Materials obtained at lower flow rates have a much more even distribution of pores, which accounts for the switch from type I N₂ sorption isotherm at high flow rates to type I/IV isotherms at low flow rates. Lastly, in Figure 10.1d, we see that there is a linear correlation between the increase in pore volume and flow rate for all three types of pores; performing a linear regression of incremental pore volume versus flow rate yields R² values of 0.87 for the micropores, 0.96 for the mesopores and only 0.74 for the macropores. The main reason for the lower linearity of the macropore volume versus the flow rate is due to the macropore volume of the 10 and 25 CCM carbon. This results show that increases in porosity due to a lower flow rate in all types of pores are linear as the flow rate is lowered—except at extremely low flow rates, where there is a disproportionate increase in macroporosity.

Following the N₂ sorption measurements, we further characterized the structures of the obtained activated carbons. All of the obtained carbon samples exhibit an amorphous atomistic structure by displaying broad (002) and (100) peaks at 2θ
Figure 10.1: a) $\text{N}_2$ sorption isotherms of different activated carbons, b) Dual plots of surface area and pore volume values versus Argon flow rates. c) Pore size distribution plot of the carbon materials d) Comparison of incremental volume of micropores, mesopores and macropores for the different activated carbon materials.

Angles of 23° and 43°, respectively. The measured d-spacings of (002) planes of the respective carbon samples do not vary much upon different flow rates, with most around 0.39 nm. However, the short-range order along the c-axis of the synthesized carbons varies greatly upon different Ar flow rate as evident from the XRD profiles. Carbons obtained at high flow rates exhibit better resolved (002) peaks than those prepared at low flow rates (Figure 10.3a & c).
Calculation by the Scherrer equation allows us to deduce the average thickness of the nanodomains along the c-axis, \( L_c \). Dividing the nanodomain thickness by the d-spacing estimates the average number of graphene layers, which decreases from 3.6 to 2.8 when the flow rate decreases from 200 to 10 CCM (Table 10.1).

When a linear regression of number of graphene layers vs. flow rate is performed, we obtain an \( R^2 \) value of 0.948, thereby showing that carbon nanodomains are thinned at low flow rates during pyrolysis. The degrees of order along the c axis can be analyzed by R calculations as well; R, an empirical parameter defined by Dahn et al.. This measurement allows quantifying the degrees of short-range order in an amorphous carbon, with higher R values implying a better degree of order. The R values obtained correlate well with the nanoporosity induced in carbon, with high-surface-area carbon having an R value of 1.2 but low-surface-area carbon exhibiting an R value greater than 1.8 (Table 10.1). Performing a linear regression analysis on flow rates vs. R values and logarithm transformed...
Figure 10.3: a) b) XRD patterns and Raman spectra of cellulose pyrolyzed for 2 h under different flow rates. c) Dual plot of the empirical R value and $I_D/I_G$ ratios vs. flow rate of Argon.

data yields a $R^2$ value of 0.817 (Figure 10.4).

We further investigate the microstructure of the resulting carbons by TEM. As Figure 3a shows, C-200 with a specific surface area of 98 m$^2$ g$^{-1}$ contains randomly
Figure 10.4: Results of BET surface area and DFT pore volume, as well as XRD and Raman results of the carbon materials obtained at different flow rates.

arranged curved graphene layers, described by the “house-of-cards” model. On the other hand, C-10, also composed of curved graphene sheets, exhibits a much lower packing density of carbon sheets (Figure 10.5).

This observation corroborates the XRD results that carbon activation occurs at low flow rate by thinning the carbon nanodomains along the c axis. SEM imaging is able to show some evidence of increased macroporosity when a low flow rate is used as opposed to high flow rate ones—though the scale of observation is too large to observe any features of the microstructure (Figure 10.6).

Raman spectroscopy provides further structural insights of the amorphous carbon materials, particularly, the disorder degree in the graphene sheets (ab plane). The $I_D/I_G$ ratios of the resulting carbon prove to be inversely correlated to the flow rate as well, with a maximum ratio of 1.10 at 10 CCM and a minimum ratio of
0.94 at 200 CCM (Figure 10.3b & c). It is evident that at a low flow rate, more defects in graphene sheets are generated. Considering that both the specific surface area/pore volume and $I_D/I_G$ ratios inversely correlate with the flow rate, a linear regression is performed for $I_D/I_G$ ratio as a function of both BET surface area and DFT pore volume. Both linear regressions show a strikingly high degree of correlation, with $R^2$ values being of 0.971 and 0.940. This implies an important message that porosity generation does occur in graphene planes. (Figure 10.7).

10.5 Self-Activation Process Mechanism

To elucidate the mechanism behind the inverse correlation of the activation process and the Argon flow rates, we monitored the evolved $H_2$, $H_2O$, CO and $CO_2$ gases during pyrolysis via TGA-MS [55-60].[156, 157, 158, 159, 160] Although there are
other larger volatile molecules possibly generated from cellulose pyrolysis, these four molecules are used here as markers to help understand the activation mechanism. As Figure 10.8a shows, the majority of the weight loss during cellulose pyrolysis occurs between 250°C and 400°C while the elimination of H\textsubscript{2}O along with
minor evolution of CO and CO$_2$ is observed. This process is often referred to as a primary reaction in cellulose pyrolysis. An important question to be answered here is how this pyrolysis process affects the overall physicochemical properties of the resulting carbon. Is the weight loss incurred from 250 °C and 400 °C inconsequential, or is it the sole reason for the self-activation reactions?

To answer this question, we pretreated cellulose at 450°C and 600°C for 6 h, respectively, under Argon at a very high flow rate of 200 CCM. The pre-treatment aims to completely remove the ‘possible’ activation reagents generated at relatively low temperatures before the following high-temperature investigation. Furthermore, the high flow rate guarantees that little self-activation reactions take place during the pre-treatment. The two obtained samples are referred to as P-450 and P-600.

After the pretreatment, P-450 and P-600 are further pyrolyzed at 1100°C for 6 h in under Argon at 10 CCM, resulting in surface areas of 1500 m$^2$ g$^{-1}$ and 730 m$^2$ g$^{-1}$, respectively.

