THE FABRICATION OF ADVANCED ELECTROCHEMICAL ENERGY STORAGE DEVICES WITH THE INTEGRATION OF ORDERED NANOMATERIAL ELECTRODES

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

Yu-Ming Chen

May, 2017
THE FABRICATION OF ADVANCED ELECTROCHEMICAL ENERGY STORAGE
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Yu-Ming Chen

Dissertation

Approved: __________________________

Accepted: __________________________

Advisor
Dr. Yu Zhu

Department Chair
Dr. Coleen Pugh

Committee Chair
Dr. Steven S.C. Chuang

Dean of the College
Dr. Eric J. Amis

Committee Member
Dr. Mesfin Tsige

Dean of the Graduate School
Dr. Chand Midha

Committee Member
Dr. Toshikazu Miyoshi

Date

Committee Member
Dr. Bryan D. Vogt
The development and commercialization of rechargeable Li-ion battery in the 1990s has triggered the advancement of modern portable technology. Currently, with the emergence of electric vehicles and more complex gadgets, conventional lithium ion intercalation based secondary batteries could no longer live up to the demands of the end-use consumers. In this dissertation, ordered carbonaceous nanomaterials were utilized to integrate with the next-generation conversion chemistry based secondary batteries. Lithium-oxygen and sodium-sulfur battery systems were tested and developed in attempt to deliver higher energy density over the conventional Li-ion battery. The main objective of the work is to fabricate advanced electrodes that are capable of providing higher capacity in order to facilitate power grids and electric vehicles, while by doing so; the effects caused by the emission of CO₂ could be significantly mitigated.

Ordered carbonaceous nanomaterials were produced by the chemical vapor deposition method. Among the wide variety of carbon materials, vertically aligned carbon nanotubes were grown on a substrate and then subsequently peeled off and used as the electrode for the lithium-oxygen battery. With the combination of 2-methyl-pyrrolidone solvent, the assembled lithium-oxygen battery could achieve specific capacity of 1200 mAh·g⁻¹ and under safe charge/discharge cycles for 50 cycles.
Carbonized metal organic framework was fabricated by mixing selected precursors. Sulfur was melt infiltrated to yield the carbon/sulfur composite. The metal organic framework structure composite cathode exhibited specific capacity of 1000 mAh·g⁻¹ for over 250 cycles for the room temperature sodium-sulfur system. In addition, nitrogen, sulfur co-doped hierarchical porous carbon was fabricated by soft template method and combined with sulfur. The N,S-HPC/S composite showed relatively lower energy density; however, with much higher cycle stability of ~10,000 cycles at a current density of 4.6A·g⁻¹.

The next generation secondary battery showed good performance yet with limited protection for the inevitable lithium dendrite growth if coupled with metallic lithium, which is an adverse phenomenon that would eventually result in the deterioration of the battery. The shortage of the battery is caused by the dendrite penetration, which could lead to safety issues including thermal runaways and explosions. Therefore, solid polymer electrolyte was designed and prepared to mechanically suppress the growth of dendrite during charging protocol. PEGDA polymer host, plasticizers and lithium salt were used to fabricate the solid ionic conducting membrane, which could achieve an ionic conductivity of $10^{-3}$ S·cm⁻¹, a value that is comparable to the liquid electrolyte counterpart. The solid polymer electrolyte was implemented in the conventional lithium-ion battery and the advanced lithium-sulfur battery.
ACKNOWLEDGEMENTS

It has been nearly four and a half years that I have been studying in the Department of Polymer Science at the University of Akron. I could not express how much I am grateful regarding the opportunity I was given to conduct research in such a prestigious institute. First of all, I would like to express my deepest gratitude to my advisor, Dr. Yu Zhu, for allowing me to carry out research projects in his group. His hardworking attitude and broad understanding in a great variety of interdisciplinary scientific areas served as an epitome to me. Under his guidance and teachings, I have acquired the ability to scientific reasoning and further utilize it in my everyday life. I would like to extend my appreciation towards my committee members including Dr. Steven S.C. Chuang (Chair), Dr. Mesfin Tsige, Dr. Toshikazu Miyoshi, and Dr. Bryan D. Vogt (Outside representative). Your valuable suggestions and constructive criticisms have urged me to pursue for more in-depth understanding in fundamental experimentation and logical reasoning.

As the first doctoral student in Dr. Yu Zhu’s laboratory, I would like to thank all the members in the group. Many things have happened in the past four and a half years; no matter good or bad, I believe that by lending from these valuable experiences I would be able to resolve any obstacles in the future. In addition, I would also like to thank the instrument managers, machine/glass/inventory shop staffs, and all university staffs who helped me out when I needed it the most.
I would also like to thank my Taiwanese friends from the NE Ohio community, especially from the universities and the Boston Heights Taiwanese Friends Church, who were there to cheer me up at my down times and to provide me with valuable advices on making life-changing decisions.

Finally, and most importantly, I would like to deeply appreciate the endless support and backing from my family. I could not have made it this far without my family’s constant spiritual support and encouragements. I feel so grateful that I have received so much assistance during my time pursuing for the degree. This achievement would not have been completed without any of you.
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CHAPTER I
INTRODUCTION

The discovery of electricity could be one of the most impactful events that eventually triggered the sudden technological advancements in the recent centuries. The generation of electricity and the subsequent harnessing of electrical power have greatly improved the living standards and allowed more advanced and intricate technologies to be developed. The invention of batteries further enabled the development of portable electronics or larger machinery to facilitate our daily lives. But, it was not until 1990 where Sony had successfully developed and commercialized the rechargeable lithium-ion batteries\(^1\); which have then predominated due to the advantageous impacts in both environmental and economic aspects. In the recent years, the development of more innovative electronics including electric vehicles and the demands for longer-lasting electrical-driven portable devices has had urged for the search for higher energy density batteries. However, the current intercalation mechanism provided by the lithium-ion battery could no longer live up to the expectations; therefore, it is essential to seek for advanced next-generation electrochemical energy storage methods in order to fulfill and perchance further become a driven-force for the development of even more complex gadgets.
A battery, regardless of what type of mechanistic chemistry or materials utilized within, or even the battery casing, has the following configuration:

![Battery Components](image)

Figure 1.1 Basic components and the configuration of a battery.

Depending on the casing of the battery which could be either coin cell, pouch cell or the 18650 battery, the battery cell configuration would consist the components shown in Figure 1.1, where the current collectors are copper or aluminum depending on the electrodes. The electrodes are coined as the cathode and the anode, in which most of the time are casted onto the current collectors. The separator is usually made of a porous thin polymeric film, which functions as an insulator to prevent the electrodes from shorting through contacting each other. Moreover, the separator should be easily wetted and able to retain electrolytes enabling the transfer of ions. Modifications and alterations could occur depending on the focus of the research, yet the overall configuration of the battery remains intact.

The aim of this research is to demonstrate higher energy density batteries compared to conventional lithium-ion batteries using conversion chemistry instead of intercalation chemistry with the integration of ordered carbonaceous materials. The lithium-oxygen battery, being considered as the Holy Grail for electrochemical energy storage devices, and the sulfur based batteries are of special interest since they exhibit much higher energy
density in comparison to the lithium-ion battery. Latter part of the research shifts focus from high energy density batteries to more safety-awareness-oriented membrane design. Safety concern is the utmost important factor to be considered if a product is to be commercialized regardless of how large the energy density could be achieved. A battery system with extremely high energy density could not be put into use if the safety standard requirements are not fulfilled.

The main incentives and objectives of this work are twofold. First is an attempt to fabricate a battery that could last longer while providing better safety protection so that our daily lives could be facilitated. Second is an indirect way to alleviate the effects of global warming, where it is based on the thought that if a better, safer, more reliable and higher capacity battery could be implemented into electric vehicles and power grids, the reliance on the green-house-gas-generating fossil fuels could be greatly reduced.

In this dissertation, ordered carbonaceous nanomaterials would be discussed and then subsequently be integrated into two different battery systems – the lithium-oxygen battery and the sodium-sulfur battery. Each chapter would consist of a brief introduction of the main themes followed by the experimental methods. Results and discussion section would focus on the interpretation of the data and the explanation of the performances. The chapters would end with a conclusion summing up the important points of the project.

In Chapter II, essential background information regarding the ordered carbonaceous materials would be covered. Subsequently, the lithium-oxygen battery would also be introduced to provide an overall understanding of the current state-of-art development in the field. The chemical vapor deposition method in growing the carbon
nanotubes and the fabrication of the battery would be thoroughly explained in the experimental part followed by the interpretation in the results and discussions section.

In Chapter III, metal organic framework and the selected crystal particle would be introduced. An overview of the sodium-sulfur battery system would also be separately described into two parts – the mechanism and the challenges. While the latter part of the chapter would follow the same logic as Chapter II in terms of experimental, results and discussions and eventually the conclusions.

In Chapter IV, another sodium-sulfur battery system would be explained. However, since the background knowledge of the battery is already being described in Chapter III, there would only be an introduction on the ordered mesoporous carbon. The subsequent sections would focus more on the experimental and the interpretation of the results.

In Chapter V, as suggested from the introduction part, the main focus would shift from engineering high energy density batteries to the modifications of safety-oriented membranes. Instead of utilizing conventional polymer separators, solid polymer electrolytic films would be used as the substitution to prevent lithium dendrite formation that leads to the shorting of the battery cell. The solid polymer electrolyte formulation process would be demonstrated, subsequent solid polymer electrolyte film characterizations would be shown to illustrate the good ionic conductivity at room temperature while providing much higher mechanical integrity compared to the liquid electrolyte counterparts. Two different battery systems – lithium-ion battery and lithium-sulfur battery were fabricated using the solid polymer electrolyte.

In Chapter VI, a general conclusion would be provided to give a brief overview of each of the chapters.
The final chapter, chapter VII, will be on the final remarks and the suggestions for future studies.
CHAPTER II

CYCLABILITY OF ALUMINIUM-OXYGEN BATTERY CONTAINING N-METHYL-2-PYRROLIDONE AND A VERTICALLY ALIGNED CARBON NANOTUBE

2.1 Introduction of carbon nanomaterials

Carbon is one of the most abundant elements existing on earth. In terms of the inorganic carbon based materials, carbon is extremely versatile in forming into many different allotropes due to its valency. Figure 2.1 illustrates some of the well-known carbon allotropes. Figure 2.1a demonstrates the amorphous carbon, which suggested by its name, is randomly oriented without exhibiting ordered crystalline structure. Figure 2.1b is diamond, in which the carbon atoms are arranged in the face-centered cubic crystal structure. Figure 2.1c shows the graphite structure, which is a material that is commonly employed into battery anode materials in the lithium-ion battery. Figure 2.1d shows sphere structure of C_{60} bucky ball, or also known as buckminsterfullerene. Figure 2.1e is graphene, which is essentially a single layer of graphite. Figure 2.1f is carbon nanotube (CNT); it could be regarded as the roll-up of a single layer or multi-layer graphene.
Figure 2.1 Selected carbon allotropes (a) amorphous carbon, (b) diamond, (c) graphite, (d) C_{60} buckminsterfullerene, (e) single layer graphene, (f) carbon nanotube.
Graphitic carbon is one of the most commonly utilized carbonaceous materials in the lithium-ion battery batteries due to its stability and cost. In the recent decades, many other carbon nanomaterials were discovered or synthesized due the advancement of better characterization tools and instrumentations. There is no universal categorization of these carbonaceous nanomaterials, but generally the materials could be identified into four groups – zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three dimensional (3D). 0D carbon materials include the C$_{60}$ fullerenes, nanoclusters or nanospheres. 1D carbon materials include the carbon nanotubes or fiber-like strands. 2D carbon materials are the films, sheets or layered structures including graphene. 3D carbon materials are graphite or some composite combinations from their lower dimensions. The nano-engineering from the scientific research acted as a driving force to push for the development innovative nano-material-related products. Among the great variety of carbonaceous nanomaterials, many products, in fact, were already been widely used in diverse commercial products such as energy storage devices, automotive coatings and interior parts, water filters, sporting goods, etc. The following sub-sections would elaborate more in-depth regarding graphene and CNTs, which are two of the most recognized and ground-breaking materials within the large subset of carbonaceous nanomaterials.

2.1.1 Graphene

Graphene, single-layer hexagonal honeycomb lattice of carbon atoms, is a two-dimensional sheet that is composed of sp$^2$-bonded carbons. Since the discovery of this extraordinary carbonaceous nanomaterial in the year 2004 by Novoselov and Geim, it has literally revolutionized and greatly impacted various fields, especially in the energy storage
and electronics field. This scientific breakthrough was once believed to be non-existence due to its thermal instability, and considered as the holy-grail material to promote the current technology into another era. Therefore, with the publication announcing successful isolation of single layer graphene from graphite, it not only stirred up the entire scientific community into pursuing for the integration of graphene into existing applications, but also triggered different processing methods in reducing the fabrication cost of the material, ultimately anticipating for commercialization. Subsequent studies and researches were also elaborated onto the isolation of 2D layered sheets from other materials which could provide further insightful perspectives in ameliorating performances of applications in various fields.

Table 2.1 Selected properties of a perfect single-layered graphene.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value [Units]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier mobility&lt;sup&gt;5-7&lt;/sup&gt;</td>
<td>&gt;200,000 [cm&lt;sup&gt;2&lt;/sup&gt;·V&lt;sup&gt;-1&lt;/sup&gt;·s&lt;sup&gt;-1&lt;/sup&gt;]</td>
</tr>
<tr>
<td>Resistivity&lt;sup&gt;8&lt;/sup&gt;</td>
<td>10&lt;sup&gt;-6&lt;/sup&gt; [Ω·cm]</td>
</tr>
<tr>
<td>Young modulus&lt;sup&gt;9&lt;/sup&gt;</td>
<td>&gt;0.5-1 [TPa]</td>
</tr>
<tr>
<td>Tensile strength&lt;sup&gt;10&lt;/sup&gt;</td>
<td>130 [GPa]</td>
</tr>
<tr>
<td>Spring constant&lt;sup&gt;11-12&lt;/sup&gt;</td>
<td>1-5 [N·m&lt;sup&gt;-1&lt;/sup&gt;]</td>
</tr>
<tr>
<td>Thermal conductivity&lt;sup&gt;13-14&lt;/sup&gt;</td>
<td>3000-4000 [W·m&lt;sup&gt;-1&lt;/sup&gt;·K&lt;sup&gt;-1&lt;/sup&gt;]</td>
</tr>
<tr>
<td>Opacity (white light absorption)&lt;sup&gt;15&lt;/sup&gt;</td>
<td>πα&lt;sup&gt;*&lt;/sup&gt; = 2.3 [%]</td>
</tr>
<tr>
<td>Surface area&lt;sup&gt;16&lt;/sup&gt;</td>
<td>2965 [m&lt;sup&gt;2&lt;/sup&gt;·g&lt;sup&gt;-1&lt;/sup&gt;]</td>
</tr>
<tr>
<td>Mass per area&lt;sup&gt;**&lt;/sup&gt;</td>
<td>≈0.76 [mg·m&lt;sup&gt;-2&lt;/sup&gt;]</td>
</tr>
</tbody>
</table>

<sup>*</sup>The constant α is defined as the fine structure constant, which is the sole factor affecting the opacity of graphene. α = e<sup>2</sup>/hc ≈ 1/137 (c ≈ 3×10<sup>8</sup> m·s<sup>-1</sup> or the speed of light)<sup>15</sup>

<sup>**</sup>Calculation based on the bond length of carbon-carbon of 0.142 nm<sup>17</sup>, and mass of a carbon atom of 1.994×10<sup>-23</sup> g.
Table 2.1 is a list of selected properties of a perfect single-layered graphene. The values of the selected properties reported are demonstrated to be one of the best in comparison to materials also possessing extraordinary properties. For instance, the thermal conductivity for copper\textsuperscript{13}, reported to be among one of the highest values within the metallic group, exhibited conductivity of \(~400 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\); whereas graphene was reported to be larger than \(3000 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\) under different circumstances. The thermal conductivity is only one of the exampled properties that demonstrated the extraordinariness of graphene.

Since the isolation of graphene from graphite via exfoliation method made public in the year of 2004, within merely a decade of research and development, the graphene could be fabricated through a great variety of procedures. Protocols include mechanical exfoliation, epitaxial growth on silicon carbide\textsuperscript{18-19} (SiC) or ruthenium\textsuperscript{20} (Ru), chemical vapor deposition\textsuperscript{21-27} (CVD), chemical reduction of graphite oxide\textsuperscript{28-29}, CNT unzipping\textsuperscript{30-33}, bottom-up synthesis\textsuperscript{34-35} etc.

Figure 2.2 illustrates the layered sheets of the graphene under high-resolution transmission electron microscope (HRTEM). The growth of the graphene was synthesized via a self-assembled CVD utilizing copper film as the catalyst substrate with gaseous carbon sources under vacuum and high temperature. Figure 2.2a depicts the layered structure of the graphene, in figure 2.2b, it could be seen from the circled edge that the synthesized graphene is multi-layered. Through counting the number of parallel lines at the edges, the number of the stacked graphene could be identified.
Figure 2.2 Graphene under high-resolution transmission electron microscope (HRTEM) (a) multi-layered graphene [scale bar = 50 nm], (b) close up at the edges of the graphene. [scale bar = 5 nm]

Figure 2.3 Raman spectroscopy of the as synthesized graphene.
Figure 2.3 is the Raman spectroscopy characterization of the synthesized graphene. Three peaks from the figure were labeled, the D peak, G peak and 2D or also known as G’ peak are corresponding to the Raman shifts at ~1310 cm\(^{-1}\), ~1580 cm\(^{-1}\), ~2700 cm\(^{-1}\), respectively. An intense D peak at ~1310 cm\(^{-1}\) is observed in defected graphite due to zone-boundary phonons\(^{36}\), which is coined as the defect peak\(^{37}\). Therefore, the lower the intensity for D peak, the less significant number of defects at the characterized sites\(^{38}\). The shape of the 2D peak from the Raman spectrum could distinct the difference between graphite and graphene. A single sharp peak is identified in the graphene Raman spectrum whereas in graphite, a combination of peaks could be observed, which would result in a shoulder at the side of the 2D peak\(^{38}\). In figure 2.3, it corresponds to the TEM results shown in figure 2.2, where the Raman spectrum exhibits the characteristic peaks of multi-layered graphene. There is a direct correlation between the layers of graphene and the ratios between the G peak and the 2D peak\(^{39}\). G/2D ratio for monolayer graphene would be < 1; G/2D ratio for bi-layer graphene would be ~ 1; and for few layered graphene, the G/2D ratio would be > 1.