The above results provide two important insights. Firstly, it confirms that the
species released below 450°C and between 450°C to 600°C do contribute to the activation, considering that when a flow rate of 10 CCM was used for the entire pyrolysis process, a final surface area of 2,600 m² g⁻¹ was obtained. Secondly, it is evident that above 600°C there are still activation reagents released during cellulose pyrolysis, considering that C-200 sample has a final surface area of 98 m² g⁻¹. Activation at above 600°C is supported by the TGA of P-600 as a significant percentage of weight loss occurs at temperatures beyond 600°C (Figure 10.8c & d). At pyrolysis temperatures below 600°C, it is known that cellulose polymer
chains are dehydrolyzed and subsequently decomposed into a plethora of volatile molecules, also referred to as bio-fuels or bio-oils. Such liquification reactions peak at around 550°C and are mostly completed by 600°C.\cite{161, 162, 163} At temperatures greater than 600°C, the pyrolysis process begins to transition towards the release of smaller non-condensable gasses, such as H\textsubscript{2}, H\textsubscript{2}O, CO and CO\textsubscript{2}.\cite{164} With this in mind, we thus propose that there are two possible self-activation reactions which can happen at higher temperatures.

\begin{align}
C(s) + H\textsubscript{2}O(g) &\rightarrow CO(g) + H\textsubscript{2}(g) \\
C(s) + CO\textsubscript{2}(g) &\rightarrow 2CO(g)
\end{align}

The occurrence of these two activation reactions are supported by the TGA-MS results, as they show a stable evolution of H\textsubscript{2}O at higher temperatures with much higher pressure than CO and CO\textsubscript{2}. The MS results imply that the removal of residual hydrogen and oxygen atoms may form H\textsubscript{2}O at a wide range of temperatures during the pyrolysis process. Furthermore, there is a distinct peak of H\textsubscript{2} evolution from 750°C to 800°C (\textbf{Figure 10.8b & c}). This is consistent to the calculated temperature of 707°C, whereby the Gibbs free energy of the syngas formation reaction (10.3) turns negative and thus the reaction becomes spontaneous. The H\textsubscript{2} peak at above 700 °C may explain what the activation reaction is at high temperatures. Furthermore, the high H\textsubscript{2} pressure leads to yet another possible activation reaction:
\[ C(s) + 2H_2(g) \rightarrow CH_4(g) \] (10.5)

Despite the possibility of self-activation via eq. 10.4 & 10.5, it is more likely that the syngas formation plays the primary role due to the vastly higher pressure of H\textsubscript{2}O.

IR spectra provide insights on the activation mechanism as well. As Figure 10.8d shows, the pyrolysis at 1100°C results in a very pure carbon, with almost no signals from oxygen-containing functional groups. Conversely, P-450 exhibits peaks from a wide range of groups, including C=O and C-O, and weaker signals of substituted aromatic rings, e.g., aldehydes and carboxylic acids. Similar C=O and C-O peaks still exist after a pre-treatment at 600°C though the signals are considerably weaker. When integrating the IR and TGA/MS results, it is evident that as the pyrolysis temperature increases, the removal of oxygen and hydrogen groups results in the release of H\textsubscript{2}O that activates carbon, thus forming H\textsubscript{2} as a by-product.

When a low flow rate is used, evolved activation gas molecules, e.g., H\textsubscript{2}O, remain in the tube furnace for a longer time period, increasing the likelihood of the reaction in Eq. 3. The concept of using a low flow rate, and its consequence of inducing self activation can better be understood through the calculation of residence times (\(\tau\)) of gas molecules in the reaction chamber. The residence time can be estimated through the equation

\[ \tau(\text{min}) = \int_{x_1}^{x_2} \frac{A_1}{F_0} \frac{T_{\text{furnace}}(x)}{T_{\text{room}}} dx \] (10.6)
Figure 10.9: Residence times (τ) as obtained through the use of equation 10.6

where τ is the residence time in min, \( A_i \) is the cross-sectional area of the reaction chamber in m\(^2\), \( F_0 \) is the inlet flow rate in m\(^3\) min\(^{-1}\), \( T_{\text{furnace}} \) and \( T_{\text{room}} \) are the temperatures in Kelvin, and \( x_1 \) and \( x_2 \) are boundaries of the alumina crucible holding the filter paper. It is evident that the residence time is inversely proportional to the flow rate. Since the flow of Argon replaces the self-activation agents, such as \( \text{H}_2\text{O} \) and \( \text{CO}_2 \), it is reasonable to believe that these self-activation agents have very similar residence time as the Argon molecules flowing through the reaction chamber. Thus, a low flow rate of Argon results in higher residence times of self-activating agents, thereby increasing the likelihood of a self-activation reaction. As we can see from Figure 5 the residence times for lower flow rates are 10 to 20 times greater than those of higher flow rates; whereas the residence time at 1100°C for a flow rate of 200 CCM is of only 12 seconds, it jumps to nearly 4 minutes when the flow rate is lowered to 10 CCM.
10.6 Electrochemical Performance in Symmetric Capacitor

We investigated the electrochemical properties of the C-10 of a surface area of 2,600 m$^2$ g$^{-1}$ in symmetrical electrochemical capacitors (ECs). Cyclic voltammetry measurements are conducted at scanning rates of 20, 200, 500 and 1,000 mV s$^{-1}$. As shown in Figure 10.10a, C-10 exhibits excellent high-rate capacitive behavior as the CV profile retains its rectangular shape even at a scanning rate of 1000 mV s$^{-1}$.

From the EIS results, the Nyquist plot shows an intercept at the real impedance (Z') of 0.6 Ω, indicating a very low equivalent series resistance (ESR). An elongated ‘semicircle’ can be attributed to the widely distributed pore sizes in the structure. The Nyquist plot was simulated using two RC circuits connected in series and a restricted diffusion element M, as shown in Figure 10.11.

Galvanostatic charge/discharge of C-10 EC cells at a current rate of 1 A g$^{-1}$ yields very symmetrical profiles, with a low voltage drop when switching from charge to discharge, thus corroborating the low ESR value seen from EIS. From the charge/discharge profiles, we observe a specific capacitance of 132 F g$^{-1}$, which is well retained at over 100 F g$^{-1}$ when the current rate is increased to 10 A g$^{-1}$ (Figure 10.11c). After 6,000 cycles, a specific capacitance of 124 F g$^{-1}$ remains, representing a 94% retention (Figure 10.11d).

Despite the much more straightforward and inexpensive preparation, the performance of the nanoporous carbon from direct pyrolysis of cellulose is better than the conventional AC that is formed by activating commercially available petroleum-derived carbon by CO$_2$. The CO$_2$ activated carbon, which was measured to have
Figure 10.10: a) CV curves of ECs with voltage scanning rates ranging from 20 mV s\(^{-1}\) to 1,000 mV s\(^{-1}\). b) Nyquist plot of a capacitor assembled with C-10 as electrodes. c) Galvanostatic charge/discharge profiles at a current rate ranging from 1 A g\(^{-1}\) to 10 A g\(^{-1}\). d) Galvanostatic cycling at a current rate of 1 A g\(^{-1}\).

Figure 10.11: Equivalent circuit used to fit the experimental Impedance Spectra.
a specific surface area of 2,400 m² g⁻¹ only exhibits a capacitance of 100 F g⁻¹ at 1 A g⁻¹.

10.7 Conclusion

In this work, we have demonstrated that high-surface-area nanoporous carbon can be synthesized in a single step pyrolysis reaction without the use of any chemical or physical activating reagents. We record strikingly linear relationships between the flow rates of Argon in the reaction and key properties of the resulting nanoporous carbon, including specific surface area/pore volume and degrees of short-range order. We identify that the high nanoporosity of the resulting carbon is due to the in-situ activation reactions between the resulting carbon and the gases, e.g., H₂O, that are evolved in situ during pyrolysis of cellulose over a wide range of temperatures. The residence time of evolving gases in the reaction chamber exerts a determining impact on the properties of the resulting nanoporous carbon.

Additionally, by simply controlling the flow rate, we are able to synthesize an AC that demonstrates a specific capacitance of 130 F g⁻¹ at 1 A g⁻¹, a performance better than that of conventional ACs that are synthesized through tedious processes. We expect that optimization of this one-step self-activation method will greatly lower the cost of ACs, which may have a profound impact on various fields that heavily rely on ACs.
Chapter 11: The Curvature of Carbon

11.1 Introduction

On a nanoscale level, characterization of materials trends towards the predictable. The ‘gold-standard’ for such a task is to index a unit cell for the material, the unit cell being infinitely repeating and predictable through physical space. This orderly approach begins to breakdown slightly when defects, and porosity are introduced in the system. Once those are introduced, the material can no longer be considered infinitely repeating, as imperfections are now present within the system. The presence of defects is routinely accounted through use of statistical probability measurements, such as a pair distribution functions (PDF), which allow to establish the deviation away from an ideal structure.

But these methods do little to quantify the issue of curvature within structures, where the only reliable way to identify it is through a visual observation in the context of a transmission electron microscopy (TEM) image. But even if visually identified, the issue of how to quantitatively assess the curvature still remains. Thus, at present, most of the information about the curvature of a structure is lost in the characterization.

Carbon materials, which have a wide range of applications such as energy storage, catalysis, sensor, and gas adsorption are a good example of this. Most of the carbon
materials used for these applications are often of the amorphous variety: they lie somewhere on the scale between graphite/graphene and diamond, all examples of neatly ordered repeatable structures. Yet in all the different characterization methods, none addresses the issue of curvature.

When characterizing these carbon materials, techniques such as X-ray diffraction (XRD), Raman spectroscopy, porosimetry, and PDF are typically used, which all yield a similar outcome: the deviation of the material from graphitic order. XRD can be used to yields average grain size and resemblance to a graphitic structure. The broader the (002) and (100) peaks are, the smaller the grain size is, and the less graphitic the structure is. Analysis of the Raman spectroscopy also allows to establish a deviation from order through a ratio of the D and G band ($I_D/I_G$) as well as the presence, or lack thereof, of the 2D band. Porosimetry, which utilizes gas adsorption to establish the overall porosity and surface area of the material, gives a broad sense of the porosity present within the carbon structure. A low porosity is interpreted as a more graphitic material, while a higher porosity implies more defects: defective sites are more adept at storing gas.

Thus far, these techniques succeed in characterizing the long range order, and bulk properties of the material. Use of high energy diffraction in order to obtain PDF measurements allow to estimate defect concentration, along with short and mid-range order. However, none of these characterization methods manage to broach the issue of curvature. Even PDF, which allows to estimate order along a lateral AB direction fails to identify curvature. Though it would invariable cause changes in the PDF spectrum it is difficult, if not impossible, to discern whether those changes are present due to the curvature alone or the presence of defects.
This issue becomes further complicated when we consider that a carbon structure with curvature in it is not per se defective. A curved structure, such as a carbon nanotube (CNT) does not possess any vacancies, and on the short range has the same characteristic C-C bond lengths for the first coordination as a planar graphene sheet. In essence, a CNT is just a cylindrical graphene sheet: still perfect, but curved. In terms of PDF analysis, if we look beyond the 1st order coordination, the subsequent coordination orders will change due to the curvature in the structure, as the sheet is no longer planar. And even then, this remains directionally dependent: a vector at perpendicular to the radius and traveling on the outside on the CNT is technically 'flat'. This difficulty in characterization almost mimics what was observed in the medieval age. Then, people had difficulty believe the earth was round, as their immediate, and limited, perception gave them every inclination that the earth was flat. Yet they knew that something was amiss – no one had ever reached the mythical 'end of the earth'. In essence, the aforementioned characterization techniques suffer from a similar affliction. They are able to show that carbon structures deviate from perfect order, but only manage to do so in the concept of "defects".

Technically curvature is a defect, as it results in differing physical properties than the 'perfect' structure. But since it isn’t a vacancy type defect our current characterization techniques fail to account for it. This is especially significant, as the curvature of graphene sheets and graphene nanodomains has an outsized impact on the properties of the materials. Its presence changes the electronic properties of the structure, which leads to further impacts on the application of the material, whether it be for energy storage, catalysis, or any of the other countless applications that carbon can be used for. A first principles examples of this effect, with
relationship to NIBs is displayed in Figure 11.1

Figure 11.1: a) Two graphene sheets with a sinusoidal curvature of periods $\pi/4$ and $\pi/5$. Details on the designing of the sheets is explained later on. b) First-principles voltage calculations. These simulations have not been ionically relaxed, and only intend to show effect of voltage on curvature.

Fortunately, unlike the scientists of yore, we can visually identify curvature at the nanoscale level through TEM analysis. In those images, we can clearly see the presence of curved graphene sheets and nanodomains, and even moreso once the images are frequency filtered as to only reveal the graphene fringes.

However, once the TEM image is obtained, the analysis usually stops there. There have been some attempts to perform quantitative analysis on TEM images. This includes attempts to measure the tortuosity, average domain length, point of inflection, and curvature – with each paper using a specific method. [165, 166, 167]

Herein, in this paper, we aim to change all of that. Using a numerical methods approach, we explore the subject of curvature using a new metric, which is effectively able to characterize theoretical carbon structures with changing curvatures. Using this as a proof of concept method, we are then able to combine it with a novel TEM-layer reconstruction (TEM-LR) technique, to generate a computa-
tional amorphous carbon structure based off of a physical TEM image. With this reconstruction in hand, we can then perform a quantitative curvature analysis, which, for the first time, enables us to quantitatively define the curvature of an amorphous carbon structure. Additionally, transforming a physical image into a digital also allows to use a physical basis for Molecular Dynamics (MD) modeling, thus enhancing our capabilities of bridging theoretical amorphous carbon models with physical amorphous carbon models. Such information can then be utilized to obtain more insightful structure-property relationships for the many different type of applications which amorphous carbon can potentially be used for. Lastly, the ideas regarding curvature analysis and TEM-LR elucidated in this paper have the potential of being used for material characterization in systems much beyond that of amorphous carbon, thus creating a new tool to utilize in material science.