2.1.2 Carbon nanotube

Carbon nanotubes (CNTs) are virtually seamless roll ups of graphene sheets. Dependent on the layers of graphene being rolled, the CNTs could be defined into single-walled CNTs, double-walled CNTs, or multi-walled CNTs. The discovery of the CNT has drawn great attention in the field of material science and continues to be a hot topic even up to date. Currently, debates on who should take credit in the discovery of CNTs remain; however, the most recognized discoverers are Iijima et al., from NEC in 1991, who submitted and later published their results on SWCNT in the Nature journal\(^{40}\). Another
group, Bethune et al., from IBM, had their results submitted roughly a month later. Regardless, the discovery has had impacted the scientific community, leading to huge activities in most areas of science and engineering since the CNTs possess exceptional physical and chemical properties.

The structure, affected by diameter and helicity, of single-walled CNTs could be defined by the chiral vector, in which how the CNT was rolled-up.

\[ C_h = (n,m) = na_1 + ma_2 \]  \hspace{1cm} (2.1)

where the values of \(a_1\) and \(a_2\) corresponds to different lattice vectors on the graphene sheet, \(n\) and \(m\) are integers \((0 \leq |m| \leq n)\). Zigzag structure occurs when \(\theta = 0\) (\(n, 0\)), armchair structure results when \(\theta = 30\) (\(n, n\)), and the chiral structure occurs when \(0 < \theta < 30\) (\(n, m\)). The intrinsic geometry structure of the CNTs could impact the physical properties, especially the electrical conductivity. The zig-zag structure and the chiral structure could range from semi-metals to wide bandgap semi-conductors; whereas the armchair structure is always semi-metallic.
Figure 2.4 (a) The different roll-up structures for the CNTs resulting from different theta angles. (b) $a_1$, $a_2$ and $\theta$ values illustrated on a graphene.\textsuperscript{42}
Similar to the two-dimensional layered graphene, the carbon based one-dimensional CNTs exhibited appealing properties that other materials that are incapable of achieving. The difference between the CNT and the graphene is the aspect ratio. The aspect ratio, also known as the length-to-diameter, could reach as high as 132,000,000:1\(^{45}\) for CNTs. Other properties, listing some values in table 2.2, also exhibited similar extraordinary values compared to its graphene counterpart; suggesting that the CNT could out-perform current existing materials that were already being placed into applications.

Table 2.2 Selected properties of a single-walled CNT.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value [Units]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier mobility(^46)</td>
<td>(10^5 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1})</td>
</tr>
<tr>
<td>Resistivity(^44)</td>
<td>(10^{-6} \text{ \Omega}\cdot\text{cm})</td>
</tr>
<tr>
<td>Young modulus(^47)</td>
<td>&gt;1 [TPa]</td>
</tr>
<tr>
<td>Tensile strength(^48)</td>
<td>63 [GPa]</td>
</tr>
<tr>
<td>Thermal conductivity(^49\text{-}51)</td>
<td>6000* [W·m(^{-1})·K(^{-1})]</td>
</tr>
<tr>
<td>Density(^47)</td>
<td>1.3 [g·cm(^{-3})]</td>
</tr>
<tr>
<td>Diameter(^52)</td>
<td>1-10(^9) [nm]</td>
</tr>
<tr>
<td>Length(^52)</td>
<td>&gt; 1 [mm]</td>
</tr>
<tr>
<td>Hardness(^53)</td>
<td>462-546 [GPa]</td>
</tr>
</tbody>
</table>

*The theoretical value of the thermal conductivity has yet to be obtained\(^54\); the highest attained value is around 3500 W·m\(^{-1}\)·K\(^{-1}\).\(^55\)
2.2 Synthesis of CNTs

Many techniques have been developed to synthesize the CNTs in order to produce them with sizable amount for commercialization. Methods including arc discharge\textsuperscript{56-57}, laser ablation\textsuperscript{58}, chemical vapor deposition (CVD), bottom-up synthesis\textsuperscript{59-60}, thermal plasma\textsuperscript{61}, and even simple incineration from flame\textsuperscript{62} are implemented to fabricate CNTs. In the upcoming sub-sections, emphasis would be on the CVD instrument and the growth mechanisms of the CNT utilizing CVD.

2.2.1 CVD method

Chemical vapor deposition method is a widely recognized technique in material processing and synthesis. The CVD process is mainly utilized in solid thin-film coating onto various surfaces, especially in the semi-conductor industry. However, it could also be attuned to produce high-purity powders or even bulk materials, and furthermore it could be used for the fabrication of composite material by infiltrating desired precursors.

The CVD instrument, with its most simple configuration, has an active material purging source that is usually gaseous, in which flows into a heated chamber that contains the desirable objects to be coated. The reacted gas would then leave the system that is connected to a vent system. The heating system could range from hundreds to several thousand depending on the desired application. Add-ons onto the CVD could greatly enhance the functionalities and versatilities of the instrument to fabricate larger variety of materials or simply improve the quality of the targeted coating material. Addition of the add-ons including plasmas, pressure controllers, ion beams, photons, lasers, combustion reactors, hot filaments etc would be coined the enhanced CVD processes; providing much more possibilities for the design of the material.
Figure 2.5 Periodic table with shaded elements, indicating reports of being deposited via the CVD method.

<table>
<thead>
<tr>
<th>IA</th>
<th>IIA</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
<th>VIII</th>
<th>IB</th>
<th>IIB</th>
<th>IIIB</th>
<th>IV</th>
<th>VA</th>
<th>VIB</th>
<th>VIIIB</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>1.008</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>6.941</td>
<td></td>
<td>4</td>
<td>Be</td>
<td>9.012</td>
<td></td>
<td></td>
<td>5</td>
<td>B</td>
<td>10.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Na</td>
<td>22.990</td>
<td></td>
<td>12</td>
<td>Mg</td>
<td>24.305</td>
<td></td>
<td></td>
<td>13</td>
<td>Al</td>
<td>26.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>K</td>
<td>39.098</td>
<td></td>
<td>20</td>
<td>Ca</td>
<td>40.08</td>
<td></td>
<td>21</td>
<td>Sc</td>
<td>44.956</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>37</td>
<td>Rb</td>
<td>85.468</td>
<td></td>
<td>38</td>
<td>Sr</td>
<td>87.62</td>
<td></td>
<td>39</td>
<td>Y</td>
<td>88.906</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>55</td>
<td>Cs</td>
<td>132.905</td>
<td></td>
<td>56</td>
<td>Ba</td>
<td>137.33</td>
<td></td>
<td>57</td>
<td>La</td>
<td>138.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>87</td>
<td>Fr</td>
<td>(223)</td>
<td></td>
<td>88</td>
<td>Ra</td>
<td>(226)</td>
<td></td>
<td>89</td>
<td>Ac</td>
<td>227.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

**LANTHANIDES**

<table>
<thead>
<tr>
<th></th>
<th>57</th>
<th>La</th>
<th>138.9</th>
<th>58</th>
<th>Ce</th>
<th>140.1</th>
<th>59</th>
<th>Pr</th>
<th>140.1</th>
<th>60</th>
<th>Nd</th>
<th>144.2</th>
<th>61</th>
<th>Pm</th>
<th>(145)</th>
</tr>
</thead>
</table>

**ACTINIDES**

|    | 89 | Ac | 227.0  | 90 | Th | 232.0  | 91 | Pa | 231.0  | 92 | U  | 238.0  | 93 | Np | 237.0  | 94 | Pu | (244)  | 95 | Am | (243)  | 96 | Cm | (247)  | 97 | Bk | (247)  | 98 | Cf | (251)  | 99 | Es | (252)  | 100| Fm | (257)  | 101| Md | (256)  | 102| No | (259)  | 103| Lr | (257)  |
CVD possess several advantages in terms of thin film deposition. The first one would be the uniformity of the thin film, which is characterized by its homogeneity without exhibiting a thickness gradient regardless of the topology of the targeted substrate. Secondly, a wide variety of materials could be used as the target to deposit thin films, and with high purity. Figure 2.5 illustrates the elements that were utilized in the CVD to deposit thin films; essentially, almost all of the transition-metals are compatible with the CVD method to deposit a thin layer of film. In addition, the deposition rate could be regulated to high values by adjusting some parameters including the temperature or flow rate. However, despite all the appealing factors mentioned, a number of disadvantages also exist with this type of processing technique. First drawback is that the target material has to be non-volatile at room-temperatures or otherwise the deposition could not be achieved; moreover, many of these target materials utilized are highly toxic, corrosive or even explosive, which could result in the production of hazardous byproducts during reactions within the CVD. Secondly, in order to deposit the target materials, the temperature usually has to be tuned up at elevated temperatures, which greatly reduces the availability of substrates to be coated. Thirdly, under such elevated temperatures, stresses in the films deposited could cause mechanical instabilities due to different thermal expansion coefficients.

Despite the simple setup of the CVD instrument, there are in fact many factors that could be controlled to affect the final outcome. Therefore, it is necessary to discuss the reaction mechanism and the processing of the CVD in order to better understand the ending results from the substrate. Regardless of the different type of various modifications that could be on the CVD, there are three fundamental capabilities that the CVD must possess (as shown in figure 2.6a): (1) a feedstock controller that enables the quantitative
measurements of precursors into the reaction chamber; (2) a source of energy that enables the reaction to take place (i.e. heating source); (3) a purging outlet that enables the removal of exhaust and reacted components from the reaction environment, preventing the possibility of side-reactions.

Figure 2.6 (a) The simplest setup for a CVD apparatus. (b) The seven mechanistic steps that were hypothesized during the deposition process.
The kinetics of the vapor deposition process is rather complex since not only the chemical reactant precursors must be taken into consideration, but also other controllable parameters including temperature, concentration gradient, geometry of the substrate, reaction zone, flow rate of the inlet gas, vacuum condition, and dependent parameters for instance the thickness of the boundary layer etc. Generally, the deposition process could be broken down into seven steps as shown in figure 2.6b. The process is explained as following:

1. Transportation of the precursor from the inlet with an inert protective carrier gas into the reaction location,
2. Pyrolysis of the precursor into intermediate reactants, or the formation of reactive intermediates under exposure to energy source,
3. Diffusion of the reactive species from the gas flow direction into the boundary layer and subsequently migrating towards the substrate,
4. Adsorption of the intermediate species onto the surface of the substrate,
5. Chemical reaction via one- or multi-step process on the surface,
6. Desorption of the gas product or exhaust gas from the substrate to the boundary layer,
7. Removal of the reacted gaseous species from the outlet through the continuous purging inlet.

The model described could further be categorized into two major classes – mass transport and surface reaction steps. At lower temperature, the rate-determining step is at the surface reaction; whereas mass-transport becomes the limit as the temperature increases.
2.2.2 Growth mechanisms of CNT using CVD

The previous section provided a succinct fundamental understanding towards the versatile use of the CVD. The CNTs are also one of the products that could be fabricated with the assistance of the CVD, and under the right circumstances, the possibility of mass-production of high-quality single-walled CNTs could be achieved. The CVD has an advantage over the other methods since it is simpler and more economical at synthesizing CNTs at lower temperature and under ambient pressure. The purity and the yield of CNT products are, especially, more superior than methods such as arc discharge and laser ablation techniques. However, in terms of the macroscopic structural control of CNT architecture, it could be only accomplished by the CVD method. The type of growth form (entangled, vertically aligned, powder etc) could be achieved by tuning different parameters or introducing add-ons into the CVD system.

![Figure 2.7 A self-assembled CVD system with an additional water-bubbling line.](image-url)
Figure 2.7 illustrates a CVD system with a water-bubbling line that is to induce the growth of vertically aligned CNTs (VACNTs), which would be discussed more in detail in the latter part of this sub-section. The CVD process involves the purging of a hydrocarbon gas (typically ethylene), liquid (ex. alcohol), or even solids at a desired flow rate via the controls of mass flow controllers, and then subsequently passing through a tube reactor (or the deposition chamber) along with a carrier gas where a heat source is supplied. The substrate is usually coated with a thin layer of catalyst material and placed at the center spot of the tube furnace reactor. The heat source would be elevated to high temperatures ranging from typically 600 – 1200 °C in order to decompose and undergo pyrolysis of the hydrocarbon. The CNT would then grow on the catalyst part of the substrate within the reactor oven; the amount of CNT growth would depend on the time interval allowed for reaction. However, it must be noted that longer time of growth does not necessarily give higher yield since the catalyst could be poisoned or simply lose its activity. In addition, pyrolysis of a catalyst vapor to isolate the nano-particles directly within the deposition chamber is also available; the process is coined as the floating catalyst method.

The growth mechanism of the CNT using the CVD, like its discoverers, is, as well, still under debate. Many different researchers have offered different mechanisms in the growth of the CNT, yet often contradicting. Hence, no single growth mechanism is non-debatable. However, there are two widely recognized and general mechanisms, shown in figure 2.8. Figure 2.8a is the bottom-growth model, in which the catalyst-substrate interaction is strong (the contact angle of the catalyst and substrate is rather obtuse). The hydrocarbon precursors would decompose allowing free carbon to diffuse into the catalyst surface (t=0 in figure 2.8a). Yet due to the strong interaction between the catalyst and the
substrate, the saturation of the carbon could not push the catalyst off the substrate. Thus instead, the CNT would emerge from the tip of the catalyst (t=1 in figure 2.8a). A hemispherical dome would first crystallize and then extend up to forming concentric (not applicable for single-walled CNT, only a cylindrical wall would form) cylinders seamlessly (t=∞ in figure 2.8a).

Figure 2.8b is the tip-growth model, in which the catalyst-substrate interaction is weak (the contact angle of the catalyst and substrate is more acute). So as the hydrocarbon precursors decomposes on the surface of the catalysts (t=0 in figure 2.8b), the free carbon would diffuse into the metal and once saturated, the CNT would precipitate out from the bottom of the catalyst and push it away from the substrate while initiate the growth of CNT (t=1, 2 in figure 2.8b). The CNT could grow indefinitely as long as fresh hydrocarbon is allowed to diffuse into the catalyst. As excess carbon covers the catalyst (also known as poisoning of the catalyst), the catalytic activity halts and thus results in the stop growth of CNT (t=∞ in figure 2.8b).

Different wall-layers or simply the single-/multi-walled CNTs are dependent on the size of the catalyst particle. The smaller the particle size corresponds to a smaller tube diameter, in which provides the opportunity to grow single-walled CNTs; typically particle sizes with several nanometers would result in the growth of single-walled CNT. Whereas particle catalysts with several tens of nanometer or larger would induce the growth of multi-walled CNT. Additionally, another factor that could affect the wall number of the CNT is temperature. At lower temperatures ranging from 600-900 °C, typically would yield multi-walled CNT. At higher temperatures ranging from 900-1200 °C, growth of single-walled CNTs is more desired; suggesting that single-walled CNTs require higher energy
to form (which is reasonable since small diameter of the tube results in higher strain energy due to high curvature).

The catalyst for the growth of CNTs is another factor to be considered. Usually transition metals are utilized for the growth of the CNTs, since the metal would not deteriorate or be destroyed at elevated temperatures. Another reason to be considered is the solubility of carbon in the metals under different temperatures and their carbon diffusion rate in the metals. Metals include Fe, Co, Ni, (which are three of the most commonly used catalysts), Ag, Ag, Al, Cr, Cu, Mg, Mn, Mo, Pd, Pt and Sn were reported to be possible for CNT growth with the CVD technique.

Figure 2.8 The generally accepted growth mechanisms of the CNT using CVD could be categorized into (a) the base-growth model (or also known as bottom-growth), and (b) tip-growth model (or also known as top-growth).
2.3 Introduction of lithium-oxygen battery

Lithium-oxygen batteries, or short as Li-O\textsubscript{2} batteries, have become one of the center of focuses in the field of next-generation energy storage devices. Recalling from Chapter I, demand to pursue for higher energy density advanced energy storage has yet to be developed. Thus, resulting in the pursuit to decipher the basic mechanisms and furthermore the development of the Li-O\textsubscript{2} batteries. The Li-O\textsubscript{2} battery has been chosen as the subject since it is well-known for its extremely high theoretical specific energy density; which is illustrated in figure 2.9, showing the highest energy density of 5217 W\textperiodcentered h\textperiodcentered kg\textsuperscript{-1}. The calculated value for the Li-O\textsubscript{2} battery is nearly ten times of that compared to the currently used LiCoO\textsubscript{2} Li-ion battery. Moreover, to further understand the potential capacity of the battery, the Li-O\textsubscript{2} battery was being placed in parallel with gasoline to compare their similarities in high energy density.

Reversible Li-O\textsubscript{2} batteries were not demonstrated until 1996 by Abraham and Jiang\textsuperscript{71}. But it was not until 2006 that Ogasawara and Bruce\textsuperscript{72} revisited the subject and developed a non-aqueous system to further validate the potential of the Li-O\textsubscript{2} battery. Since then, hundreds and thousands of research articles flourished in attempt to solve the problems existing in the Li-O\textsubscript{2} battery and subsequently aiming for its commercialization. Despite extensive and elaborated research and experimentation in the field, the Li-O\textsubscript{2} battery has yet to exhibit a breakthrough to put the technology into practical use in the near future. In the sub-sections, the mechanism of the Li-O\textsubscript{2} battery will be discussed and then shift to the challenges of the Li-O\textsubscript{2} battery.
2.3.1 Mechanism of the lithium-oxygen battery

Presently, four different types of reversible Li-O₂ batteries were demonstrated and categorized by the use of electrolyte – non-aqueous, aqueous systems, solid-state, and a hybrid of the non-aqueous/aqueous system. Regardless of the system, the Li-O₂ battery requires an open system in order to allow the flow of oxygen into the electrode. In addition, currently lithium metal must be used as the metal electrode and as the reservoir for lithium ion supply. This sub-section would be mainly focusing on the non-aqueous (or aprotic) mechanism.
The specific energy density of the aprotic-electrolyte based Li-O₂ battery is calculated from the provided reaction:

\[ 2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2 \]  \hspace{1cm} (2.2)

where a lithium would be supplied to react with the oxygen to form the discharge product of lithium peroxide (\(\text{Li}_2\text{O}_2\)). The open circuit voltage (OCV) of the system usually lies around \(2.96\text{V}^{75-76}\).
In figure 2.10, the Li-O_2 battery configuration is basically similar to the generalized battery configuration with some modifications. A lithium metal must be utilized as the metal electrode for the supply for lithium. A separator membrane is used to prevent the short circuit between the two electrodes, with the capability of retaining the electrolyte. On the cathode side of the Li-O_2 battery, a conductive porous material, usually porous carbons, must be employed to house the insoluble discharge products, where Li_2O_2 from equation (2.2) is the desired reversible discharge product. The conductive porous material acts as the three-phase boundary for the reaction to take place; the material itself only acts as a catalyst.