11.2 Numerical Approach to Building Curved Structures

One of the issues mentioned in the introduction was the difficulty with distinguishing between curvature and defect concentration when utilizing PDF measurements. With a curved structure, the length between atoms with a coordination greater than 1 varies depending on the radius of the curved structure. As a result, this leads to PDF peaks of differing intensities and widths – though some of those changes could well be attributed to the presence of vacancy type defects.

To establish a proof of concept on measuring curvature in carbon materials, we first needed curved carbon structure. However, even those structures proved elusive. Typically, most studies which explore the curvature of carbon utilize known carbon
structures such as CNTs or buckyballs, or generate a curved carbon structure through a MD simulation. Yet both of these come with inherent flaws.

A basis utilizing predictable curved structures such as CNTs and buckyball, has the issue of uniform curvature. Both CNTs and buckyballs have a fixed gaussian curvature, which in the case of the CNT is 0. This poses a problem, and a challenge: curvature in amorphous carbon structure is not uniform, and thus a CNT/buckyball approach will be limited. We could technically apply a local radius to various parts of the curved graphene sheet, and model it as a collection of CNT curvatures, in a fractal type analysis, but that would come with many more challenges, both in theory, and in practice.

Additionally, such an approach would not give a good estimation of the tortuosity present within the sheet. Through curved, a CNT can be described at an order structure, and can easily be defined as a function of its radius. A theoretical "sine-wave" graphene sheet is also curved. However, it has a changing curvature, which cannot be defined by a single radius. Moreover, such a structure is a lot more tortuous and disordered than a CNT: it cannot be recreated or characterized through a unit cell approach.

The use of MD to build curved structure solves the issue of uniform curvature. Depending on the conditions and constraints applied to the MD model, a plethora of curvatures can be obtained, without having to worry about uniformity. No two systems will be alike, and there will be plenty of variety in the local curvature or an individual system. Yet this too poses a problem. The dependence on the conditions used to make the system takes the focus away from the characterization of the curvature, and shifts it towards the MD simulation. Furthermore, there is
no guarantee that the outcome of the MD simulation matches what is obtained in real-life, thus we could run the risk of developing a model that can only be theoretically applied.

To overcome this problem, we devised a numerical method way of designing curved graphene structures, which does depend on CNTs, buckyballs, or MD simulations. Our novel approach involves defining a mathematical function of any type (sinusoidal, polynomial, logarithmic ...) and 'overlaying' a sheet of graphene on such a function. The procedure, which was done using MATLAB, is relatively straightforward and goes as follows

1. A function is defined (Figure 11.2a).

2. A point of reference is chosen at the root of the function (Figure 11.2a).

3. A semi-circle with a radius typically of a 2nd coordination C-C length, determined to be 0.244 nm \((2d \cdot \sin(\frac{\pi}{3}))\), is drawn from the point of reference (Figure 11.2a).

4. The points on the semi-circle are scanned in reference to the points on the function. With the interesting point of reference being stored as the new reference point (Figure 11.2a).

5. The semi-circle/reference point scan is repeated until the function has ended, or the user has defined enough points (Figure 11.2b-c).

6. If periodic boundary conditions are desired, this process needs to be repeated many times, until an endpoint after one period can match one of coordinates from a starting point: if the initial point has a z-value of 0, a z-value of 0
after one period implies periodic boundary conditions. It is also important
to make sure to delete the last atom if this is the case. In this case, the sine
wave can be tuned by adjusting the period, the amplitude, or both.

7. Steps 2-5 are repeated for a 2nd time, though the initial point of reference
has to be offset at the start by a factor of $d \cdot \sin\left(\frac{\pi}{6}\right)$. The offsetting point
needs to be found through a numerical scan to account of the amplitude and
period of the sine wave (Figure 11.2d-e).

8. Now that two characteristic lines have been defined, the lines 1 and 2 can be
tiled accordingly to create an overlaid graphene sheet on the function. Such
a graphene sheet will be of the 'zigzag' edge variety. A similar procedure
could be utilized to create an 'armchair' edge graphene sheet, but that would
involve some additional complexity in the semi-circle/reference point scan,
as the semi-circle would change radius every other scan (Figure 11.2f).

Utilizing this method, the types of graphene sheets which can be drawn are only
limited by one’s mathematical imagination. Even more complicated functions, such
a heavyside functions, dirac-delta functions, and bessel functions could be fitted.
In this paper, sinuosoidal functions are used for the sake of obtaining periodic
boundary conditions. Though the process is the same, a few additional steps are
added to numerically vary either the amplitude, or the period of the function, as
to make sure the endpoints are periodic.
Figure 11.2: a) Defining a function, a drawing a semi-circle of desired length from a determined reference point. b) Repeating the semi-circle step, using the newly found reference point. c) Completely fitted function, after many recursive steps. d) In a graphene sheet, there are two characteristic lines, the starting point for the second line needs to be offset by a factor of $d \cdot \sin\left(\frac{\pi}{6}\right)$ from the initial reference point. e) Fitting of the second characteristic line. f) Tiling of the lines, respecting the zigzag edge arrangement.

11.3 Defining Curvature

Once the curved graphene structures have been established, the next step involves coming up with a way to quantitatively characterize their curvature. Such a method requires two things. First it must be able to define curvature as an average. Additionally, it must also reflect if the curvature of the structure is changing, thus accounting for tortuosity.

Looking at the structure, one of the potential ways of defining curvature is through the “out-of-plane” distance. Given that there are no vacancy defects in the graphene structure, every carbon atom is guaranteed to have three nearest neighbors at a
characteristic C-C bond length. In this manner, the central carbon of reference is much like it would be in a graphene sheet, as it is equidistant from all of its 1st order coordination. However, if we are to build a plane from the basis of the three nearest neighbors, we can quickly see that the central atom does not always lie in the plane like it would in a pristine graphene sheet, especially in the case of the peaks and valleys of the sine wave. The distance of the central atom away from this plane is then defined at the “out-of-plane” distance, which gives us a way to estimate curvature (Figure 11.6).

A corollary to the “out-of-plane” measurement is the “sum-of-angles” measurement. If bonds from the three nearest neighbors to the central carbon atom are considered, the sum of the three angles, in the case of a graphene sheet, should be 360°. If the central atom is gradually pulled further and further out of the plane defined by the nearest neighbors, the sum of the three angles will begin to add up to values smaller than 360°. This gives us yet an additional way of characterizing curvature (Figure 11.6).

![Figure 11.3: a) Schematic representation of both the "out-of-plane" and "sum-of-angles" curvature definitions. b) Plot of the sum-of-angles versus the out-of-plane distance, showing the close relationship between the two.](image)

Both of these previously mentioned methods yield a value for each atom in the
system. By taking the average/median of the values, we meet the first criteria for our measurement of curvature: obtaining an average for the structure. But such a number does little to give us an idea of tortuosity/changing curvature. However, taking all the values and plotting them as a cumulative distribution function (CDF) changes that. Through the use of a CDF the value at the 50th percentile represents the average, while the standard deviation present within the CDF serves to give an idea of the tortuosity and the changing curvature present within the structure.

This can easily be seen using a CDF with the sum of angles measurement. For this proof of concept, we made three different theoretical graphene sine waves, with respective periods of $\frac{\pi}{4}$, $\frac{\pi}{5}$, and $\frac{\pi}{6}$. The amplitude of the sine waves was adjusted numerically as to obtain periodic boundary conditions, and the cell size was adjusted to have a similar density of atom/nm$^3$, as to avoid any bias in the pair-correlation function measurements. As we can see from Figure 11.4a, the PDF measurements allow for little distinguishements between the three graphene sheets. Furthermore, there is the added doubt that any differences could be due to vacancy defects. While this is not a problem for us, as these are theoretical structures with no vacancy defects, it is more of a problem in physical measurement, as there is no way to tell whether the changes seen in the PDF are due to defects or curvature – especially when they are that small. However, when looking at the CDF plots, we can easily tell the graphene sheets of different curvatures apart by looking at the distribution between 0 and 1 on the CDF. The graphene sheet with the most abrupt curvature with the $\pi/4$ period, has the broadest distribution, while the sheet with the shallowest curvature, has a CDF that stays at 0 until the very end, thus causing it to have a very narrow distribution (Figure 11.4b).
Figure 11.4: a) PDF of graphene sheets of different periods. b) CDF of sum-of-angles measurements of graphene sheets of different periods. c) CDF of sum-of-angles measurements of CNTs of different diameter.

Additionally, these sum-of-angle measurements allow us to distinguish between structure of different tortuosity. In addition to the curved graphene sheets, we also computed the sum of angle measurements for CNTs of various diameters. Looking at the sum-of-angles measurements from the CNTs, we observe two things: first that there is a heavyside like 'jump' from 0 to 1 for all CNTs, and second, that the average curvature for CNTs is greater than for the sinusoidal waves (Figure 11.4c). These observations show the robustness of this curvature measurement approach, as it is able to separate out curvature and tortuosity. From the data, it is obvious that CNTs have a greater curvature than the graphene waves, yet, CNTs are ordered structure with a uniform curvature – something which the graphene waves are not.

11.4 TEM Layer Reconstruction

Having established a proof of concept for defining curvature in theoretical carbon structures, the next step becomes how to apply it to physical carbon structure. As state previously in this paper, the only way to evaluate curvature was through
a qualitative analysis of a TEM image. However, using a combination of image filtering techniques, pixel analysis and numerical analysis, it becomes possible to construct a digital layer of amorphous carbon from a TEM image, which can then be analyzed for curvature using the process highlighted in the previous section.

The process for TEM-LR is numerically based, and is a lot like the previous process of building curved graphene structures out of mathematical functions. The steps that were taken were as follows

1. Use a combination of frequency filters and image processing to transform the TEM image (Figure 11.5a) into a black and white image exposing the graphene fringes (Figure 11.5b).

2. Skeletelize the graphene fringes by rendering them just a few pixels thick (Figure 11.5c).

3. Obtain a conversion factor between the physical length in the picture, as obtain by the scale bar, and the pixel length.

4. Once the conversion between physical length and pixel length is obtained, "seeding" points need to be created for each individual fringe. Seeding points are the equivalent of the reference point at the beginning of the mathematical function used in the previous section. The seeding point is contrasted from the rest of the picture by giving it a numerical value not equal to 0 (black), or 255 (white) – at least if using 8 bit gray scale mode (Figure 11.5d).

5. Once of the seeding points have been made, semicircles with a 2nd order C-C radius are to be traced from the reference points, and then scanned for
a intersection point with the same fringe. If such a point is found, it will then become a new reference point, its pixel value will change from 0 to the arbitrary value, and the process will start over. Since the orientation of the fringe is random, there is the case that the semicircle will not intersect the fringe for fault of being in the wrong orientation. Thus, the process is repeated twice, the 2nd time with the semi circle being oriented in the other direction (Figure 11.5d).

6. Once this process is finished, the image needs to be cleaned up. There are many cases of stray pixels which arise due to the semi circle coming into contact with a fringe it was not originally connected to. These stray pixels, which would represent unphysical carbon atoms, have to be deleted (Figure 11.5e).

7. The stray pixels being deleted, the \([x,y]\) pixel coordinates are then changed into their corresponding spatial values, using the predetermined conversion factors.

8. Having obtained the spatial values of the carbon atoms, the layer is then tiled a few layers deep, giving an ‘zigzag’ edge slab of amorphous carbon (Figure 11.5f).

To save time in the short run, steps 2, 4, and 6, are done manually, as they have not yet been automated. However, whether they are done manually, or automated, they still are aimed towards completing the same goal.

Following this process, we have created a digital representation of an amorphous carbon structure, based on a physical observation. It is important to note that it
Figure 11.5: The steps necessary in TEM-SR a) Raw TEM image. b) Frequency filtering of noise from TEM image, and contrasting of the graphene fringes. c) Skeletelizing of the graphene fringes into lines just a few pixels thick. d) In a subset area of (c) the seeding of the graphene fringes, followed by the numerical pixel fitting of the graphene fringes is shown. We can see the potential for ‘overlap’ problems, as the semi-circles have the chance of broaching onto neighboring graphene fringes if not spaces far enough apart. e) After the numerical fitting, the image is cleaned up to a set of individual pixels, which will eventually become the atomic coordinates in two dimensions. f) Representation of the TEM slab once the pixel positions have been transformed into atomic coordinates.

would be unwise to project such a structure indefinitely in one direction. TEM images, which utilize electrons that go through the sample, only represent a thin length of the sample. As such our 3D slab can only be of limited length in the z-direction. Never-the-less, this methods gives us, for the first time, a way to bridge
a physical representation of an amorphous carbon structure, with a digital one.

Using the digital representation, in conjunction with the curvature analysis method developed earlier, we now have a quantitative way of defining curvature between two different carbon TEM images. Additionally, utilizing this method also allows us to directly transform the digitized image into a PDF output, thus allowing comparison with both experimental PDF’s, as well as MD models (Figure ??a). Though the two model show similar characteristics, the intensity of the peaks are markedly different, showing that the agreement between the two models is not robust. Additionally, as we can see from the curvature estimation, the TEM-SR shows much more significant curvature than the MD model, which could be both due to inaccuracies in the TEM-reconstruction, as well as the MD model parameters.