Figure 2.11 Basic discharge/charge mechanisms for the Li-O_2 battery.
Similar to the CNTs, the mechanistic reaction understandings toward the Li-O\textsubscript{2} batteries are relatively in the infancy stage. In addition, the operation of the battery also varies by the battery design, but generally, the reaction pathway follows the one illustrated in figure 2.11. Under discharge, the metal lithium will dissociate into a lithium ion and an electron, the lithium ion will migrate from the metal through the electrolyte layer and then reach the cathode material to react with the radical oxygen (See scheme 2.1). The electron that was dissociated will travel from the external circuit to do work and react with the oxygen from ambient air to undergo r\textsubscript{1} reaction pathway to generate the radical oxygen. The presence of carbonates or some other impurities would lead the radical oxygen to follow pathway r\textsubscript{2} to form undesirable byproducts. The desired reaction pathway is to follow r\textsubscript{3}, where the radical oxygen encounters the lithium ion at the cathode of the battery to form the intermediate discharge product of lithium super oxide (LiO\textsubscript{2}).

![Scheme 2.1 Reaction scheme of an aprotic electrolyte Li-O\textsubscript{2} battery – oxygen reduction reaction]
The intermediate discharge product could undergo three different reaction pathways of \( r_4, r_5, \) and \( r_6 \). When it goes through \( r_4 \), the intermediate LiO\(_2\) products combine and form the reversible discharge product of lithium peroxide (Li\(_2\)O\(_2\)) while releasing oxygen back to the atmospheric environment. If the reaction path follows through \( r_5 \), another pair of lithium ion and electron would react with the LiO\(_2\) to form the reversible discharge product Li\(_2\)O\(_2\). If the reaction follows \( r_6 \) reaction path, di-lithium oxide (Li\(_2\)O) would form along with the release of a single oxygen atom, which would eventually be adsorbed onto another free lithium ion to form LiO, and then subsequently result in the discharge product Li\(_2\)O with another contact with free lithium ion. Reaction pathway \( r_7 \) could also occur with addition of two lithium ions and electron pairs, where Li\(_2\)O would be the final discharge product as well.

When the Li-O\(_2\) battery is under charging protocol, or undergoing oxygen evolution reaction, the discharge products of Li\(_2\)O\(_2\) (which is the desired reversible discharge product) would decompose with the addition of electrons; in which the lithium ion will migrate via the electrolyte layer back to the lithium metal, while the oxygen would be released back to the atmosphere. Ideally, the battery charge protocol reaction pathways should follow the reverse order of the discharge protocol. Therefore, eventually the Li\(_2\)O\(_2\) discharge products would be returned back to its most original state of Li metal and oxygen.

Currently, the anode of the Li-O\(_2\) battery focuses mainly solely on Li metal. The reaction that occurs at the anode is as following:

\[
\text{Li} \rightarrow \text{Li}^+ + e^- \quad (2.3)
\]

where the half reaction of lithium provides a high specific capacity of 3842 mAh·g\(^{-1}\), in comparison to the already commercialized zinc-air battery (815 mAh·g\(^{-1}\)) and multi-
valency aluminum (2965 mAh·g⁻¹)⁷⁸, it is obviously seen that the Li possesses much higher potential in energy density to other systems. Similar to battery systems with different chemistries, a solid electrolyte interphase (SEI)⁷⁹ would form upon operation on the Li metal anode. This SEI layer would act as a barrier between the Li metal anode and the aprotic electrolyte, with the function of corrosion inhibition; however, as the SEI layer grows thicker, the reaction kinetics between the Li metal anode and the electrolyte would be hindered⁸⁰. Uneven distribution of the SEI layer upon charge/discharge is likely to further promote the issue regarding the Li dendrite formation that would eventually lead to the shortage of the Li-O₂ battery. The SEI layer will be further discussed in Chapter V.

The cathode of the Li-O₂ battery could vary greatly from carbonaceous materials to metal catalysts, or combined as a composite material. Currently, carbon materials including, listing a few, mesoporous carbon⁸¹, CNT⁸², graphene⁸³, metal catalysts and derivatives⁸⁴ and so on were utilized as the cathode. The two possible half-reactions occurring at the cathode are as following:

\[
\text{Li(s)} + \frac{1}{2} \text{O}_2 \rightarrow \frac{1}{2} \text{Li}_2\text{O}_2 \quad (2.4)
\]

\[
\text{Li(s)} + \frac{1}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{LiO}_2 \quad (2.5)
\]

where these two reactions are mainly the results from the utilization of an aprotic electrolyte. As shown in scheme 2.1, the discharge product LiO₂ equation (2.5) would proceed onto the Li₂O₂ reaction pathway or also the formation of Li₂O due to its instability. Both reaction from (2.4) and (2.5) are able to provide energy densities of 11,457 Wh·g⁻¹ and 11,248 Wh·g⁻¹, respectively⁷⁸. However, it must be noted that the practical achievable energy density for the Li-O₂ batteries is far less since it is strongly dependable on the
amount of area that is available on the porosity of the air electrolyte and also the electrolyte that is utilized\textsuperscript{85}.

The electrolyte is also an important factor in the design of the Li-O\textsubscript{2} battery. The first demonstrated Li-O\textsubscript{2} battery utilized carbonized based solvent (ethylene carbon (EC), and propylene carbon (PC)) with a lithium salt (lithium hexafluorophosphate (LiPF\textsubscript{6}))\textsuperscript{71}. Other solvent combinations with salt include using ionic liquids\textsuperscript{86}, ether\textsuperscript{87}, dimethylformamide (DMF)\textsuperscript{88}, DMSO\textsuperscript{89}, dimethylacetamide\textsuperscript{90}, etc. The listed solvents are usually combined with salts including LiPF\textsubscript{6}, LiClO\textsubscript{4} (lithium perchlorate), LiAsF\textsubscript{6} (lithium hexafluoroarsenate), LiBF\textsubscript{4} (lithium tetrafluoroborate), lithium triflate (LiSO\textsubscript{3}CF\textsubscript{3}), lithium bis(trifluoromethyl sulfonylimide (LiN(SO\textsubscript{3}CF\textsubscript{3})\textsubscript{2}) etc. It was reported that the carbonate-based electrolytes are susceptible to the formation of unwanted discharge products, which will be discussed further in the latter part of Chapter II.

2.3.2 Challenges of the lithium-oxygen battery\textsuperscript{77}

Decades of studies on the Li-O\textsubscript{2} battery were attempted to resolve the issues from this particular system. However, many challenges still exist and remain as milestones for scientists and researchers to achieve. The challenges could be categorized into three different parts in the Li-O\textsubscript{2} battery component.

From the lithium metal anode side, two of the most important factors to consider are the formation of lithium dendrites, which is in fact the obstacle in every lithium-metal-based battery system. The formation of the lithium dendrites from the lithium metal could result in serious safety issues that must be addressed before it could even be commercialized. The second factor is also another problem regarding the safety of the Li-
O₂ battery. Since the Li-O₂ battery needs to be in an open system to the atmosphere, it increases the threat for possible moisture and humidity to attack the pure lithium metal; which could result in serious hazardous reaction that ultimately lead to the failure of the battery itself.

The selection of the electrolyte could also have negative impacts on the stability and performance of the Li-O₂ battery. Since the electrolyte must be exposed to the ambient environment, it increases the chances for moisture to be dissolved into the electrolyte; especially for hygroscopic type of solvents. The common carbonate based electrolytes that are widely implemented in Li-ion batteries could not be utilized in the Li-O₂ batteries due to possible side reactions. Another fundamental problem causing the electrolyte to be unstable is during the charging, the charge over-potential is much higher, generally at a value around 4.0 V - 4.5 V. The high charge voltage could deteriorate certain electrolyte systems by inducing electrochemical side-reactions; thus making it difficult to find a suitable solvent candidate for Li-O₂ electrolytes. Low oxygen solubility of the solvent is also problematic; several solvents are innately low in oxygen solubility; which adversely impacts the reaction opportunities between oxygen and lithium. Until now, there has yet to be demonstrations of stable solvents for Li-O₂ electrolytes.

Most of the researches are focusing on the development of cathode material, attempting to provide a good porous conductive structure to house the discharge products. However, the nature of the discharge product coating on the cathode material could cause issues regarding the transport kinetics and reaction kinetics, thus resulting in the low cycle stability and poor rate capability, respectively.
2.4 Experimental

The following subsections would be focusing on the experimental part in the growth of the VACNT, the fabrication of the Li-O\textsubscript{2} battery and the characterization methods.

2.4.1 Growth of vertically aligned carbon nanotube using chemical vapor deposition

The growth of the orderly aligned CNTs was made available with the use of the CVD. The quality growth of the VACNT critically depends on the preparation of the catalysts.

2.4.1.1 Preparation of the catalyst on silicon wafer

A silicon wafer (4” in diameter, p-type, University Wafer) was sonicated using an Ultrasonic cleaner (GB-2500B, Bringnew) in ethanol for 10 minutes followed by acetone for another 10 minutes. The washing process was repeated for more than three times to ensure the cleanliness of the silicon wafer. After washing with acetone, the silicon wafer was blow-dried using compression gas to remove possible wetted areas on the surface. Then, the as-prepared silicon wafer is placed into an electron-beam evaporator (Denton vacuum DV-502 A and Denton vacuum deg-2 mini-gun modified). The chamber was vacuumed to at least $5 \times 10^{-5}$ Pa prior to the deposition of the buffer layer. The buffer layer was coated by using aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) with a thickness of 10 nm; the evaporation rate of the Al\textsubscript{2}O\textsubscript{3} should be less than 1.0 Å·s\textsuperscript{-1}. Subsequently, another 1 nm of iron (Fe) was deposited as the catalyst at a rate less than 0.5 Å·s\textsuperscript{-1}. The Fe is used as the catalyst for the growth of CNTs.
2.4.1.2 Growth of the VACNT using CVD

Vertically aligned carbon nanotubes (VACNTs) were grown using a self-assembled and designed chemical vapor deposition (CVD) system, which was shown in figure 2.7. The growth of the VACNT was under atmospheric pressure. Prior to turning on the CVD system, the catalyst coated silicon wafer was placed in a moving quartz tube inside the CVD mother quartz tube. Argon (5.0 UHP grade 99.999%, Praxair) was firstly purged into the CVD system while the vacuum pump is on to ensure all contaminations are removed from the quartz tube. Then, hydrogen (5.0 UHP grade 99.999%, Praxair) was purged into the system at once when the argon is turned off; the hydrogen flow rate was tuned at different ratios to give the best results of VACNT growth. Finally, the vacuum was discontinued by shutting down the pump, and the growth tube chamber was refilled back to atmospheric pressure by the continuous purging of hydrogen. The furnace is turned on and set to a temperature of 750 °C for the pyrolysis of the carbon source. The catalyst coated silicon wafer was loaded into a cool zone first to wait for the furnace to reach the desired temperature. Once the temperature reaches 750 °C, the catalyst specimen was hot-loaded into the center of the tube using a magnet without breaking the hydrogen gaseous atmosphere in the tube. Meanwhile, water vapor (bubbled through by using a hydrogen source), was introduced into the CVD tube. The annealing time was controlled to three minutes. Ethylene (2.5 grade 99.5%, Praxair) along with the water vapor and hydrogen carrier gas were introduced into the reaction chamber to grow VACNTs upon the ending of annealing time. The growth time was also an independent variable that was controlled to provide different lengths of VACNTs.
If the VACNT was to be peeled of the silicon wafer, a facile etching procedure was carried out to weaken the bonds between the VACNTs and the substrate. After the VACNT growth, the carbon source was turned off while the hydrogen and water-vapor supply were kept on for a minute. Next, the hydrogen and the water-vapor supply were shut down and the growth sample specimen was unloaded to the original standby cool region. The vacuum pump was turned on to remove residual gas in the tube to the gas sink reservoir. After removal of the hazardous gases, inert argon was filled into the chamber to restore atmospheric temperature prior to taking out the sample specimen. After this etching procedure, a free-standing VACNT could be easily obtained by simply peeling the sample using mechanical force using a stainless-steel sheet.

Figure 2.12 Images of the stainless steel sheet to peel of free-standing VACNT from the substrate.
2.4.2 Fabrication of the Li-O_2 battery

Swagelok®-type cell case (shown in figure 2.13) was used for the Li-O_2 battery fabrication. The whole process in making the Li-O_2 cell was in an argon glovebox (Labstar, MBraun) at a controlled environment with H_2O level < 0.5 ppm and O_2 level < 0.5 ppm. Lithium foil (1 mm thickness, 99.9% metal basis, Alfa Aesar) was punched into 12.7 mm (or ½”) round discs and employed as the anode of the cell. Two Celgard® membranes were also punched into pieces at larger sizes of 14.3 mm (9/16”) and used as the membrane separators. The as-grown free-standing VACNTs were placed as the working cathode and fully immersed in 1M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, 99.6%, Matrix Scientific) with self-distilled anhydrous N-methyl-2-pyrrolidone (NMP, semi-grade, VWR). The prepared cell was left in the glovebox overnight to ensure the electrolyte to fully wet the two membrane separators and the VACNT cathode. The stainless tube placed at the cathode side of the Swagelok cell to provide flow of oxygen into the battery whereas the rod is placed at the anode side of the cell. The assembled cells were then transferred out from the glovebox and connected to O_2 (5.0 Research Grade, Praxair) at a pressure slightly higher than atmospheric pressure.

![Figure 2.13 Illustration of the Swagelok Li-O_2 battery configuration.](image.png)
2.4.3 Electrochemical measurements

The Li-O₂ batteries are connected as shown in figure 2.14 for electrochemical measurements. Galvanostatic charge and discharge characterizations were performed using an 8 Channel battery Analyzer BST-8A (1mA) from MTi. Chemical window of the battery cell was set from the range of 2.25 V – 4.25 V. The charge/discharge current density applied on the Li-O₂ battery for the long cycle runs were at 250 mA·g⁻¹ at a temperature of 25 °C. Cyclic voltammetry (CV) was conducted using a CHI 608E electrochemical analyzer (CH Instruments). The scanning range was from 2.2 V - 4.3 V with a scan rate of 0.1 mV·s⁻¹.
2.4.4 Post-electrochemical analysis

Raman spectroscopy was used to characterize the surfaces of the cathode material. It was carried out on a HORIBA LabRAM HR high resolution Raman microscope. The wavelength of the excitation laser was 523 nm, green-colored laser. The electrodes were disassembled and then taken out from the Swagelok cell within the glovebox. The cycled electrodes were not treated with solvent at all to ensure the detection of all elements and particularly the discharge products that were on them. Then, the electrodes were heated on a hotplate at 135 °C for at least 48 hours to remove any residual electrolyte solvent from electrolyte that is still in the electrode. Subsequently, the dried electrodes were cut into smaller pieces and sealed onto a glass micro-slide using a cover-slip as the cap and superglue sealing the edges of the cover-slip; this was done inside the glovebox to make sure the discharge products on the electrode do not react with any other materials from the environment during characterization. Scanning electron microscope (SEM) was carried out on a JEOL-7401 field-emission scanning electron microscope. The same dried electrodes were attached onto a column mount and then vacuumed overnight before characterization. X-ray diffraction (XRD) studies were carried out on a Bruker AXS dimension D8 X-ray system, the dried electrode was taped onto the mount holder with the 2θ set to 40°, where the CuKα radiation was used.

2.5 Results and discussions

It was mentioned in previous sub-sections that carbonate-based electrolytes would result in the promotion of reactions with superoxide species91-94, and subsequently would form irreversible by-products that will aggravate the charge/discharge process95-96. Therefore, in this research, non-conventional type of electrolyte solvent was utilized in
order to replace carbonate-based electrolytes to provide better cycle stability. A series of solvents were evaluated due to their capability of withstanding larger electrochemical windows and also the ability against superoxide anion radicals. As mentioned in the former section, different electrolyte solvents were utilized to provide a more stable system than the carbonate-based solvents; the carbonate-based solvents are slightly acidic. Therefore, in other words, the different electrolyte solvents are more resistant against strong basic superoxide anion radical reaction; consequently, the side-reactions and by-products generation could be reduced and suppressed. NMP, mostly used as battery slurry thinner, was among the suggested solvent that is capable of resisting superoxide anion radical tests\textsuperscript{97}. Despite suggested to be stable against the superoxide anions and possessed higher boiling point (203 °C) compared to other organic solvents being used in Li-O\textsubscript{2} batteries including dimethylformamide (DMF, 153 °C), dimethoxyethane (DME, 85 °C), not much has been reported regarding the use of NMP as a solvent for Li-O\textsubscript{2} battery.

One study on the use of NMP as the solvent of electrolyte did not exhibit good cycle stability\textsuperscript{98}, the poor performance could possibly be owing to the use of amorphous carbon to prepare the cathode. It was elucidated that the superoxide radicals react with carbons that contain activated double bonds or aromatics to form epoxy groups and carbonates\textsuperscript{94}. Therefore, VACNTs that were grown by using CVD are more suitable candidate, since the VACNTs are free of oxygen-containing groups and exhibit nearly perfect sp\textsuperscript{2} structure.

2.5.1 Material characterization

The VACNTs were grown by utilizing different flow rates of inlet gases controlled by mass flow controllers. The carbon source utilized was ethylene (C\textsubscript{2}H\textsubscript{4}). Hydrogen (H\textsubscript{2})
was used as the carrier gas to push the carbon sources into the system and also act as a concentration diluent. Argon (Ar) was also attempted as carrier gas to dilute the concentration as well, but in the trials from table 2.2, Ar was not used since the flow rate of H₂ was relatively large already; in fact, from preliminary trials, the Ar did not affect much on the growth of the CNT. The growth time was controlled from 3 minutes to 15 minutes in order to determine the growth length of the CNTs. The annealing time of the catalysts was fixed at 3 minutes to remove possible surface contamination and also acted as reactivation of the catalysts (reducing the possible iron oxide back to metallic iron). The expected length was based on empiricism; the previous trials are not included since they are based on trial-and-error.

Table 2.3 Selected trials for the growth of the VACNTs.

<table>
<thead>
<tr>
<th>Trial</th>
<th>C₂H₄ (scm)</th>
<th>H₂ (scm)</th>
<th>Ar (scm)</th>
<th>H₂O (scm)</th>
<th>Grow time (min)</th>
<th>Anneal time (min)</th>
<th>Expected Length (μm)</th>
<th>Actual Length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>400</td>
<td>0</td>
<td>10</td>
<td>3</td>
<td>3</td>
<td>50</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>400</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>3</td>
<td>100</td>
<td>89.6</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>400</td>
<td>0</td>
<td>15</td>
<td>15</td>
<td>3</td>
<td>150</td>
<td>246.8</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>400</td>
<td>0</td>
<td>10</td>
<td>15</td>
<td>3</td>
<td>200</td>
<td>297.6</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>400</td>
<td>0</td>
<td>20</td>
<td>10</td>
<td>3</td>
<td>250</td>
<td>152.9</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>400</td>
<td>0</td>
<td>20</td>
<td>15</td>
<td>3</td>
<td>300</td>
<td>369.0</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>400</td>
<td>0</td>
<td>50</td>
<td>10</td>
<td>3</td>
<td>400</td>
<td>~450</td>
</tr>
</tbody>
</table>
Figure 2.15 SEM images from the VACNT growth trials from table 2.3.
It could be seen that in spite of the availability in many controllable parameters to
tune the VACNTs, it is still relatively difficult to grow the desired height at their exact
proposed values. However, overall, the trend of increasing the growth time, carbon source
flow rate and the water vapor bubbling flow rate would result in a direct proportional
relationship with the height of the VACNTs according from table 2.3. As seen from figure
2.15, it is clearly seen that the CNTs were grown in a vertical direction with very high tube
to tube density. The lowest height that could be achieved was using 25 sccm ethylene flow
rate, 400 sccm hydrogen flow rate, 5 minutes growth time and 3 sccm water vapor bubbling
rate.

Figure 2.16 SEM images from the lowest height VACNT growth using 25 sccm ethylene,
3 sccm water vapor bubbling, 400 sccm hydrogen and 5-minute growth time.
Figure 2.17 (a) Raman spectrum of the VACNT grown with the lowest height achieved.
(b) Raman spectrum of the VACNT from trial 6 in table 2.2.

From figure 2.17, it must be noted that as the height of the VACNTs decreases, the G peak of the Raman spectrum became more intense (figure 2.17a) compared to the taller VACNT counterparts (figure 2.17b). The increase in intensity from the D peak from taller VACNTs could result from the more disorderliness as the CNTs grow, the taller the growth
the higher the possibility where contaminations and impurities could take part and thus the increase in D peak. The VACNTs that were grown are multi-walled CNTs, because the single-wall CNTs would exhibit a sharp 2D peak similar to that measured here for graphene\textsuperscript{38}, which is not observed from the Raman peaks these figures.

Figure 2.18 The Raman spectrum from trial 7 in table 2.3, which is the VACNT specimen that was implemented into the Li-O\textsubscript{2} battery\textsuperscript{82}. 
In figure 2.19, the VACNT height could grow up to 450 μm with the intense purging of water vapor. The VACNTs were enabled to grow at such length with vertical orientation and additionally same height level for each CNT is because of the introduction of water vapor bubbling. The utilization of water vapor in the CVD is coined as water-assisted CVD growth or also “super growth”. Use of the water vapor could dramatically enhance the activity and life time of the catalysts, which could be attributed to the inhibition of Ostwald ripening. Ostwald ripening is a phenomenon where larger particles would agglomerate and grow in the size while the smaller sized particles would shrink in their sizes and disappear due to higher strain energy\textsuperscript{99}. Therefore, with the purging of water vapor into the growth chamber, the empty areas on the surface of the substrate (the empty areas between the catalysts particles) would be occupied by the hydroxyl functional group; in which restricts the movement of catalyst particles from diffusing, and thus the ripening rate reduces whereby the life of the catalysts extends. The similar carpet height of the VACNT could be explained by the mechanical drag force that was applied on the parallel...
growing CNT, which is due to interlocking and van der Waals forces\textsuperscript{99}; so when one of the CNT stops growing, the others adjacent would terminate as well, thereby giving a relative homogenous height growth of VACNTs.

2.5.2 Electrochemical characterization

Galvanostatic charge and discharge were applied by two methods. The first one is to deeply discharge and charge the Li-O\textsubscript{2} battery to exhibit the maximum capacity. However, by running full charge and discharges, despite providing extremely high capacity, the Li-O\textsubscript{2} battery lacks the stamina to cycle for more than even five cycles while retaining its capacity.

Figure 2.20 Galvanostatic full discharges without capacity limitation\textsuperscript{82}. 

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The first two initial discharge curves of the Li-O₂ battery indicated a specific capacity of nearly 6000 mAh·g⁻¹, which was close to several reports in the literature\(^{85,100}\). However, the full discharge could result in a capacity loss, which could be seen from the second discharge curve in figure 2.20, where a specific capacity of around 5622 mAh·g⁻¹ was demonstrated. The significant fade away in specific capacity resulted in the change in charge/discharge protocols to the capacity limitation method (safe charge/discharge), where another set of parameters were added in addition to the voltage control.

Figure 2.21 Galvanostatic safe discharges and safe charges with capacity limitation\(^{82}\).
In figure 2.21, the safe discharge and safe charge with capacity limitation was employed. The control in the specific capacity is based on limiting the amount of discharge product of Li$_2$O$_2$ generation during the charge and discharge processes. It was conjectured that the non-conductive Li$_2$O$_2$ discharge product coating on the cathode electrode will increase the charge over-potential, and thus result in the degradation of both the solvent and electrolyte as the voltage is increased\textsuperscript{101}. According to previous research, the Li$_2$O$_2$ film conductivity is strongly dependent on its thickness, where the critical thickness film is only around 5-10 nm\textsuperscript{102}. The thicker the coated film would result in the mal-conductivity of the cathode material, and thus result in the clogging of the electrode that causes inability to perform further electrochemical reactions. As shown in figure 2.21, it can be seen that the Li-O$_2$ battery had been cycled for around 50 rounds at a controlled specific capacity of approximately 1200 mAh·g$^{-1}$. The initial discharge plateau remained at a voltage of about 2.7 V; yet as cycles proceed, the discharging voltage decreased gradually to 2.5 V at the 40$^{th}$ cycle. The charging process exhibits a first charging plateau around 3.6 V; but as the charge cycle continues, a plateau of 3.8 V was achieved at the 40$^{th}$ cycle. The charge and discharge could continue on to slightly more than 50 cycles. However, as seen from figure 2.21, sluggishness and shakiness from both the charge and discharge curves could be observed. The sluggishness and shakiness of the discharge or charge curves indicate the breaking down of the Li-O$_2$ battery.

2.5.3 Identification of discharge products

In order to identify the discharge products of the Li-O$_2$ battery, four different types of galvanostatic charge and discharge protocols were utilized to contrast the discharge products that are deposited on the surface of the electrode. Safe charge and safe discharge
are the terms used when the battery is charge or discharged at a controlled specific capacity, in this case, the specific capacity is controlled at 1200 mAh·g⁻¹. Full charge and discharge protocols are used to explain the phenomenon when the battery were charged up to the maximum set voltage of 4.25 V or discharged to the minimum set voltage of 2.25 V, respectively; without the specific capacity control.

![X-ray diffraction spectra for four different charge/discharge protocols](image)

Figure 2.22 X-ray diffraction spectra for four different charge/discharge protocols.\(^8\)

In figure 2.22, the X-ray diffraction spectra (XRD) were obtained for the four different charge and discharge protocols. The background in the figure is a cathode that has yet to be charge or discharged. The peaks at 44° and 52° belong to the background peaks. It could be seen from the full discharge protocol that at 2θ = 33°, 35°, and 58°, three
strong intensity peaks could be observed\textsuperscript{103-104}. These peaks are identified as the Li\textsubscript{2}O\textsubscript{2} peaks. While in full charged spectrum, no peaks could be identified except for the background. This indicates that the Li\textsubscript{2}O\textsubscript{2} crystals are removed and dissociated upon charging; therefore the discharge product characteristic peaks could not be observed. In the safe discharge, the intensities of the Li\textsubscript{2}O\textsubscript{2} peaks are weak, barely visible; suggesting that the Li-O\textsubscript{2} battery has good reversibility without accumulating thick layer of Li\textsubscript{2}O\textsubscript{2}. The discharge products were removed upon safe charging, where it is exhibiting very similar curve behavior as the full discharged protocol. The use of the XRD validated the formation of the Li\textsubscript{2}O\textsubscript{2} during the discharge process. In addition, the differences in the spectra indicated that during safe discharge procedure, the amount of discharge products deposited on the surface of the cathode was significantly less compared to that on the full discharged cathode.

Figure 2.23 Raman spectra for four different charge/discharge protocols\textsuperscript{82}.  

\textsuperscript{51}
Another characterization method other than XRD was utilized to characterize the Li$_2$O$_2$ crystal formation on the surface of the cathode electrode. Since the Li-O$_2$ battery was not solvent treated and cleaned, so after heating up the electrode, there should be only LiTFSI salt and the reacted products on the electrode. Hence, a LiTFSI salt reference was taken to compare with other spectra. From all four samples, it could be clearly seen that the existence of LiTFSI salt was still observable. Similar to the XRD shown in figure 2.22, the full discharge procedure exhibited a strong peak at the Li$_2$O$_2$ shift region, which is ranging from approximately 780-808 cm$^{-1}$. However, the region for the safe discharge could not be observed very clearly, which could be explained that a very thin layer of Li$_2$O$_2$ was deposited on the cathode, which could not generate peaks strong enough to be detected by Raman. In both the safe charged and full charged cathode material, there is no Li$_2$O$_2$ intensity peak, suggesting the complete removal of the discharge product during the charging step. In all of the cathode specimens, side-reaction discharge products of lithium carbonate (Li$_2$CO$_3$)$^{92}$ could not be detected or even observed; indicating that the NMP-based electrolyte did in fact suppress the development of carbonate-based byproducts under the test conditions. The Li$_2$CO$_3$ is an undesired discharge that is difficult to reverse; it would require much higher voltage charge over-potential to dissociate once it is formed. However, under higher voltage conditions, the cathode or the electrolyte could deteriorate due to instability. In the Raman spectra, it could be seen that the Li$_2$CO$_3$ could not be identified as well on any of those charge/discharge protocols.
Figure 2.24 Two ways the Li$_2$O$_2$ discharge product could disable the functioning of the VACNT.

In figure 2.24, a pictorial demonstration of how the discharge product could disable the VACNTs from working. The first way is when the Li$_2$O$_2$ grows too thick, when the discharge product goes beyond maximum 10 nm, the VACNT would be insulated and not be able to transfer the electrons to the reaction sites. Once the electrons are hindered from moving to the surface reaction sites, the three phase boundary would fail and thus result in the incomplete of the reaction, which ultimately causes the failure of the Li-O$_2$ battery. On the other hand, even if the thickness of the coated discharge products is controlled, the surface of the VACNTs could be blocked due to the connection of Li$_2$O$_2$ crystals from one tube to another tube; therefore, preventing the penetration of the reactants in reaching the
three phase boundary. Eventually, the Li-O\textsubscript{2} would fail as well due to the accessibility to reaction active sites.

Figure 2.25 SEM images of (a) and (c) charged cathode; (b) and (d) discharged cathode\textsuperscript{82}.

From figure 2.25, the images of the cathode electrode after full charge and full discharge were shown. It could be seen from figure 2.25a and figure 2.25c that the fully charged cathode electrode has a relatively clean surface compared to the ones exhibited
from figure 2.25b and figure 2.25d. Tiny crystal-like particles could be observed on the surface of the discharged electrode, which could be attributed to the Li$_2$O$_2$ discharge products. Therefore, the SEM images could be some evidences showing the possible removal of the discharge products on the surface of cathode electrode; demonstrating the reversibility of the Li-O$_2$ battery.

2.6 Conclusions

It was demonstrated that the utilization of the free-standing, binder-free VACNT cathode electrode and the integration of NMP as the solvent of the electrolyte could provide better performances in the Li-O$_2$ battery. The battery could achieve a capacity of approximately 1200 mAh·g$^{-1}$ at a current density of 250 mA·g$^{-1}$ for nearly 50 cycles before degrading. When the Li-O$_2$ battery was fully discharged, it could reach a capacity of around 6000 mAh·g$^{-1}$. Subsequent characterizations were conducted to demonstrate the formation of the reversible Li$_2$O$_2$ discharge products excluding possible formation of irreversible Li$_2$CO$_3$. The Li-O$_2$ battery was enabled to provide better cycle stability and the generation of reversible discharge product due to the utilization of superoxide-resistive solvent – NMP. The use of VACNT also provided much higher surface area for reaction sites and fewer defects for that could induce by-product reactions. This work suggests that in order to develop reversible Li-O$_2$ batteries, it is necessary to take the factors of - the stability of the electrode; the solvent; and the electrochemical reaction dynamics into account.
CHAPTER III
A NITROGEN DOPED CARBONIZED METAL-ORGANIC FRAMEWORK FOR HIGH STABILITY ROOM TEMPERATURE SODIUM-SULFUR BATTERIES

3.1 Introduction of metal organic framework

Metal-organic framework (MOF), or porous coordination polymer (PCP), is a type of crystalline material that possesses coordination bonds between transition-metal cations and organic linkers. Therefore, with the possession of both inorganic and organic parts, the hybrid MOF acts as a bridge connecting the gap between pure organic and inorganic materials. One of the first MOF structures was developed by Yaghi and Li in the year of 1995\textsuperscript{105}, ever since, the field of MOF has flourished and attracted many researchers due to its unique structure, versatile pore size tuning capability, and the final utilization in various applications. The material could be tuned to provide extremely high porosity up to 90% free volume with ultrahigh surface areas that could reach 6000 m\textsuperscript{2}\cdot g\textsuperscript{-1} and even beyond\textsuperscript{106}; typical surface area of these MOFs range from 1000 to 10,000 m\textsuperscript{2}\cdot g\textsuperscript{-1}, which exceeds the conventional porous materials such as carbons and zeolites\textsuperscript{107}. With the coupling of high porosity and surface area, it makes this unique type of structure very appealing to different types of applications including the energy storage devices.

The MOF is synthesized by the combination of two components – a metal ion or cluster, and an organic linker. The possibility of final MOF product is essentially endless.
since there are so many different selections of metal part and especially the organic linker part; with the permutation of these two types of materials, there could be tens of thousands of formulations, each possibly yielding a different MOF with different properties. The covalent coordination links of these MOFs could form one-dimensional, two-dimensional or three-dimensional structural frameworks. The unique configuration and topology of this material have, especially, induced researchers from the field of the electrochemical energy storage devices to use the MOFs as sacrificial templates to produce ordered nano-structure with high surface area\textsuperscript{108}.

Zeolitic imidazole framework (ZIF) is a sub-family of the MOFs, which has the following secondary building units:

\[
M\text{−Im−M}
\]

where the M is the Zn and Co cation, and the Im stands for the imidazolate linker. This ZIF structure obtained its named due to the similarity in the aluminosilicate zeolites (Si-O-Si), where the Zn\textsuperscript{2+} ions and the imidazolate anion form bonding similar to the silicon and oxygen in zeolites, with a bonding angle of \(\sim145^\circ\)\textsuperscript{109-110}. However, as of 2010, there are more than 105 topologies of ZIF being discovered\textsuperscript{111}, many of the ZIFs do not strictly follow the bonding angle yet still being categorized into the ZIF sub-section. The ZIF structure is advantageous due to the combination of appealing properties from both the MOFs and the zeolites, where the ZIF structure exhibits ultrahigh surface area, unimodal micropores, high crystallinities, high functionalities, excellent thermal stability, and exceptional chemical stability\textsuperscript{112}, making the ZIF a great candidate in many end-use applications, especially in catalysis.
Amongst the ZIF family, the ZIF-8 structure is the most widely recognized and studied due to its stability and flexible framework, the flexibility is resulting from the thermal rotation of the methylimidazole linkers\textsuperscript{113}. The ZIF-8 structure has a \textit{sod (sodalite)} topology (shown in figure 3.1), with four and six member ring of ZnN\textsubscript{4} clusters with internal cavities\textsuperscript{114}.

![Figure 3.1 The topological illustration of the ZIF-8 structure, with the center being the metal ion and the surrounding being the imidazolate ion linkers.](image)

The ZIF-8 is greatly studied and its properties demonstrate that the crystals could be put into good use. As shown in table 3.1, it could be seen that the pore size and the channel aperture is in the nano-meter scale range; while exhibiting high surface area and exceptional thermal and chemical stability.
<table>
<thead>
<tr>
<th><strong>Property</strong></th>
<th><strong>Value [Units]</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size diameter</td>
<td>11.6 [Å]</td>
</tr>
<tr>
<td>Channel aperture size</td>
<td>3.4 [Å]</td>
</tr>
<tr>
<td>Surface area (Langmuir)</td>
<td>1810 [m²·g⁻¹]</td>
</tr>
<tr>
<td>Surface area (BET)</td>
<td>1630 [m²·g⁻¹]</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>~500 [°C]</td>
</tr>
<tr>
<td>Chemical stability*</td>
<td>Boiling benzene, Methanol, Water, Aqueous sodium hydroxide</td>
</tr>
</tbody>
</table>

*The ZIF-8 crystals were suspended in selected solvents and conditions that reflect extreme parameters from typical industrial processes.