![Figure 11.6](image)

Figure 11.6: a) Comparitive PDF plots, obtained from the TEM-SR method, as well as a molecular dynamics simulation. b) Plot of the sum-of-angles versus the out-of-plane distance, showing the difference in curvature obtained from the MD model, and TEM model.
11.5 Conclusion

This work, though not yet finished, shows the power in merging computational power with modern materials characterization methods. In the context of amorphous carbon, this is of great importance: curvature proves very difficult to quantify using traditional characterization methods, yet they do have a big impact on the properties of the carbon material, as it pertains to its specific application. Thus, this work develops both a way of designing curvature from mathematical equations, and physical measurements, as well as a way of quantifying it. Future work should aim to explore the relationship between theoretical structures, TEM measurements, and more traditional PDF measurements – hopefully leading to a more thorough understanding of the amorphous carbon structure.
Chapter 12: Development of a Cylindrical Diffusion Model Using CITT

This chapter on a cylindrical diffusion with the CITT model was worked on jointly with Kristin Marshall. The work is not yet completed as of the publishing of this PhD, but hopefully, we’ll get to keep working on it, along with many other things :)

12.1 Introduction

Earlier in the thesis, different diffusion models for sodium atoms were discussed, including one for CITT. The CITT model was actually explored, and yielded results that were comparable to those found with GITT (Figure 12.1).

However, before any substantial conclusions or validations could be made, there were two outstanding issues. First, the diffusion model that was used assumed a spherical particle geometry, while the particle geometry of the carbon used for the test was cylindrical. Additionally, some of the assumptions made in the previously published model were also suspect, and had in fact come under questioning from another paper in the literature. That being the case, this was an attempt at creating a new diffusion model with cylindrical coordinates from first principles.
Figure 12.1: a) Sodiation curve for CITT diffusion measurements. b) Desodiation curve for CITT diffusion measurements.

12.2 Experimental

The following model is developed with the intent of describing the diffusion process of intercalary species within insertion type materials, such as a carbon anode hosting sodium. It is based on the CITT method, first elucidated by Tang et al. [115], which makes use of a ratio comparing the potential sodiation capacity,
with the galvanostatic sodiation capacity, in order to determine diffusion rate. As the CITT experiment was performed on Lyocell based anode, which exhibits a cylindrical shape, a cylindrical geometry will be used.

Model Assumptions

1. Cylindrical coordinates
2. Unidirectional flux in the r-direction (inward in the cylinder)
3. Radial outward flux is positive, radial inward flux is negative
4. Transport is isothermal, and heat produced in negligible
5. Diffusion coefficient is assumed to be constant
6. Electrolyte concentration is assumed to be constant

Starting from first principles, we assume the following model

\[ \text{Input} - \text{Output} + \text{Generation} = \text{Accumulation} \quad (12.1) \]

\[-D_A(2\pi h)r \frac{\partial C_A}{\partial r} \Delta t - (-D_A(2\pi h)r \frac{\partial C_A}{\partial r} \Delta t + 0 = C_A \Delta V|_{t+\Delta t} - C_A \Delta V|_t \quad (12.2)\]
\[ -D_A(2\pi h)r \frac{\partial C_A}{\partial r}|_r \Delta t - (D_A(2\pi h)r \frac{\partial C_A}{\partial r}|_r + \Delta r) \Delta t + 0 = C_A(2\pi h)r \Delta r|_{t+\Delta t} - C_A(2\pi h)r \Delta r|_t \] 
(12.3)

\[ -D_A r \frac{\partial C_A}{\partial r}|_r \Delta t - (D_A r \frac{\partial C_A}{\partial r}|_r + \Delta r) \Delta t + 0 = C_A r \Delta r|_{t+\Delta t} - C_A r \Delta r|_t \] 
(12.4)

\[ D_A \left( \frac{(r \frac{\partial C_A}{\partial r}|_{r+\Delta r} - r \frac{\partial C_A}{\partial r}|_r)}{\Delta t} \right) + 0 = \frac{C_A r|_{t+\Delta t} - C_A r|_t}{\Delta t} \] 
(12.5)

Taking the limit

\[ \lim_{\Delta r \to 0} D_A \left( \frac{(r \frac{\partial C_A}{\partial r}|_{r+\Delta r} - r \frac{\partial C_A}{\partial r}|_r)}{\Delta t} \right) \] 
(12.6)

\[ \lim_{\Delta t \to 0} \frac{C_A r|_{t+\Delta t} - C_A r|_t}{\Delta t} \] 
(12.7)

\[ D_A \frac{\partial C_A}{\partial r} + D_A r \frac{\partial^2 C_A}{\partial r^2} = r \frac{\partial C_A}{\partial t} \] 
(12.8)

This yield the equation
\[
\frac{1}{r} \frac{\partial C_A}{\partial r} + \frac{\partial^2 C_A}{\partial r^2} = \frac{1}{D_A} \frac{\partial C_A}{\partial t} \quad (12.9)
\]

with boundary/initial conditions

1. Initial Condition: \( C_A(r,0) = 0 \) (no intercalation at time \( t=0 \))
2. BC 1: \( \frac{\partial C_A}{\partial r} \bigg|_{r=0} = \text{finite for all values of } t \)
3. BC 2: \( D_A \frac{\partial C_A}{\partial r} \bigg|_{r=R} = \frac{i}{nF} \) for all values of \( t \)

Where, for the second boundary condition

1. \( i \) is the current of a single particle
2. \( n \) is the charge number of the intercalating ion (for Na, \( n \) is equal to 1)
3. \( F \) is Faraday’s constant
4. \( S \) is the surface area of a particle (\( A=2\pi Rh \))

Since the boundary conditions are inhomogenous, we will rewrite the concentration equation as

\[
C_A(r,t) = u(r,t) + w(r) + v(t) \quad (12.10)
\]

which defines \( u(r,t) \) with homogeneous boundary conditions. The \( w(r) \) satisfies the inhomogeneous boundary conditions. Plugging eq. 12.10 into eq. 12.9 and separating the the variables yields
\[ \frac{1}{r} \left( \frac{\partial}{\partial r} \left( r \frac{\partial U}{\partial r} \right) \right) = \frac{1}{D_A} \frac{\partial U}{\partial t} \]  

(12.11)

\[ \frac{1}{r} \left( \frac{\partial}{\partial r} \left( r \frac{\partial w}{\partial r} \right) \right) = \frac{1}{D_A} \frac{\partial v}{\partial t} \]  

(12.12)