3.2 Introduction of sodium-sulfur battery

Similar to the Li-O₂ battery system, the sodium-sulfur (Na-S) battery system is also considered as one of the next-generation advanced electrochemical energy storage systems. The energy density of the Na-S battery is less than that of the Li-O₂ battery; however, still significantly larger than that of the currently prevailing Li-ion battery. As shown in Chapter II, figure 2.9 exhibited different capacities from various battery systems; the theoretical capacity of the Na-S battery is still at least three to five times larger than the Li-ion battery. The sulfur can theoretically take in two electrons per atom, which provides a cathode capacity of 1675 mAh·g⁻¹ and also being extremely abundant and environmental friendly, making it desirable for energy storage in both economical and environmental perspectives. On the other side of the battery, the sodium metal is significantly cheaper than that of lithium. It was calculated that based on the abundance of sodium resources, the price of the
sodium is only $1/25^{th}$ that of lithium$^{115}$. Therefore, even if the theoretical energy density of the Na-S battery is lower than the Li-S battery, the energy cost per kW·h$^{-1}$ is more favorable for the Na-S battery systems, with better cost-performance of 10 $ energy cost per kW·h$^{-1}$; in comparison to the 16.4$ for the Li-S batteries. (Shown in figure 3.2)

![Figure 3.2 The energy cost of the LiCo$_2$O/graphite, Li-S, and Na-S battery systems$^{115}$.](image)

In fact, Na-S batteries were already being commercialized and used as smart energy grid storages. The Na-S battery was first released by Ford Motor Company in the year 1996 and remained as one of the most promising candidate to be developed since the 1980s$^{116}$. However, the Na-S battery that was implemented in the smart grid system needs to be operated at an elevated temperature. The operation temperatures for the system are at the range from 300 - 350 °C, so that the electrode materials are sustained at the molten state. Keeping the electrodes at a molten state enables the reduction of resistance of the sodium
ions passing through a solid electrolyte membrane\textsuperscript{117}. Even though under higher temperatures the mobility and kinetics of the materials are greatly enhanced, it is considered as a major drawback. In order to maintain the system at an elevated temperature, extra energy would be needed; thus, in terms of the energy efficiency perspective, it is unfavorable. Another issue that must be addressed is the safety. Since the sulfur and sodium under the mentioned temperature is at a liquid state, corrosion (resulting from the sodium polysulfides, which is highly corrosive by nature) and potential explosion could arise\textsuperscript{118}. An incident regarding the Na-S grid plant occurred in September 2011 at Tsukuba Japan, where the NGK-manufactured (NGK Insulator, Ltd.) NAS batteries caught fire during the operation of the storage plant. Therefore, the risk of running the Na-S battery at elevated temperature is high despite the maturity in the technology and the additional preventative installations surrounding the battery systems. Moreover, the high temperature Na-S batteries could only be utilized in smart grid applications; applications including EVs and portable electronics that surround our daily lives would need to be at room temperature. Therefore, the development of a room temperature Na-S battery could make it more viable for a larger range of applications.

Understanding the potential hazard that could be caused by the Na-S battery under high temperature conditions, lending from the past research experiences and concepts with the lithium-sulfur battery (Li-S battery) while combining the traditional high temperature Na-S batteries, room temperature sodium-sulfur battery (RT-Na-S) batteries have recently regained the attention in the field of electrochemical energy storage due to several reports\textsuperscript{119-127} regarding successful reversible cycles of high specific capacities.
3.2.1 Mechanism of the sodium sulfur battery

The Na-S battery is essentially akin to the Li-S battery, where the only difference is at the metal-ion. According to several literature surveys, the Na-S battery mechanism is believed to be similar to that of Li-S battery. Therefore, in the following paragraphs, the general battery mechanism concepts would be taken from various Li-S literatures, yet converting the lithium ion part to sodium ion.

Figure 3.3 Basic charge and discharge of a sodium-sulfur battery.
The Na-S battery, analogous to other advanced electrochemical energy storage devices, has different systems that could yield different type of mechanistic routes due to the type of electrolyte used. In the following sections, only the non-aqueous or aprotic electrolyte would be discussed.

During the discharge of the battery, the reactions occur:

It is much simpler at the anode electrode,

\[ \text{Na} (s) \rightarrow \text{Na}^+ + e^- \]  

(3.2)

where the sodium electrode is dissociated into a sodium ion and the electron went through the external circuit to do work, and eventually returned to the other side of the battery to complete the reaction.

At the cathode electrode,

\[ 2\text{Na}^+ + n\text{S} + 2e^- \rightarrow \text{Na}_2\text{S}_n \]  

(3.3)

where equation (3.3) is a simplified general reaction. The sodium ions migrated through the electrolyte layer and then pass the diffusion layer to reach the sulfur within the catalyst matrix. The sodium ions would react with the sulfur, typically a cyclo-\(S_8\) ring, and form the discharge product sodium polysulfide while combining with the electrons that passed through the external circuit. Generally, the reaction of the sodium ions with the sulfur to form sodium polysulfides is a step-wise reaction process.

\[ 2\text{Na}^+ + \text{S}_{8(s)} + 2e^- \rightarrow \text{Na}_2\text{S}_{8(l)} \]  

(3.4)

\[ 2\text{Na}^+ + \text{Na}_2\text{S}_{8(l)} + 2e^- \rightarrow \text{Na}_2\text{S}_{6(l)} \]  

(3.5)

\[ 2\text{Na}^+ + \text{Na}_2\text{S}_{6(l)} + 2e^- \rightarrow \text{Na}_2\text{S}_{4(l)} \]  

(3.6)
\[
\text{Na}^+ + \text{Na}_2\text{S}_4(\text{i}) + e^- \rightarrow \text{Na}_2\text{S}_3(\text{s}) \quad (3.7-1)
\]

\[
2\text{Na}^+ + \text{Na}_2\text{S}_4(\text{i}) + 2e^- \rightarrow \text{Na}_2\text{S}_2(\text{s}) \quad (3.7-2)
\]

\[
\text{Na}^+ + \text{Na}_2\text{S}_2(\text{s}) + e^- \rightarrow \text{Na}_2\text{S}(\text{s}) \quad (3.8)
\]

Figure 3.4 Typical discharge and charge curve of a conventional sodium-sulfur battery with aprotic electrolyte. The sulfur undergoes a series of structural changes as the reaction moves forward.

Figure 3.4 exhibits the charge and discharge curves of the Na-S battery. It must be noted that the curves are not drawn accordingly to a particular Na-S system; it is only used as a generic illustration to provide better understanding regarding the charge and discharge protocol. Commencing from the discharge curve, the reaction initiates with the cyclo-sulfur ring, where it is in the insoluble region. The cyclo-sulfur would react with the sodium ions...
that migrated from the anode and form the soluble discharge products of sodium polysulfide. The long chain sodium polysulfide (Na$_2$S$_x$, where $4 \leq x \leq 8$) are typically soluble in the aprotic electrolyte after the ring-opening reaction with the cyclo-sulfur. The sodium polysulfide would further react with the sodium ions step-wisely to form shorter chain polysulfide (Na$_2$S$_y$, where $1 \leq y \leq 3$), which are insoluble for most of the aprotic electrolyte systems; however, otherwise in some reported aqueous system$^{128}$. The series of equations of (3.4), (3.5), (3.6), and (3.7-2) exhibited reactions with the addition of two sodium ions to provide the next-stage discharge products. However, the existence of other intermediate sodium polysulfides is still possible. Intermediate discharge products including Na$_2$S$_7$ and Na$_2$S$_5$ are also detected but less common. The final discharge product ends at the Na$_2$S when fully discharged.

When the Na-S battery is under charging protocol, ideally the discharge products would follow the same procedure in reverse to reduce the sulfur back to the solid state cyclo-sulfur ring. The dissociation of the sodium polysulfides would occur upon an input of energy while releasing the sodium ions back to the anode electrode as the shorter chains of sulfides would merge together; eventually restoring the cyclo-sulfur ring.

3.2.2 Challenges of the sodium-sulfur battery

Following up from the previous mechanism section of the Na-S battery, the sodium polysulfide is supposed to ideally restore back to its cyclo-sulfur ring formation. However, ideal cases never happen. This section would address the three main challenges for the sulfur-based next generation batteries. The three main challenges of a sodium-sulfur battery are as following$^{129}$. 

65
1. The conductivity of the sulfur cathode material is extremely poor, only exhibiting an electrical conductivity of around \(1 \times 10^{30} \Omega\).  

2. Huge volume change of at least 80% expansion occurs as the electrochemical reactions proceeds, in which could induce adverse structural and morphological changes.  

3. Undesired polysulfide shuttling phenomenon during charge and discharge protocol, where unfavorable reaction could occur at the electrode causing infinite charging.  

The first issue could be simply resolved with addition of conducting agents including carbon black, CNTs, graphene, conducting polymers etc. to enhance the conductivity of the sulfur. The second issue could be addressed by employing a sturdier structure as the cathode to trap the sulfur, or possibly a flexible structure to accommodate the severe volume change. It was reported that with a yolk-shell morphology (instead of having the sulfur being fully encapsulated by a conducting structure – or also known as the core-shell, the yolk-shell morphology only fills up the pores partially, leaving space for the sulfur to expand so that it would not pulverize the external structure) could greatly reduce the adverse structural damage due to volume expansion. The method is shown in figure 3.5, from the top path, the sulfur would just expand and polysulfide would move around freely without restriction. The core-shell morphology would pulverize due to the expansion from the conversion of sulfur to sodium polysulfide. The final pictorial illustration shows the yolk-shell, where the limited amount of initial sulfur expands but not enough to break the shell; in addition, the polysulfide is also entrapped within the shell.
The third issue is the polysulfide shuttling phenomenon, where it is mainly due to the higher-order soluble polysulfide (the longer chain polysulfide) penetrating through the separator of the Na-S battery to the sodium metal electrode. The movement of these higher-order soluble polysulfides would react at the sodium metal electrode and be reduced to form lower-order polysulfides (the insoluble shorter chain polysulfide). As the concentration of these lower-order polysulfides increases, these lower-order polysulfides would diffuse to the other side (the cathode electrode) and then be oxidized back to higher-order polysulfides; which causes the loss of the sodium active material due to deposition of lower-order polysulfides. The phenomenon would result in low Coulombic efficiency, low use of the sulfur at the cathode electrode, and severe degradation of the battery which is reflected on the cycle stability\textsuperscript{133}. The third issue is the major problem that must be
addressed since the formation of the polysulfide is inevitable. The polysulfide would have to be separated from the sodium metal anode part, so that it would not result in the deterioration of the Na-S battery. Moreover, the liquid flowing nature of the polysulfide would migrate freely within in the electrolyte, so it is also necessary to entrap the discharge product polysulfide at the cathode side; in which the electrons could conduct through the catalyst matrix to react with the polysulfide (if the polysulfide is not near a conductive catalyst, the electrons would not be able to reach them and thus electrochemical reactions would not be able to occur).

3.3 Experimental

The following subsections would be on the preparation and characterization of the active and then the subsequent testing of the Na-S battery.

3.3.1 Materials and characterizations

The following chemicals were utilized to synthesize the ZIF-8 crystals and to formulate the electrolyte as received without further purification or treatment: zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, 98%, STREM CHEMICAL), 2-methylimidazole (C$_4$H$_6$N$_2$, 97%, Alfa Aesar), methanol (>99.8%, Sigma-Aldrich), hydrochloric acid (HCl, ACS GR, EMD Millipore), sublimed sulfur (S, 99.5%, Alfa Aesar), polyvinylidene fluoride (PVDF, M$_w$ = 530 000 g·mol$^{-1}$,Scientific Polymer Products Inc.), carbon black (Super P, Timcal), N-methyl-2-pyrrolidone (NMP, 99.5% EMD Millipore), sodium perchlorate (NaClO$_4$, 98%, Sigma Aldrich), and tetraethylene glycol dimethyl ether (TEGDME, 99%, Acros Organics)
SEM images and their energy dispersive X-ray (EDS or EDAX) mapping were obtained by using a JEOL-7401 field emission scanning electron microscope. TEM images were taken by the use of JEOL JSM-1230 with an accelerating voltage of 120kV. High-resolution TEM (HRTEM) and their subsequent EDS mapping were obtained by using a Tecnai G2 F20 TEM, which was equipped with an EDAX SUTW (super ultrathin window) from FEI; the accelerating voltage for the HRTEM was 200kV. Surface area characterizations were done after the treatment of the powder samples. The powder was degassed for 15 hours at 110 °C (Micromeritics VacPrep 061). N₂ adsorption-desorption isotherms were collected with the assistance of a Micromeritics Tristar II instrument, where the specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. XRD patterns were measured by a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation (λ = 1.604Å). TGA analyses were taken by a Q500 (TA Instruments) under N₂ environment with a heating rate of 5 °C per minute. X-ray photoelectron spectroscopy (XPS) was performed on a PHI5000 Versa Probe II Scanning XPS Microprobe (ULVAC-PHI, Inc.). The survey and high-resolution spectra associated with Cls and N1s were obtained by a 0.05 eV step size and a passing energy of 11.75 eV. The scans were recorded at a takeoff angle of 45°. Raman spectroscopy was conducted by using a HORIBA LabRAM HR High-resolution Raman Microscope to identify the characteristic peaks of the N-doped carbon. The laser that was applied to the sample for the Raman spectrum was at 523 nm. Galvanostatic charge and discharge characterizations were performed on an 8 Channel Battery Analyzer BST-8A (1mA) from MTi with a chemical window ranging from 1.2 V to 2.7 V (vs. Na/Na⁺). Cyclic voltammetry (CV) was carried out by using an electrochemical workstation (CHI608E) with a scan rate of 0.5 mV·s⁻¹. Electrochemical
impedance spectroscopy (EIS) was conducted using the same CHI608E electrochemical station with 5 mV perturbation voltage amplitude ranging from 100 kHz to 0.1 Hz.

3.3.2 Synthesis of the carbon-sulfur composite cathode

![Scheme 3.1 The fabrication scheme of the cZIF-8/S composite.](image)

ZIF-8 crystals were synthesized by reported literature. In a typical fabrication protocol, 810 mg of Zn(NO$_3$)$_2$·6H$_2$O was dissolved in a beaker with 40 mL of MeOH, and 526 mg of 2-MeIm was dissolved in another beaker with 40 mL of MeOH. Both of these two mixtures were vigorously mixed under stirring separately prior to merging these two mixtures together. The combined mixture was then left at room temperature overnight without stirring to yield the ZIF-8 nano-crystals. The resulting white powder was then collected, washed with methanol several times using centrifugation and eventually dried at
100 °C to remove the residue solvent within. The structure of the collected ZIF-8 resembles the one shown in scheme 3.1.

The as-synthesized dried ZIF-8 white powdery crystals were then collected and then placed in a ceramic boat prior to placing it in a tube furnace. The tube furnace was purged with argon gas for 30 minutes first before initiating the carbonization protocol. The purging of the argon is to ensure an inert environment in the tube. The ZIF-8 crystals were then thermally converted to carbonized ZIF-8 (denoted as cZIF-8) under Ar flow at a temperature of 800 °C for 2 hours with a heating rate of 2 °C per minute. The cZIF-8 was then allowed to cool down with the continuation of the flowing of Ar gas. The collected cZIF-8 was collected from the ceramic boat and placed in a plastic centrifugal tube simultaneously with HCl. The HCl functions as an etchant to remove the residual Zn species. Further addition of de-ionized water was to wash away the traces of HCl that is remained in the cZIF-8 by centrifugation for several times. After ensuring the removal of the HCl, the etched cZIF-8 was dried at 100 °C in an oven to obtain the final product for the preparation of the carbon-sulfur composite.

The treated cZIF-8 was degassed in an oven overnight to remove moisture prior to mixing with sublimed sulfur. The sulfur and the cZIF-8 were mixed together at a weight ratio of 1:1 with pestle and mortar in an Ar filled glovebox (Labstar, MBraun) at O₂ and H₂O levels < 0.5 ppm. The mixed sulfur and cZIF-8 composite product was then placed in a sealed vial in the glovebox, and then heated up to 155 °C at a heating rate of 1 °C per minute in a heating chamber. The composite material was maintained at 155 °C for 12 hours to acquire the final cZIF-8/S composite material.
3.3.3 Fabrication of the sodium-sulfur battery

The cZIF-8/S composite was mixed with carbon black and PVDF at weight ratio of 7:2:1, respectively. The powder mixture was first mixed thoroughly before the addition of NMP. Vigorous mixing by using pestle and mortar was applied in order to ensure homogenous thick slurry. The slurry was then casted on an aluminum foil current collector using a doctor blade. After leaving the slurry casted aluminum foil in ambient air for one or two hours, it is then placed in an oven at 50 °C overnight to remove the NMP. 2032 coin cells were utilized for the fabrication of the Na-S half cells. The fabrication of the cells was conducted in the same Ar glovebox. Sodium metal was employed as the counter electrode, Celgard® 3501 and GF/B glass fiber (Whatmann™) as the separator with 1M of NaClO₄ in TEGDME as the electrolyte. The cathode was punched into 5/16” circular discs; each punched electrode typically has a mass loading of approximately 0.7 - 0.9 mg·cm⁻².

3.4 Results and discussions

The following subsections would be focusing on the obtained results and discussions on the Na-S battery.

3.4.1 Identification of the carbon-sulfur composite

The ZIF-8 crystals were synthesized successfully, which could be identified by using the XRD shown in figure 3.6. It could be seen that the as-synthesized ZIF-8 crystals are coherent with the peaks that came from the simulated.
Figure 3.6 XRD patterns of the simulated ZIF-8 and as synthesized ZIF-8 structures.

Figure 3.7 The SEM images of (a) ZIF-8 and (b) cZIF-8.
The SEM images of the ZIF-8 and the cZIF-8 are shown in figure 3.7, where it could be seen that the morphological structure does not change drastically upon carbonization.

![Figure 3.8 The TEM images of (a) ZIF-8 and (b) cZIF-8.](image)

Similarly, from figure 3.8, it could be seen that the ZIF-8 crystals retain the morphological structure after carbonization under TEM characterizations. In fact, the structure actually became more distinct, sharp and slightly smaller after heat treatment. The reason to that is because the cZIF-8 was graphitized during thermal annealing, in which provided higher electrical conductivity and thus resulted in the decrease in charging phenomenon in the electron micrographs. The structure of the cZIF-8 remained as the standard rhombic dodecahedral morphology yet at the nanometer range. Moreover, from the TEM images from figure 3.8, the crystals clearly exhibit homogeneous size controls. The crystal sizes could be achieved by controlling and tuning the ratio of the zinc nitrate hexahydrate and 2-methylimidazole; further modifications in size could be accomplished
by attuning the reaction conditions of the solvothermal reaction, for instance the temperature and time of reaction etc.

Figure 3.9 (a) High-resolution STEM images of a single cZIF-8 particle, the inset shows the area of the particle where it was enlarged. (b) HAADF STEM images of the single cZIF-8 particle and its EDS elemental analysis.

From figure 3.9a, the cZIF-8 structure was investigated using the HRTEM. The inset on the upper right of the figure 3.9a shows a single cZIF-8 particle under the scale bar of 100 nm. The red square is the enlarged area that is shown for figure 3.9a. The image showed a clear view of the surface morphology. It is worth mentioning that the thickness of the cZIF-8 particle is thinner at the near-edge areas and it could be seen that there is no apparent short-range order in the structure. Moreover, the surface roughness exhibited from the cZIF-8 particle indicated the high porosity property. It was reported that the cZIF-8 has the shown morphology is due to the constitution of graphene sheet assembly\textsuperscript{135}; which means that the cZIF-8 crystal structure was actually composed of graphene stacks into the
rhombic dodecahedral morphology. In figure 3.9b, the elemental distribution and the composition of the cZIF-8 particles were shown – characterized by EDS mapping. The TEM is operated under scanning mode for figure 3.9b. According to the STEM HAADF the distinctive hexagonal structure from the top view is seen; suggesting the structural stability after carbonization. Three selected elements of carbon, nitrogen and oxygen were demonstrated to show homogeneity distribution within the single particle; it could be seen that elemental aggregation or gradient dispersion could not be observed.

![HRTEM-EDS quantification results of existing elements.](image)

Figure 3.10 HRTEM-EDS quantification results of existing elements. The weight percentage quantifications of important elements are as following: C 68.18%, N 9.23%, O 1.34%.
From figure 3.10, the HRTEM-EDS elemental analysis was conducted at several spots from different cZIF-8 samples, weight percentages of the carbon, nitrogen and the oxygen are 68.18%, 9.23% and 1.34%, respectively. These values do not add up to 100% since residue Zn and Cu from the TEM grid could be detected and taken into account. The important result from the HRTEM-EDS is the high nitrogen-doping content, which is around 10 wt%. Further confirmation on the nitrogen doping was also conducted using different characterization methods – XPS and Raman spectroscopy.

Figure 3.11 Survey scan of the cZIF-8. Elemental analysis was conducted on the four elements C, N, O and Zn with atomic ratios of 75%, 18.3%, 4.6% and 1.5%, respectively.
From figure 3.11, the XPS analysis of the cZIF-8 was carried out. The illustration indicated a high N-doping content, along with some other atomic quantitative elemental analysis provided: carbon with 78%, nitrogen with 18.3% and oxygen with 4.6%. A small amount of Zn could be observed with an atomic loading of 1.5%, which could be from the residual trace amount from the precursor material.

Figure 3.12 High-resolution scan from 395 to 404 eV was performed to better understand the binding energy of the nitrogen.
Nitrogen contents provided as stacked columns, where the pyridinic-N, pyrrolic-N and quaternary-N give atomic ratios contribution of 10.2%, 5.4%, and 2.7%, respectively. The total adds up to the overall 18.3%.

Nitrogen-doping content was further examined in figure 3.12. The de-convoluting of the N1s peaks was assigned to three different sub-peaks that are fixed at 398.21 eV, 399.75 eV and 400.79 eV. Each of the sub-peaks corresponds to the pyridinic-N (55.75 atomic %), pyrrolic-N (29.53 atomic %), and the quaternary-N (14.72 atomic %) or also known as the graphitic-N, respectively\textsuperscript{135-136}. In addition, the calculated pyridinic-N, pyrrolic-N and the quaternary-N each contributes 10.2%, 5.4% and 2.7%, respectively to the total 18.3% of nitrogen doping, which is shown in figure 3.13 as stacked columns.
The Raman spectra were used to characterize the difference between the S, cZIF-8, cZIF-8/S composite and ZIF-8. It could be seen that the ZIF-8 has various peaks especially from the range of 500-1500 cm\(^{-1}\). The pure sulfur component also showed several strong intensity peaks at spectrum below 500 cm\(^{-1}\). After thermal carbonization of the ZIF-8 crystals, the cZIF-8 exhibited the characteristic peaks of the carbon showing as the G peak, D peak and 2D peak, which was already discussed in Chapter II. The appearance of carbon characteristic peaks and the disappearance of the ZIF-8 peaks in the cZIF-8 demonstrated that the cZIF-8 was successfully converted into carbonized materials. The high intensity at the D peak area could be due to the imperfections such as substitution.

Figure 3.14 Comparison of the Raman spectra between S, cZIF-8, cZIF-8/S composite and ZIF-8. The C-N bond is designated at 2217 cm\(^{-1}\).
of nitrogen heteroatoms within the cZIF-8 structure\textsuperscript{137}. Since it was characterized by the XPS and the TEM EDS mapping that there is nitrogen-doped content within the carbon matrix, the utilization of the Raman spectroscopy further provided qualitative evidence for the nitrogen-doping. From figure 3.14, a peak at 2217 cm\textsuperscript{-1}, which is relatively less intense compared to the D and G peaks, is attributed to the C-N bond. The peak is only observable only when the nitrogen doping level is relatively high\textsuperscript{137}. In addition, another piece of information that could be extracted out from the Raman spectrum is the intensity ratio between the D and G peak, denoted as (I\textsubscript{D}/I\textsubscript{G}). The parameter provides information on the quantification of disorder\textsuperscript{138}. The maximum intensity peak was calculated to be approximately 1.11, suggesting the nanoporous cZIF-8 structure possessed both disordered and graphitic structures\textsuperscript{139}. The higher value the I\textsubscript{D}/I\textsubscript{G} ratio results in the higher amount of N-doping within the nanoporous cZIF-8 structure, since the nitrogen heteroatom is considered as a substitution defect that disrupts the graphitic carbon configuration.
Figure 3.15 Comparison of the powder x-ray diffraction between S, cZIF-8, cZIF-8/S composite and ZIF-8. The overlapping peaks of cZIF8/S from S and cZIF-8 indicated successful melt-infiltration of the composite material.

Four different powder XRD patterns are shown in figure 3.15. The sulfur and the ZIF-8 are used as the reference to compare with cZIF-8 and cZIF-8/S. In the cZIF-8, two peaks could be observed at $2\theta = 25^\circ$ and $45^\circ$. The broad peak for cZIF-8 that appears at $25^\circ$ is a typical (002) graphite carbon nanosheet interlayer peak. The weaker and less observable peak at $45^\circ$ is the (101), which is related to the hexagonal lattice in single-layer graphene. The two peaks indicate the complete carbonization of the ZIF-8 material. For cZIF-8/S composite, the peaks are essentially an overlap between the sulfur and the cZIF-8 peaks.
Figure 3.16 The BET results between cZIF-8 and cZIF-8/S. No volume absorbed was observed for the cZIF-8/S, indicating the complete filling of the sulfur into the cZIF-8.

Figure 3.17 The BET result of ZIF-8.
Figure 3.16 and figure 3.17 are obtained from nitrogen adsorption/desorption isotherm at 77 K. These two figures are to investigate the specific surface areas of the materials. The ZIF-8, shown in figure 3.17, provides a Brunauer-Emmett-Teller (BET) specific surface area of around 1213 m²·g⁻¹, whereas the cZIF-8 exhibits a specific surface area of 627 m²·g⁻¹. The cZIF-8 appeared to be the type I isotherms, which is typical for microporous materials. In figure 3.16, it is shown that the cZIF-8/S does not have any volume absorbed, indicating that the pores are completely filled with sulfur.

![Figure 3.18](image)

**Figure 3.18** The pore size distribution for (a) ZIF-8 and (b) cZIF-8.

The pore size distributions of the ZIF-8 and cZIF/8 were determined by the NLDFT model using CO₂ as the absorbent. The ZIF-8 in figure 3.18 shows a homogeneous pore diameter of approximately 1 nm, whereas in cZIF-8 the pore diameter is rather larger in the range. The ZIF-8 with homogeneous sub-nanometer pores indicated the high specific surface area. The larger pore distribution for the cZIF-8 could be ascribed to the thermal
annealing procedure, where several parts of the structure could have been altered due to collapse or shrinkage of pores; therefore, resulting in the decrease in specific surface area.

Figure 3.19 Thermogravimetric analysis of the sulfur, cZIF-8 and cZIF-8/S.

Thermogravimetric analysis (TGA) was carried out to determine the amount of sulfur that was melt-infiltrated into the cZIF-8. The sulfur has a sublimation point at 300 °C. So at 300 °C, the sulfur should have been completely removed. The cZIF-8 shows very little mass loss even up to 600 °C. The slight mass loss could be due to the high amount of N-doping, where the carbon matrix is not as resistant towards thermal treatments compared to its pure carbon counterparts. The cZIF-8/S composite shows two steps deterioration. The first slope could be observed around 250 – 300 °C, where it is due to the sublimation of the
sulfur that is deposited on the surface of the cZIF-8. The second slope initiated from 300 °C and stabilized at 425 °C. The second slope could be ascribed to the nitrogen-doping; where the nitrogen within the carbon matrix could be an enhancing factor in trapping the sulfur inside the nano-porous carbonaceous matrix. Additionally, there could be a stronger interaction between the sulfur itself with the microporous carbon matrix.  

3.4.2 Electrochemical characterizations

![Graph showing specific capacities and coulombic efficiency](image)

Figure 3.20 C-rate testing exhibited specific capacities of approximately 1000 mAh·g⁻¹, 850 mAh·g⁻¹, 650 mAh·g⁻¹, 480 mAh·g⁻¹, 220 mAh·g⁻¹, and 850 mAh·g⁻¹ at corresponding current densities of 0.1 C, 0.2 C, 0.5 C, 1.0 C, 2.0 C, and 0.1 C, respectively.
The cZIF-8/S cathode material was installed in the Na-S batteries and tested for their electrochemical performances. The rate performance of the cZIF-8/S electrode is shown in figure 3.20. The chemical window range was set from 1.2 V - 2.7 V, and the open circuit voltage of the battery is typically around 1.9 V - 2.0 V. The initial capacity could reach up to 1650 mAh·g⁻¹, which is in proximity to the theoretical value of sulfur (1675 mAh·g⁻¹). For the rate performance of the battery, each of the protocols was run for 10 cycles prior to the next protocol step. The reversible specific capacities of approximately 1000 mAh·g⁻¹, 850 mAh·g⁻¹, 650 mAh·g⁻¹, 480 mAh·g⁻¹, 220 mAh·g⁻¹, and 850 mAh·g⁻¹ at corresponding current densities of 0.1 C, 0.2 C, 0.5 C, 1.0 C, 2.0 C, and 0.1 C, respectively. The specific capacity decreases as the current densities increases; yet it could be seen that when the current density is returned to 0.1C, the cell is able to return back to provide similar specific capacities at 850 mAh·g⁻¹.

Figure 3.21 Discharge/charge profile of the Na-S cell at different C-rates.
The initial discharge shows an obvious discharge plateau at around 1.6 V, which is assigned to the conversion of the long-chain sodium polysulfide into shorter-chain sodium polysulfide (shown in figure 3.21). The good c-rate performance could be explained by the interconnected microporous/mesoporous hierarchical structures that provided accessible pathways for the sodium ion diffusion. Moreover, the doped nitrogen within the carbon matrices assisted the trapping of the long-chain polysulfide to prevent shuttling through the differences in electrostatic charges between nitrogen doped carbon matrix and long polysulfide chains. The non-trapped sulfur reaction with the sodium ion could only be clearly distinguished in the first initial discharge. Subsequent discharge profiles did not show similar distinctive discharge plateaus as the first one; however, all subsequent discharges have only one sloping region that could be identified, suggesting the confinement of sodium polysulfide within the nanoporous nitrogen-doped cZIF-8.

Figure 3.22 Long discharge of Na-S cell at 0.1 C for 5 cycles and then 0.2 C for the rest of the cycles.
Long cycle galvanostatic discharge and charge were carried out to determine the cycle stability of the Na-S batteries. It could be seen from figure 3.22 that the Na-S batteries have achieved 250 cycles. The first five cycles were running at 0.1 C with subsequent cycles running at 0.2 C. The first five cycles showed a capacity of nearly 1000 mAh·g⁻¹. The cycles at the beginning of 0.2 C exhibited initial capacity of 873 mAh·g⁻¹. After cycling up to the 250th charge/discharge protocol, the battery retained a specific capacity of around 500 mAh·g⁻¹. As mentioned previously, the exceptional cycle stability could be attributed to the nitrogen doping that can have a strong interaction with the long sodium polysulfide chains, therefore preventing the sodium polysulfide from shuttling. Similar heteroatom doping immobilization techniques were reported for the Li-S batteries in preventing the polysulfide shuttling. Additionally, the microporous hierarchical structure of the cZIF-8 also provided a confined space that allowed only the entry of small sulfur molecules (sizes smaller than the S₈ ring) into the carbon, where similar discharge profile curves are observed. Synergy between the high nitrogen doping and the presence of microporous hierarchical structure enable the superior electrochemical performance of the Na-S battery with the cZIF-8/S as the cathode.

3.4.3 Post-electrochemical analysis

After over 100 cycles of galvanostatic charges and discharges, the battery was disassembled and the cathode was taken out for further characterizations. The morphology of the surface of the cathode was the main focus of study in this case to determine and to provide an explanation regarding the cycle stability of the Na-S battery.
Figure 3.23 SEM images of the Na-S battery. (a) and (b) are reference electrode, without undergoing charge or discharge; (c) and (d) are the electrode after cycling for more than 100 cycles.

Figure 3.23a and b are SEM images of the electrode without undergoing charge or discharge. Figure 3.3c and d are SEM images of the electrode that went through 100 cycles. The reference electrode shows homogeneous coating of individual distinctive cZIF-8 particles attached by a binder material and conductive fillers. After cycling for more than 100 cycles, it could be seen that the individual cZIF-8 particles remain intact. The composite cathode did not deteriorate or fail in structure upon long cycling performances.
The phenomenon could provide the reason for the superior cycling performance of the Na-S batteries.

![Figure 3.24 XPS of the Na-S battery after (a) discharge and (b) charge.](image)

XPS spectrum of the sulfur species (S2p) was shown in figure 3.24 for the discharged and the charged electrodes. In figure 3.24a, the discharged cathode has two peaks, whereas in figure 3.24b the charged cathode has only one single peak. The peak illustrated at 160 eV -162 eV is an extra peak that could be assigned to the sodium polysulfide component; in which the sulfide terminal bonding with sodium is 161.5 eV and Na2S is 160.4 eV\(^{149}\). The broad peak that is visible from 164 eV to 168 eV on both figure 3.24ab could be assigned to the active material. The XPS binding energy provided is larger than that of the elemental sulfur (at 164 eV\(^{150}\)); the shift could be due to the higher positivity of the sulfur compound, which could result from the formation of covalently bonded sulfur. Moreover, the nitrogen-doping could also assist the formation of the covalently bonded sulfur. Nitrogen doping was found to enhance the formation of the bonds between sulfur...
atoms and oxygen functional groups on the carbon, which is suggested to play a key role in sulfur immobilization. The nitrogen doping was also reported to provide chemical adsorption of sulfur within the carbon matrix, where a synergistic effect with the microporous framework together to immobilize the sulfur within the space. Therefore, the XPS peak of 166 eV - 170 eV could be due to the formation of sulfur bonding on the oxygen function groups that is on the carbon.

3.5 Conclusion

The microporous nitrogen doped cZIF-8 was synthesized by simply mixing zinc nitrate hexahydrate and 2-methylimidazole solutions, and the directly carbonized in a tube furnace. The cZIF-8/S composite was fabricated by melt-infiltrating sulfur into the cZIF-8, and then subsequently made into Na-S batteries. The cZIF-8/S composite cathode showed good rate performances at different current densities, where specific capacity of 1000 mAh·g⁻¹ could be reach at a rate of 0.1 C. Long charge and discharge showed a specific capacity of 500 mAh·g⁻¹ at 0.2 C at its 250th cycle. The exceptional performances could be ascribed to the synergistic effect of the nano-level dimensions of the carbon hierarchical structure and the relatively high nitrogen doping amount; where they can act together to entrap the sulfur molecules and the subsequent sodium polysulfide inside the carbon matrix. The reversible capacity and the excellent rate performance of the RT-Na-S illustrate the potential use of MOF for advanced electrochemical storage devices. Table 3.2 is the comparison of the cZIF-8/S cathode with the other current state-of-art RT-Na-S batteries.
Table 3.2. Comparison of the Na-S batteries with cathode composition, electrolyte, rate, capacity and cycles.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Cathode Composition</th>
<th>Electrolyte</th>
<th>Rate</th>
<th>Capacity (mA·h·g⁻¹)</th>
<th>Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ryu et al.⁹⁸</td>
<td>S:Carbon:PEO (60:20:20)</td>
<td>1M NaCF₃SO₃ in TEGDME</td>
<td>0.144 mA·cm⁻²</td>
<td>240</td>
<td>10</td>
</tr>
<tr>
<td>Yu et al.¹¹⁰</td>
<td>MWCNT fabric with Na₂S₈ catholyte</td>
<td>1.5M NaClO₄ and 0.3M NaNO₃ in TEGDME</td>
<td>0.1 C</td>
<td>~400</td>
<td>30</td>
</tr>
<tr>
<td>Yu et al.¹²⁰</td>
<td>Na₂S/MWCNT (8:2)</td>
<td>1.5M NaClO₄ and 0.3M NaNO₃ in TEGDME</td>
<td>C/10</td>
<td>560</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C/3</td>
<td>380</td>
<td>50</td>
</tr>
<tr>
<td>Yu et al.¹²¹</td>
<td>CNF/AC Composite/Na₂S₈</td>
<td>1.5M NaClO₄ and 0.2M NaNO₃ in TEGDME</td>
<td>C/5</td>
<td>~550</td>
<td>100</td>
</tr>
<tr>
<td>Xin et al.¹²²</td>
<td>S/(CNT@MPC):Super P:PVDF (8:1:1)</td>
<td>1M NaClO₄ EC/PC (v:v = 1:1)</td>
<td>0.1 C</td>
<td>~1000</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1 C</td>
<td>~600</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 C</td>
<td>~580</td>
<td>200</td>
</tr>
<tr>
<td>Wang et al.¹²³</td>
<td>(S+carbonized PAN composite):acetylene black:PTFE (70:20:10)</td>
<td>1M NaClO₄ in EC/DMC (v:v = 2:1)</td>
<td>0.1 mA·cm⁻²</td>
<td>~500</td>
<td>18</td>
</tr>
<tr>
<td>Kim et al.¹²⁴</td>
<td>S/C(Activated carbon):Super P:PVDF (6:2:2)</td>
<td>1M NaCF₃SO₃ in TEGDME</td>
<td>1/64 C</td>
<td>521</td>
<td>104</td>
</tr>
<tr>
<td>Kim et al.¹²⁶</td>
<td>SPAN webs</td>
<td>1M NaPF₆ in EC/DEC (v:v = 1:1)</td>
<td>0.1 C</td>
<td>266 (gelectrode)</td>
<td>200</td>
</tr>
<tr>
<td>Hwang et al.¹⁸²</td>
<td>c-PANS NF₅:Super P:PVDF (70:15:15)</td>
<td>0.8M NaClO₄ in EC/DEC (v:v = 1:1)</td>
<td>0.22 A·g⁻¹</td>
<td>219 (gelectrode)</td>
<td>&gt;500</td>
</tr>
<tr>
<td>Yu et al.¹²⁷</td>
<td>Na₂S/AC-CNF</td>
<td>1.5M NaClO₄ and 0.2M NaNO₃ in TEGDME</td>
<td>C/5</td>
<td>~600</td>
<td>100</td>
</tr>
<tr>
<td>Bauer et al.¹⁸³</td>
<td>S:Carbon:MWCNT:PTFE (42.5:42.5:12:3)</td>
<td>1M NaClO₄ in TEGDME</td>
<td>0.1 C</td>
<td>350</td>
<td>20</td>
</tr>
<tr>
<td>This Work</td>
<td>cZIF-8/S:Super P:PVDF</td>
<td>1M NaClO₄ in TEGDME</td>
<td>0.1 C</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 C</td>
<td>~850</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 C</td>
<td>~650</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 C</td>
<td>~500</td>
<td>250</td>
</tr>
</tbody>
</table>
CHAPTER IV

ULTRA-LONG CYCLE LIFE ROOM TEMPERATURE SODIUM-SULFUR BATTERIES ENABLED BY HIGHLY DOPED (N,S) NANOPOROUS CARBONS

FOR STATIONARY ENERGY STORAGE

In this chapter, since the same Na-S battery system was utilized, there would be no introduction part for the Na-S battery system. Instead, the introduction would be focused more on the material and the incentive on why the particular system was chosen and studied.