Since \( w = w(r) \) and \( v = v(t) \), the only way that eq. 12.11 & 12.12 is feasible is if both sides are equal to a constant

\[ \frac{1}{r} \left( \frac{\partial}{\partial r} \left( r \frac{\partial w}{\partial r} \right) \right) = \frac{1}{D_A} \frac{\partial v}{\partial t} = A \]

\[ \frac{1}{r} \left( \frac{\partial}{\partial r} \left( r \frac{\partial w}{\partial r} \right) \right) = A \]

\[ \frac{\partial}{\partial r} \left( r \frac{\partial w}{\partial r} \right) = Ar \]

\[ \frac{\partial w}{\partial r} = \frac{A}{2} r + \frac{C_1}{r} \]

If we recall that \( w(r) \) satisfies the inhomogeneous boundary conditions

\[ BC-1 \]

\[ \frac{\partial w}{\partial r} = \frac{A}{2} 0 + \frac{C_1}{0} = finite \]
so that $C_1 = 0$

BC-2

\[ \frac{\partial w}{\partial r} = \frac{AR}{2D_A} = \frac{i}{nFS} \]

so that

\[ A = \frac{2D_A i}{nFSR} \]

IC

\[ v(t) = A \cdot D_A 0 + C_2 = 0 \]

so that $C_2 = 0$

Thus

\[ w(r) = \frac{i}{nFSR} + B \]

Where $B$ is an arbitrary constant, and

\[ v(r) = it \]

Now that $w(r)$ and $v(r)$ have been determined, we solve for $u(r,t)$

with boundary/initial conditions
1. Initial Condition: \( u(r,0)=0 \) (no intercalation at time \( t=0 \))

2. BC 1: \( \frac{\partial u}{\partial r} \bigg|_{r=0} = \text{finite for all values of } t \)

3. BC 2: \( D_A \frac{\partial u}{\partial r} \bigg|_{r=R} = 0 \) for all values of \( t \)

Assume that \( u(r,t) \) takes the following form

\[
 u(r,t) = F(r)T(t)
\]

\[
 \frac{1}{r}T(t)F'(r) + T(t)F''(r) = \frac{1}{D_A}T'(t)F(r)
\]

\[
 \frac{1}{r} \frac{F'(r)}{F(r)} + \frac{F''(r)}{F(r)} = \frac{1}{D_A} \frac{T'(t)}{T(t)}
\]

Since \( F = F(r) \) and \( T = T(t) \), the only way that the above relationship is feasible is if both sides are equal to a constant.

\[
 \frac{1}{r} \frac{F'(r)}{F(r)} + \frac{F''(r)}{F(r)} = \frac{1}{D_A} \frac{T'(t)}{T(t)} = -\lambda^2 \quad (12.13)
\]

Evaluating the first part of expression 12.13

\[
 \frac{1}{r} \frac{F'(r)}{F(r)} + \frac{F''(r)}{F(r)} = -\lambda^2
\]
\[ rF''(r) + F'(r) + r\lambda^2 F(r) = 0 \]

For which the solution to a second order differential equation using cylindrical coordinates is

\[ F(r) = C_1 J_0(\lambda r) + C_2 Y_0(\lambda r) \]

And the second part of equation 12.13

\[
\frac{1}{D_A} \frac{T'(t)}{T(t)} = -\lambda^2
\]

\[ T'(t) + D_A \lambda^2 T(t) = 0 \]

Which is solved using the equation

\[ T(t) = T_0 \exp(-\lambda^2 D_A t) \]

Combining the two solutions from above, and renaming the constants \( C_1 \cdot T_0 \cdot A \) and \( C_2 \cdot T_0 \cdot B \), we get

\[ u(r, t) = (A J_0(\lambda r) + B Y_0(\lambda r)) \exp(-\lambda^2 D_A t) = \text{finite} \]
Applying the first boundary condition \( \frac{\partial u}{\partial r} |_{r=0} = \text{finite} \), for all values of \( t \)

\[
\frac{\partial u}{\partial r} |_{r=0} = -\lambda (A J_1(0) + B Y_1(0)) \exp(-\lambda D_A t)
\]

with \( B \) equal to 0, so there is no singularity at 0

Applying the second boundary condition \( \frac{\partial u}{\partial r} |_{r=R} = 0 \), for all values of \( t \)

\[
\frac{\partial u}{\partial r} |_{r=0} = -\lambda A J_1(\lambda R) \exp(-\lambda^2 D_A t) = 0
\]

\( J_1(\lambda R) = 0 \)

Thus, \( \lambda_N \) is so that \( \lambda R \) are the roots of \( J_1(r) \)

\[
 u(r, t) = \sum_{1}^{\infty} A_N J_0(\frac{\lambda_N}{R} r) \exp(-\frac{\lambda_N^2}{R^2} D_A t)
\]

Now solving for the initial condition eq. 12.10 At \( t=0 \), \( u(r,t)=-w(r) \)

\[
 u(r, 0) = \sum_{1}^{\infty} A_N J_0(\lambda_N r) = -w(r)
\]

\[
 \sum_{1}^{\infty} A_N \int_{0}^{R} J_0(\frac{\lambda_N r}{R}) J_0(\frac{\lambda_N r}{R}) r dr = \int_{0}^{R} -w(r) J_0(\frac{\lambda_N r}{R}) r dr
\]
\[ A_N = \frac{R^2}{2} J_1^2(\lambda_N) = \int_0^R -\left(\frac{i}{nFSR} r + B \right) J_0\left(\frac{\lambda_N r}{R}\right) r dr \]

\[ A_N = \frac{2}{R^2} J_1^2(\lambda_N) \int_0^R -\left(\frac{i}{nFSR} r + B \right) J_0\left(\frac{\lambda_N r}{R}\right) r dr \]

\[ A_N = -\frac{2i}{nFSS} \int_0^R J_1^2(\lambda_N) r^2 J_0\left(\frac{\lambda_N r}{R}\right) dr - B \int_0^R J_0\left(\frac{\lambda_N r}{R}\right) r dr \]

\[ A_N = -\frac{2i}{nFSS} \frac{2a - \pi H_0(\lambda_N)}{R^3 J_1^2(\lambda_N)} - \frac{BR^2}{\lambda_N} J_1(\lambda_N) \]

\[ A_N = -\frac{2i}{nFSS} \frac{2\lambda_N - \pi H_0(\lambda_N)}{2\lambda_N^2} - \frac{BR^2}{\lambda_N} J_1(\lambda_N) \]

If \( R << 1 \) then the second part of the equation should be negligible, which simplifies things, and thus the equation becomes

\[ A_N = -\frac{2i}{nFSS} \frac{2\lambda_N - \pi H_0(\lambda_N)}{2\lambda_N^2} \]

Thus \( u(r,t) \) is equal to

\[ u(r,t) = \sum_{1}^{\infty} \frac{2i}{nFSS} \frac{2\lambda_N - \pi H_0(\lambda_N)}{2\lambda_N^2} J_0\left(\frac{\lambda_N r}{R}\right)J_0\left(\frac{\lambda_N r}{R}\right) \exp\left(-\frac{\lambda_N^2}{R^2} D_A t\right) \]
Recalling eq.12.10, and filling in for \( w(r) \) and \( \nu(r) \) we can then write

\[
C_A(r, t) = \sum_{i=1}^{\infty} -\frac{2i}{nFS} \frac{2\lambda_N - \pi H_0(\lambda_N)}{J_1(\lambda_N)} \frac{\lambda_N}{2\lambda_N^2} J_0(\frac{\lambda_N}{R} r) \exp(-\frac{\lambda_N^2}{R^2} D_A t) + \frac{i}{nFS} r + B + it
\]
Chapter 13: Contributions to the Science

In the course of this thesis, contributions were made towards both the understanding of electrochemical structure-property relationships of amorphous carbon anodes for Na-ion batteries, as well as a more thorough investigation of amorphous carbon, and methods of characterizing it.