For the Na-S battery, decent specific capacities were reported under a various range of current densities. However, in terms of the cycle stability, or the possible cycle runs that could be achieved, not much has been reported for the Na-S to be operated under room temperature and cycled over 1000 cycles; where the capacity fading issue is still a major problem\(^\text{154}\). In this chapter, a RT-Na-S battery was reported to cycle more than 10,000 cycles. Despite with lower capacity, the battery exhibits good cycle stability with much less degradation.

4.1 Introduction of the ordered mesoporous materials

It is known from previous chapters that the surface area plays a crucial role in the performance of the electrochemical storage devices. Since the first report in 1990 regarding the fabrication of mesoporous silica\(^\text{155-156}\) for high surface areas, many material scientists delved into the development of novel materials in order to fabricate innovative hierarchical
designs for futuristic energy storage devices; since in principle, larger number of interaction sites could be provided with higher surface areas. The previously mentioned nano-materials’ morphology could be controlled to some extent yet the overall structure and porosity were not deliberately manipulated to provide the best architecture for the purpose.

Porous materials, especially the ordered mesoporous materials, have drawn tremendous attention due to the potential practical applications not only limited to the energy storages, but also catalysis, sensors, separation, adsorption and so on\textsuperscript{157}. The pores of the solids could be categorized as given in table 4.1.

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Pore Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropore</td>
<td>&lt; 2 [nm]</td>
</tr>
<tr>
<td>Mesopore</td>
<td>2–50 [nm]</td>
</tr>
<tr>
<td>Macropore</td>
<td>&gt; 50 [nm]</td>
</tr>
</tbody>
</table>

*Definition from International Union of Pure and Applied Chemistry (IUPAC).

It is important to have high surface area, yet the high surface area does not necessarily convert into improved performances if these interfacial reaction sites are not accessible. The distribution of the pores, the sizes of the pores, volume and void spaces provided by the porous material could directly affect the performances of the application\textsuperscript{158}. Moreover, the capability in creating uniformity and orderliness of the abovementioned parameters could lead to exceptional application properties. It was provided that larger pore volumes with better accessibility exhibited promising loading of intermediate species and
also the capability in accommodating expansion/contraction during repeated charge/discharge protocols. Therefore, with more tuned and designed pathways for the reaction species, the mesoporous materials could greatly reduce the transport channeling for ions and electrons, which pose as the major enhancement for energy storage device applications.

There are several methods in the synthesis of mesoporous materials\textsuperscript{159}, shown in figure 4.1.

![Image](https://example.com/image.png)

*Figure 4.1 Various methods in the synthesis of mesoporous materials\textsuperscript{158}.*
In hard-templating method, or also known as nano-casting, mesoporous structures are made from preformed hard templates by filling the precursors into the pores in the template structure initially. Subsequent conversion of the precursor into desired material and then the removal of the template would result in the final hard-templated hierarchical product. Soft-templating method is the utilization of surfactant molecules and guest species co-assembling into ordered meso-structured composites. The removing of the template would provide ordered mesoporous materials with opened pores. The interaction between the surfactant and the guest species is crucial to form the desired hierarchical structures; the method is not restricted to aqueous or aprotic system. The combination of the hard-templating and soft-templating methods could generate sophisticated hierarchical porous materials that could not be achieved by one-step with the previously two mentioned techniques. *In-situ* templating pathway could be formed by using solution phases’ separation, where the solvents themselves act as a template to create mesoporous structures. However, the mesopores that are fabricated are usually disordered and randomly distributed due to the flow nature of the liquid phase. The template free method essentially uses the mesopore voids stem from nanoscale building blocks’ agglomeration. Of all the techniques that were mentioned, the tasks in determining the resulting pore architectures still remain complicated. By the use of reticular chemistry, or coordination chemistry, mesoporous materials could be fabricated with homogeneous porosity and expected structural architecture. The fabrication of ZIF-8 MOF was demonstrated in Chapter III; however, despite the homogeneity of the ZIF-8, the structure is not continuous. The advantages and the disadvantages of the mesoporous materials using different fabrication techniques are listed in table 4.2.
Table 4.2 Comparison in the advantages and the disadvantages of the mesporous materials under different methods of preparation\textsuperscript{158}.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard Templating</td>
<td>• Low sensitive to reaction conditions</td>
<td>• Use of preformed hard templates</td>
<td>Carbons, metal oxides, zeolites, non-oxide ceramics, metals...</td>
</tr>
<tr>
<td></td>
<td>• High quality product</td>
<td>• Time consuming</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Large scale manufacturing</td>
<td>• High cost</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Tunable morphologies</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Ease of process</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High quality product</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Large scale manufacturing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soft Templating</td>
<td>• Controllable pore sizes and structures</td>
<td>• Use of surfactants</td>
<td>Polymer, organosilica, carbon, metals, phosphates, silica, aluminosilicates...</td>
</tr>
<tr>
<td></td>
<td>• Tunable morphologies</td>
<td>• Highly sensitive to reaction conditions</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Ease of process</td>
<td>• Lower crystallinity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High quality product</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Large scale manufacturing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multi-Templating</td>
<td>• Hierarchical porous structure</td>
<td>• Multiple templating</td>
<td>Silica, carbon, metal oxides, zeolites</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• High cost</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Time consuming</td>
<td></td>
</tr>
<tr>
<td>In-situ Templating</td>
<td>• Simple</td>
<td>• Low quality</td>
<td>Silica, carbon, metals, polymers, metal oxides</td>
</tr>
<tr>
<td></td>
<td>• No preformed templates</td>
<td>• Difficult to form ordered structures</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• No surfactants</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Low cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Template-free Packing</td>
<td>• Simple</td>
<td>• Difficult to form ordered structures</td>
<td>Carbon, metal oxides, metal sulfides</td>
</tr>
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4.2 Experimental

The following subsections would be on the experimental methods in the synthesis of the active material and subsequent electrochemical testing.

4.2.1 The synthesis of ordered mesoporous carbon and the N,S-doped hierarchical porous carbons

First, 9.6 g of Pluronic F127 (Sigma Aldrich) was dissolved in 8 g of 0.2M HCl and 24 g of ethanol at a temperature of 45 °C for 2 hours. Then, 12 g of resol solution (50 wt % in ethanol, low molecular phenolic resin and 15 g of tetraethyl orthosilicate (TEOS, Sigma Aldrich) were added into the solution. After stirring for 2 hours at 40 °C, the solution was then casted on a PET film substrate (125 m, Terphane Inc.) by a doctor-blade at a rate of 50 cm·min⁻¹. The film along with the casted slurry was heated up to 50 °C and then equilibrated for 3 hours. Further thermal treatment at 100 °C for 3 hours was applied in order to crosslink the resol. The crosslinked film was subsequently peeled off from the PET substrate and grinded into powder.

Ordered mesoporous carbon (OMC) was synthesized by carbonizing the previously as-prepared grinded powder in a tube furnace (SentroTech Inc.) under continuous N₂ flow at 700 °C at time duration of 90 minutes. Nitrogen and sulfur co-doped hierarchical porous carbon (N,S-HPC) was fabricated by firstly placing the as-prepared grinded powder in the same abovementioned tube furnace under N₂ atmosphere at 350 °C for 90 minutes to undergo calcination process in order to remove the residual surfactants. Then, the powder was mixed and grinded with melamine (Sigma Aldrich) and benzyl disulfide (Sigma Aldrich) at a mass ratio of 1:25:5. The powder was subsequently carbonized in the tube
furnace under with N\textsubscript{2} as a protection gas at 700 °C for 3 hours. The silica within the OMC and N,S-HPC were then etched out by 3M KOH in ethanol/de-ionized water (1:1; v:v%) mixture solution for 4 days while changing the etchant daily. The final etch-treated powder was washed with de-ionized water and then dried in a vacuum oven at 80 °C for 24 hours. The synthesis of the N,S-HPC is shown in scheme 4.1.

Scheme 4.1 The synthetic route for the fabrication of nitrogen, sulfur co-doped hierarchical porous carbon (N,S-HPC).
4.2.2 Fabrication of the composites cathode using ordered mesoporous carbon and nitrogen, sulfur co-doped hierarchical porous carbon

The OMC with sulfur composite (OMC/S) and N,S-HPC with sulfur composite (N,S-HPC/S) cathodes were fabricated by the typical melt-diffusion sulfur impregnation method. The carbon materials of OMC and N,S-HPC were firstly mixed with sublimed sulfur powder at a mass ratio of 1:2 (carbon to sulfur) by ball milling. Then, the mixture was placed in a sealed vial at 1 °C ramping temperature per minute up to 155 °C, and equilibrated at that temperature for 12 hours duration in order to diffuse sulfur into the mesopores. The sulfur/carbon composite was then placed in a vacuum oven with at an elevated temperature of 200 °C to remove the excess sulfur on the surface of these carbon materials.

4.2.3 Coin cell fabrication

The as-prepared porous carbon and sulfur composites were mixed with carbon black and styrene butadiene rubber: sodium salt of carboxymethyl cellulose (SBR:CMC) at a weight ratio of 7:2:1 using mortar and pestle to form aqueous slurry. The slurry was then casted on the aluminum foil with a doctor blade before drying in an oven at 60 °C overnight. The aluminum with slurry coating foil was punched into circular electrodes with the size of 5/16” with an area mass loading of 1.0~1.1 mg·cm$^{-2}$. Coin cells (CR2032, MTI Corp., USA) were assembled using sodium ingot as the counter electrode and 1M of sodium perchlorate (NaClO$_4$, Sigma Aldrich, >98%) in ethylene carbonate/propylene carbonate (EC/PC, 1:1 v/v%) as the electrolyte. Porous polypropylene (Celgard® 3501, Celgard, LLC Corp., USA) and glass fiber (GF/B, Whatman®, USA) were used as the separator. Electrochemical performances were conducted on an 8 Channel Battery
Analyzer (BST-8A, 1mA, MTI Corp., USA) at room temperature. Specific capacity is calculated based on the weight of active sulfur within the composite material.

4.2.4 Material characterizations

Scanning electron microscope (SEM) images were acquired by JOEL-7401 field-emission scanning electron microscope, the energy dispersive X-ray mapping (EDX mapping) from the SEM was also taken from the same equipment. HRTEM images and EDX mappings were taken by Tecnai G2 F20 with an EDAX SUTW (super ultrathin window) from FEI. The TEM was running under an accelerating voltage of 200kV. N\textsubscript{2} adsorption-desorption isotherms were carried out using Micromeritics Tristar. The specific surface area was determined from the typical Brunauer-Emmett-Teller (BET) method and the pore size distributions were calculated from the adsorption isotherms using the Barret-Joyner-Halenda (BJH) model. Transmission small angle X-ray scattering (SAXS) was performed on Rigaku MicroMax 002+ instrument using 0.154 nm wavelength X-rays. X-ray diffraction (XRD) carried out by Rigaku instrument equipped with an 18 kW rotating anode X-ray generator in the transmission mode. The X-ray photoelectron spectroscopy (XPS) was conducted on PHI5000 Versa Probe II Scanning XPS Microprobe (ULVAC-PHI, Inc.). A passing energy of 11.75 eV at a 0.05 eV step was applied for both survey and high-solution spectra associated with C1s, N1s and S2p. The scans were recorded at a takeoff angle of 45°. Quantitative analyses and results were obtained by using software (Igro Pro, Wavemetrics) after applying a Shirley background subtraction. Detailed characteristics of various chemical bonds in each sample were characterized by Fourier transform infrared spectroscopy (Thermo Scientific iS50 FT-IR) in integration with KBr discs. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were
conducted by CH Instruments CHI608E. The CV was performed at a scan rate of 0.5 mV·s⁻¹ from the range 0.8 V - 2.7 V. EIS measurements were taken within the frequency range of 100 kHz to 0.1 Hz with a 5 mV amplitude perturbation voltage. H-cell testing was conducted by coating the OMC material or N,S-HPC with PVDF binder at a ratio of 8:2 on a Celgard® using a doctor blade. Sodium polysulfide was fabricated mixing 7 mols of sulfur (S) with 1 mol of disodium sulfide (Na₂S) in TEGDME solvent; the polysulfide was further diluted and mixed until no solid content could be observed. The polysulfide was injected into the left hand side of the H-cell; pure TEGDME was injected onto the right hand side of the H-cell. Images were then taken at different selected time intervals to observe the migration of the polysulfide.

4.3. Result and discussion

The following sections would be on the results and discussions on the characterization of the active material and the electrochemical performances.

4.3.1 Characterization of the ordered mesoporous carbon and nitrogen, sulfur co-doped hierarchical porous carbon

The N,S-HPC was prepared by a roll-to-roll technique, a technique that is enables the capability of scalable production. Demonstrated in scheme 4.1, this synthesis route could be separated into five steps: (1) the formation of ordered mesophases through tri-consitutent self-assembly of organic-inorganic composites; (2) the polymerization of resol to solidify the thermosetting framework; (3) the calcination to remove the surfactants; (4) the reaction of resol with dopants (melamine and benzyl disulfide) and conversion to doped carbon and (5) the removal of silica nanoparticles for introducing the micropores.
The N,S-HPC in figure 4.2a exhibited a typical Type IV/H3 reversible hysteresis loop and the increasing adsorption from \( p/p_0 \) is 0.8 to 1 indicates the presence of macropores due to the defects formed during the doping reactions\textsuperscript{163-164}. The pore size distribution of N,S-HPC figure 4.2b further validates the existence of the micropores that were obtained from the removal of silica and mesopores that were from F127 in the N,S-HPC.

Figure 4.3 (a) \( \text{N}_2 \) adsorption-desorption isotherm of OMC and (b) BJH pore-size distribution derived from the adsorption isotherm.
The mesopore size of N,S-HPC (4.2 nm) is smaller than the OMC (5.8 nm) that is shown in figure 4.3a. The reason to the decrease in pore sizes could be due to the incorporation sulfur and nitrogen heteroatoms, in which the carbon framework was expanded; therefore, causing the pores of the nanostructure to shrink.

![Graph showing comparison of small angle X-ray scattering patterns between the OMC and the N,S-HPC.]

Figure 4.4 Comparison of small angle X-ray scattering (SAXS) patterns between the OMC and the N,S-HPC.

Small angle X-ray scattering (SAXS) that is shown in figure 4.4 confirms the observed expansion in the carbon matrix framework; where there is an increase in the domain-spacing between the N,S-HPC and the OMC. The N,S-HPC has a domain spacing of 10.4 nm, whereas OMC has a domain spacing of 9.8 nm. The broad peak that is observed at $q^* \approx 0.06$ nm for the N,S-HPC indicated the partially ordered nanostructures that consistent with the transmission electron microscopy (TEM) images (see figure 4.5a); where the alignment of walls could be clearly observed.
From figure 4.5bcd, it could be seen that the EDAX results provided homogeneous elemental doping on the N,S-HPC. The nitrogen, sulfur and carbon elemental mapping all exhibited the equal distribution of the material over the structure without any gradient difference. Further EDAX elemental analysis using line scanning technique provided the evidence of carbon with nitrogen doping, where they exhibited a constant carbon to nitrogen doping ratio (shown in figure 4.6). The regular fluctuations in the lines indicated the morphology of the hierarchical structure. The areas with higher counts suggested the scanning on the solid wall structure, where the areas with lower counts means the scan was
at the pore (the top is still covered with a thin layer of N,S-OMC shell). The coherence between the carbon and nitrogen counts intensity indicated the uniform doped heteroatom throughout the carbon matrix framework.

Figure 4.6 (a) STEM image of the N,S-HPC and line scanning intensity for detecting carbon and nitrogen at (b) and (c).

Additional elemental doping evidence was also provided by the X-ray photoelectron spectroscopy (XPS) (Shown in figure 4.7). The atomic elemental doping of heteroatoms was provided by the XPS showing carbon, nitrogen and sulfur with atomic percentage doping of 40%, 39.1% and 0.9%, respectively. The nearly 40% nitrogen doping for the N,S-HPC structure was significantly higher than previous literature reports\textsuperscript{165-166} due to direct carbonization in the porous carbons by heteroatoms-containing precursors or gas treatment methods. The nitrogen doping content is significantly higher than the sulfur
doping counterpart. The reason for the lower amount of sulfur incorporation in the carbon framework is due to their reactivity level\textsuperscript{167}.

Figure 4.7 The survey scan of the N,S-HPC using the XPS.

In figure 4.8abc, the high-resolution XPS was de-convoluted for the species of C1s, N1s and S2p. For the C1s, the binding energies 284.8 eV, 286.3 eV, 287.9 eV and 289.9 eV are attributed to the C-C (47.1 atom%), C-N (28.2 atom%), C=O (16.7 atom%) and C-O species (3.7%), respectively. For N1s, the binding energies of 398.1 eV, 399.7 eV and 401.0 eV are assigned to pyridinic-N (41.3 atom%), pyrrolic-N (51.9 atom%) and graphitic-N (6.8 atom%), respectively. It was reported that pyridinic-N and pyrrolic-N could enhance pseudo-capacitance, while graphitic-N could provide better electrical conductivity. For the S2p, the binding energies at 163.49 eV and 164.8 eV belong to S-S/S-C bonds (61.6 atom%) and S-O species (38.4 atom%), respectively. These co-existing functional groups were reported to improve the affinity and binding energy of the non-polar carbon atoms with polar polysulfide; therefore result in the cycle stability of the metal-S batteries\textsuperscript{168-169}. 
Figure 4.8 High resolution XPS spectra for the sample N,S-HPC, where the deconvoluted peaks for (a) C1s, (b) N1s and (c) S2p are shown.
4.3.2 Battery fabrication and electrochemical measurements

Sulfur/N,S-HPC composite electrode was prepared as previous reported\(^{170}\). Taking a step further to remove the sulfur that is existing on the surface of the N,S-HPC, the sulfur/N,S-HPC was placed in a vacuum oven at 200 °C for 12 hours; in which the external surface sulfur would be removed while a 22 wt% sulfur is trapped within the pores of the N,S-HPC. The nanopores and channels provided by the N,S-HPC, as demonstrated in Chapter III, exhibited synergistic effect from both the nitrogen doping and the nanoporous hierarchical structure; which is suitable for highly stable Na-S batteries. From figure 4.9, the pores of the N,S-HPC was completely filled according to the adsorption-desorption isotherm, where no hysteresis loop and low total adsorption was observed.