13.1 Inverse Correlation Between Porosity Measurements and Capacity of Hard Carbon Anodes

In chapter 6, an inverse correlation between capacity and porosity values of hard carbon anodes in NIBs was uncovered. This set a guideline that amorphous carbon materials for NIB anodes should be of lower surface area (e.g. 25 m$^2$ g$^{-1}$ or less) in order to have high capacity and a high coulombic efficiency. It also showed that using CO$_2$ activation to increase capacity was ineffective, contrary to what would be assumed using the falling-card model for sodium ion storage.

The work was published in *Carbon*:

13.2 New Na Atom Storage Mechanism in Non-graphitizable Carbon

Using advanced characterization methods, as well as detailed electrochemical measurements, a new mechanism for sodium atom storage in non-graphitizable carbon materials was demonstrated (chapter 7). This enables a more focused ‘materials by design’ approach to making carbon anodes for NIBs, which will hopefully help to optimize performance. The work was published in *Nano Letters*


13.3 DFT Investigation of Sodium Atom Storage Mechanism

Using DFT simulations, the mechanism proposed in chapter 7 was investigated from a theoretical perspective in chapter 8. The DFT results point to many of the same conclusions that were drawn in the experimental paper: storage at defect sites at higher voltages, intercalation at low voltages, and lastly, a shift towards plating at very low voltages. Additionally, the results were able to show that sodium can intercalate graphene bilayers, if they are defective, and that the ability to expand to fit the sodium ion is more important than the overall d-spacing. Additionally, this paper was able to show that the sodium storage mechanism proceeds through two routes: ionic interactions, and Na/Na interactions, especially at high Na concentrations. This suggests that the theoretical limit for reversible capacity in carbon anodes is the sodium plating limit. This work is under preparation to
13.4 Investigation of the Fading Mechanism of Carbon Anodes

In chapter 9, it was shown that in a half-cell setting, the degradation of the electrolyte is the primary reason for capacity fading. Additionally, it was also shown that replacing the electrolyte and the sodium metal counter electrode lead to drastic capacity recovery, which confirms the electrolyte was the problem all along. This was also demonstrated using diffusivity measurements, as well as electrochemical measurements. This work is significant in a few ways: it shows the perils of testing long-term cycling in a half-cell setting, it shows the electrolyte should receive more consideration when designing a battery cell, and it shows that what we consider to be ‘SEI’ might not be SEI at all, but just degraded electrolyte. This work was published in *Advanced Materials Interface*.


13.5 Self Activation of Mechanisms During Pyrolysis

In chapter 10 an self-activation mechanism, dependent on inert gas flow rates during pyrolysis was demonstrated. This is a significant development, as it shows obtaining carbon from organic sources is not a straightforward process, and that
if one is not careful, a carbon with different properties will be synthesized. This shows the importance of maintaining flow rates, and heating rates at the same level if results are to be repeatable. Additionally, it also shows that highly porous material from organic sources is obtainable with a one-step pyrolysis reaction. This work was published in *Nano Energy*:


13.6 The Curvature of Carbon

In this work, a new method of measuring the curvature of carbon was devised, using an “out-of-plane” angle approach. This was done by making curved structures using a numerical methods approach, which allows to make sine-like graphene sheets, with periodic boundary conditions. Additionally, the numerical methods approach was taken a step further, and adapted to work with pixels, as to transform TEM images into digitized atomic coordinates. To the best of my knowledge, this is the first time this has been achieved for carbon materials, and leaves the door open towards merging structural characterization data with TEM and computational data. A paper is under preparation.
13.7 CITT Cylindrical Diffusion Model

This work represents a new type of diffusion model for cylindrically shaped particles using CITT. This could have applications to supplement GITT and PITT diffusion coefficient estimates for carbon nanofiber anodes, in all types of electrochemical cells.
Chapter 14: Future Directions

During my time in graduate school, a lot of progress has been made towards bringing NIBs to be a more commercially viable technology. But, like all battery technology, the answer is still ‘5 years away’, just like it was when I first started, 5 years ago. So how to bridge this gap?

First off, the expectations of batteries need to be brought to scale. This might sound like a defeatist attitude, but at some point, we have to come to terms that there is no Moore’s law for batteries. Unlike computer technologies, which have doubled in computing power every two years or so for the past 50 years, the same is not true of batteries. Progress with batteries is a lot slower, and more incremental. Unlike computer chips, we cannot make atoms smaller and smaller every year. They will always remain the same size, which limits the improvements we can have in the battery. Additionally, we cannot change the thermodynamic aspects of the interactions with the electrode materials. We can use materials that have different thermodynamic aspects with the desired ion, but we still cannot control it all the same. One cannot ‘will’ graphite to have a lithium storage capacity greater than 372 mAh g⁻¹.

The NIB research field is still young enough that ‘theoretical limits’ are still often disregarded. But just because they are disregarded doesn’t mean they don’t exist. Thus a key priority should be to pursue research in order to determine is
a theoretical limit to capacity storage does indeed exist: the sooner we realize our weaknesses, the sooner we can do something about them. This should be done through two methods: statistics, and computation. There is a lot of data currently in the literature, but no one has yet to comprehensively review it, and mine it for statistically significant trends. Doing so would be a good idea, and would be sure to yield interesting insights. Additionally, using modern computational tools one could establish, without experimental biases, whether or not a theoretical limit does exist.

The second key area of research is finding ways to improve the cycle life and increase the efficiency on the first cycle. It is important to remember what NIBs are ultimately supposed to be used for large scale grid level storage, not powering cars and cell phones. As such, the most important thing about these batteries is not to make them small, compact and energy dense. The most important thing is that they last a while, and be of low cost. Thus, pursuing research interest focusing on long lasting batteries, electrolytes that do not decay, or even solid state electrolytes, might be something worthwhile.
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