![Figure 4.9](image)

Figure 4.9 The comparison of N\(_2\) adsorption-desorption isotherm between N,S-HPC and N,S-HPC/S composite.
As shown in figure 4.10, the XRD exhibited three different samples. The sulfur and N,S-HPC are used as the reference, whereas the N,S-HPC/Sulfur active material is the comparison group. The as-purchased sublimed sulfur showed multiple sharp diffraction peaks, which is attributed to the crystalline structure of the cyclo-S\textsubscript{8}. For the N,S-HPC, the two broad peaks at $2\theta = 24^\circ$ and $43^\circ$ correspond to the graphitic crystallite planes (002) and (100) for turbostratic carbon\textsuperscript{171}. Unlike the combination peaks of sulfur and the active carbon material that was demonstrated from the previous chapter, the diffraction patterns for the N,S-HPC/S composite could not be differentiated from the pure N,S-HPC. First reason is that the surface sulfur was completely removed; therefore, the cyclo-S\textsubscript{8} could not be observed from the surface. Secondly, it indicates that the sulfur exist in a smaller molecular form in the N,S-HPC other than the cyclo-S\textsubscript{8}. The sulfur is trapped in the N,S-HPC due to the strong polar interaction between sulfur and the N,S-co-doped carbon framework.
Figure 4.11 X-ray diffraction spectra for sulfur, OMC and the composite OMC/Sulfur.

From figure 4.11, instead of the N,S-HPC, the non-heteroatom OMC was used as the subject for comparison. It is seen that under the same protocol, the OMC/S composite that the sulfur remains in a rather crystalline form that is similar to the cyclo-$S_8$; indicating the absence of the interactions that were demonstrated by the N,S-HPC.

The coin cells were fabricated to evaluate the effects of high-nitrogen concentration doping of N,S-HPC on the electrochemical properties for the Na-S batteries. The detailed fabrication method was mentioned in the experimentation part of this chapter, where simply, N,S-HPC/S as the active material at the cathode side and sodium metal as the anode side. Another reference battery using pure OMC/S as the cathode active material was tested simultaneously to demonstrate the effects of the nitrogen doping on the electrochemical properties as a control.
Figure 4.12 Discharge profile comparison between the N,S-HPC/S and the OMC/S.

It could be seen that there is a significant difference from the discharge profiles exhibited from figure 4.12. The galvanostatic discharge curves for the OMC/S shows an initial discharge plateau at the voltage near 1.90 V, which was reported\textsuperscript{172} to be the voltage at forming the discharge products of Na\textsubscript{2}S\textsubscript{3} and Na\textsubscript{2}S\textsubscript{2} for the RT-Na-S batteries. The capacity for the OMC/S active material cathode in the first cycle is near 380 mAh\textperiodcentered g\textsuperscript{-1}. However, the deterioration in the capacity was severe, upon the second cycle, the specific capacity degraded to only approximately 20 mAh\textperiodcentered g\textsuperscript{-1}. The huge loss in specific capacity in comparison from the first cycle and the cycle indicated the loss of active material, the sulfur, due to dissolution and possibly side reactions from the sodium polysulfides; which was also reported from several literatures of RT-Na-S battery systems\textsuperscript{170, 173-174}. On the other hand, the N,S-HPC/S composite cathode could deliver an initial capacity of 450 approximately mAh\textperiodcentered g\textsuperscript{-1} with a voltage plateau in proximity at 1.4 V, which was reported to be the cleavage of S-S bonds in the composite cathode\textsuperscript{175}. The discharge capacities remained to be reversible at 380 mAh\textperiodcentered g\textsuperscript{-1} after the second and up to fifth cycle in the figure.
Conventional RT-Na-S batteries and also the Li-S batteries (at different voltage range in comparison to the Na-S batteries) would exhibit two regions of voltage plateaus as following:

(1) a steep sloping region (2.7 V – 1.65 V), where the reaction is the liquid-liquid transition from the Na$_2$S$_8$ to the Na$_2$S$_4$.

(2) a smoother second sloping region (1.65 V - 0.8 V), where the reaction is from the further addition of sodium into Na$_2$S$_4$ to form Na$_2$S$_2$.

The discharge profile is different from what was reported, in which a plateau could be observed at 2 V$^{122, 172}$. The missing plateau in this type highly nitrogen-doped cathode material could be associated with the lack of reaction between Na$^+$ and elemental sulfur. In other words, the series of reactions exclude the possible formation of cyclo-S$_8$ even when the Na-S battery is fully charged; the reduction reaction could not be fully reversed back into the pure elemental sulfur. In addition, from figure 4.12, it could be seen that there is only two sloping regions, the absence of the third sloping region indicated that the reaction with Na$_2$S$_2$ is not possible, where further Na$_2$S discharge product is not obtained in the N,S-HPC/S cathode. The inability to further oxidize into Na$_2$S means lesser specific capacity could be extracted; however, it was reported that it is limited on the observation of the Na$_2$S in the Na-S battery$^{122}$. Therefore, understanding that the final discharge products could not be Na$_2$S, instead, the final discharge products exist in mixtures of Na$_2$S$_3$ and Na$_2$S$_2$. The theoretical capacity of the Na-S cell is between 558 mAh·g$^{-1}$ and 837 mAh·g$^{-1}$, which are the theoretical capacities for Na$_2$S$_3$ and Na$_2$S$_2$, respectively.
Figure 4.13 C-rate electrochemical testing for the Na-S battery using N,S-HPC/S as the cathode.

The c-rate performance for the N,S-HPC/S composite cathode is shown in figure 4.13. The Na-S battery was charged and discharged under the following current densities: 115 mA·g⁻¹, 230 mA·g⁻¹, 575 mA·g⁻¹, 1150 mA·g⁻¹, 2300 mA·g⁻¹, and then switched back to 115 mA·g⁻¹. Each of the current densities was executed for 10 cycles before switching to the other current density. The specific capacities corresponding to the current densities were 455 mAh·g⁻¹, 380 mAh·g⁻¹, 345 mAh·g⁻¹, 285 mAh·g⁻¹ and then 196 mAh·g⁻¹. After the rapid discharging current density at 2300 mA·g⁻¹, the battery could still retain and recover almost most of the initial specific capacities. The retention of the specific capacities exhibited values of ~443 mAh·g⁻¹ while the current density is set back to 115 mA·g⁻¹. The exceptional c-rate performance of the N,S-HPC/S cathode could be attributed to the hierarchical nanoporous structures, where the sodium ions were easily accessible to the sulfur molecules that were entrapped within the carbonaceous matrices.
Figure 4.14 Long discharge cycles that was run under the current density of 230 mA·g⁻¹.

In figure 4.14, the Na-S battery was run under a current density of 230 mA·g⁻¹ for over 350 cycles exhibiting a specific capacity initially near 400 mAh·g⁻¹. When the cycle number reached up to 350, there is still retention in the specific capacity with the value of 378 mAh·g⁻¹; which is calculated to be approximately 2% of capacity fading. The 2% fading in capacity is much less compared to previously reported for the RT-Na-S batteries. The ultra-long term cycle stability of the Na-S cell is provided in figure 4.15, which was conducted under a current density of 4600 mA·g⁻¹. Upon initial discharge, the capacity exhibited approximately 128 mAh·g⁻¹ with merely 3% fade in capacity after 8000 cycles while showing nearly 100% Coulombic efficiency. After charging and discharging for over 10,000 cycles which is shown in figure 4.15, the discharge capacity is still able to give around 84 mAh·g⁻¹. The sample of N-HPC, which has 34 atom% nitrogen-doping without the sulfur also shows a very stable cycle performance after 1000 cycles (see figure 4.16) with a slightly lower capacity at 112 mAh·g⁻¹ compared to the N,S-HPC, indicating that the polysulfide shuttling was inhibited due to the high amount of nitrogen-doping. Whereas for the sulfur atom doping, it could be contributing to the pseudo-capacitance thus
providing slightly higher specific capacity compared to the purely nitrogen-doping hierarchical porous carbon frameworks. The large fluctuations in the curve could be ascribed to the temperature of the environment, so if the battery cell was modulated within an iso-thermal chamber, the spikes could be reduced.

Figure 4.15 Discharge capacity of the N,S-HPC/S at a current density of 4.6mA·g⁻¹ exhibiting over 10,000 cycles.

Figure 4.16 Discharge capacity of the N-HPC/S at a current density of 4.6mA·g⁻¹ exhibiting for 1000 cycles.
4.3.3 Post-electrochemical analysis

The high cycle stability could be due to the 21 atom% of pyrrolic-nitrogen that is bonding with Na\(^+\) through lone pair electrons with a favorable Na-N interaction, which is shown by the high-resolution XPS spectra in figure 4.17.

![Figure 4.17](image)

**Figure 4.17** High resolution XPS spectra of N1s for the pure N,S-HPC cathode and the fully discharged N,S-HPC.

The N1s spectrum of the electrode after fully discharge shows a broad asymmetric widening towards lower binding energy, which could be due to the change in chemical environment. The peak at 397.2 eV can be assigned as the Na-N interactions. This Na-N interaction enables N,S-HPC to effectively trap sodium polysulfides during cycling.
Figure 4.18 The diffusion of the sodium polysulfides using the H-cell configuration under different time intervals for (a) OMC coated Celgard® membrane, and (b) N,S-HPC coated Celgard® membrane.

In order to provide evidence for the sodium polysulfide entrapment, the H-cell configuration with ultra-high concentrated sodium polysulfide at one side and pure solvent on the other side was used (illustrated in figure 4.18). The diffusion phenomenon of the liquid sodium polysulfide is due to the concentration gradient. From figure 4.18a, the OMC coated Celgard® membrane could not entrap the polysulfide diffusion that much, where it could be seen that the polysulfide has already initiated to diffuse from one side to the other solvent side. As for the N,S-HPC coated Celgard® membrane, it could be seen that the polysulfide has been significantly mitigated, where only traces amount of polysulfide diffused to the other side even after 300 minutes.
In order to further validate the Na-S battery, pure N,S-HPC was fabricated as the electrode to further confirm that all the specific capacity came from the sulfur that was impregnated into the composite cathode. As it could be seen that the specific capacity for the N,S-HPC is significantly lower than that of the N,S-HPC/S composite cathode, signifying that the N,S-HPC has minimal contribution to the specific capacity.

In addition, electrochemical impedance spectroscopy (EIS) was utilized to identify the discharge and charge statuses of the Na-S battery. As shown in figure 4.20, the resistivity of the fully charged battery ($R \approx 230 \ \Omega$) is lower than the fully discharged ($R \approx 395 \ \Omega$), which was found to be opposite from previously reported literature regarding the metal-sulfur battery$^{176}$. Regardless, this phenomenon is coherent with the acquired data, where fully charged product was the $\text{Na}_2\text{S}_8$ instead of pure insulating sulfur when the upper chemical window was reached. The long chain polysulfides of $\text{Na}_2\text{S}_8$, due to its liquid
phase, exhibited better mobility and conductivity compared to the shorter chain sodium polysulfides (which is in solid phase). The step change in resistance after each galvanostatic charge/discharge protocol is provided in figure 4.20, where a “breathing-like” phenomenal behavior was observed.

![Graph showing resistance changes](image)

Figure 4.20 The fully charged and fully discharged resistance for different cycles.

The enhanced cycle stability in the N,S-HPC/S composite cathode compared to previously reported could be summed up as following: First, the ordered mesoporous walls were able to confine the volumetric expansion of sulfur during the transition to sodium polysulfides; second, the removal of excess sulfur that are mostly deposited on the surface prevents the loss of active materials during cycling; third, introduction of nitrogen and sulfur heteroatoms into the ordered hierarchical carbon matrices change the electronic band of carbon framework that improves the immobilization capability of the polysulfide; and fourth, the strong interaction from sodium-nitride during discharge could constrain the sodium polysulfides in the pores and thus greatly mitigates the dissolution of polysulfide into the electrolytes.
Another piece of evidence to support the sodium polysulfide entrapment from polysulfide shuttling phenomenon, the Na-S batteries were disassembled for both N,S-HPC/S cathode and OMC/S cathode after 1000 cycles. From the inset images, it could be seen that after the 1000 cycles, the N,S-HPC/S battery’s glass fiber separator remained to be relatively clean without the dark yellowish tint. However, for the OMC/S cathode, it could be clearly seen that the dark yellowish sodium polysulfide has tinted the white glass fiber. The UV-vis at around 400 nm could be seen for the OMC that there is a larger, steeper and broader shoulder compared to the N,S-HPC and the electrolyte reference (which is a clear, transparent liquid), which is possibly due to the result of the sodium polysulfide.
4.4 Conclusions

A roll-to-roll facile method of fabricating hierarchical porous carbon with high heteroatoms concentration (>40 atom%) was used as the carbon matrix host for sulfurs and eventually made into the composite cathode for the RT-Na-S battery. The high level of nitrogen-doping in the carbon framework led to sodium-nitride interactions during discharge protocol, thus preventing the dissolution of sodium polysulfides within electrolytes that is primarily responsible for capacity fade in Na-S batteries due to polysulfide shuttling phenomenon. The Na-S batteries using N,S-HCP/S composite cathodes exhibited ultra-long cycle stability for more than 10,000 cycles with less than 20% decay in capacity (where for the first 8000 cycles, the decay was only 3%). This high doping strategy for ordered porous carbons provides a promising candidate to enable the possible commercialization for RT-Na-S batteries, which could be as an improvement for stationary, grid-level energy storages.
CHAPTER V
HIGH IONIC CONDUCTIVITY
TERNARY-COMPOENTS SOLID POLYMER ELECTROLYTE AT ROOM TEMPERATURE FOR DIFFERENT BATTERY SYSTEMS

The previous chapters have demonstrated different battery systems with high specific energy densities compared to the state-of-art Li-ion battery systems. The energy density of the next-generation batteries does indeed exhibit superior performance when placed in parallel in terms of the projected specific capacities; however, safety concerns become one of the most, or in fact, chief important factor, in the realization for actual commercialization. Just recently, in the interim of writing up this dissertation, several explosion issues and thermal runaway incidents were reported regarding the battery product in Samsung Galaxy Note 7 mobile phones. Despite only several tens of battery failure cases being recorded, Samsung, due to fears of battery explosion from the public, was forced to initially recall the products and then eventually discontinue the production and sales of the hazard-associated products; in which resulted in perhaps several tens of billions of dollars in loss. The cause of battery faults and failures has yet to be disclosed, but lending from this case study, it is understood that safety is of paramount importance regardless the amount of the exceptional capacity the battery could deliver. Therefore, while focusing on the actualization of the theoretical capacities from these next-generation
batteries, in this chapter, safer battery configuration would be discussed, in which the solid-state electrolyte would be introduced. The experimentation, as suggested by the title of the chapter, would be focusing on the ternary solid polymer electrolyte system.

5.1 Introduction to lithium-ion battery

It has been stressed in the previous chapters regarding the importance of energy storage devices. Many advanced electrochemical energy storage batteries including Li-O₂, Li-S and Na-S were described yet the currently prevailing Li-ion battery system has yet to be discussed in full detail; therefore, this section would be focusing on some of the basic backgrounds of the Li-ion battery.

5.1.1 Mechanism of the Li-ion battery

Lithium based batteries have rudimentary advantages over the other metal related battery chemistries. First advantage is that the Li has the lowest reduction potential in the whole periodic table, which allows Li-based batteries to give out the highest possible cell potential. Other appealing factors include having the smallest ionic radii and being one of the lightest elements, which turned out to provide high gravimetric/volumetric capacity and power density. Lithium, despite only being a mono-valency ion, is more superior in terms of the ion mobility, which could beneficially affect the power density.

In figure 5.1, the simplified Li-ion battery system using lithium cobalt oxide (LiCoO₂) as the cathode and carbon as the anode to depict the general Li-ion mechanism. The main reaction occurs as the reversible Li-ion intercalation and de-intercalation cycles between the layers of cathode and anode, following the cathode equation listed below:

\[
\text{LiCoO}_2 \leftrightarrow \frac{1}{2} \text{Li}^+ + \frac{1}{2} \text{e}^- + \text{Li}_{0.5}\text{CoO}_2
\]  

(5.1)
The cathode LiCoO$_2$ acts as a Li-ion reservoir to provide the amount of Li-ions needed for the necessary intercalation reaction. The use of LiCoO$_2$ could provide better prolonged shelf-life and superior safety features$^{178}$ in comparison to the pure Li-metal battery; however, the drawback would be the decrease in amount of capacity that the cathode could provide. The first protocol of the full battery is always charging, where the Li-ions would migrate from the LiCoO$_2$ pass the electrolyte/membrane layer to the graphite carbon matrix, where the intercalation product of LiC$_6$ would be formed as following:

$$\text{C}_6 + \text{Li}^+ + e^- \leftrightarrow \text{LiC}_6$$  \hspace{1cm} (5.2)

where LiC$_6$ means that every six carbons could accommodate up to one carbon.
The intercalation of the Li-ion into the carbon graphite matrix, resembling other battery systems, also occurs in different stages where LiC_{24}, LiC_{27}, LiC_{12} intermediate phases could be observed\textsuperscript{179}. The carbon matrix that is most commonly implemented is graphite; however, many other different types of carbons are also reported\textsuperscript{180} as the anode material as well. Since the graphite carbon theoretically is capable of providing a specific capacity of 372 mAh·g\textsuperscript{-1}, which is larger than all of the cathode materials that are currently available, most of the researches would focus on the development of the cathode side in attempt to provide a specific capacity that could pair up with the graphite counterpart while ensuring the safety. As the cathode part, mostly the transition metal oxides\textsuperscript{181} and phosphates\textsuperscript{182} were employed. The most commonly ones are LiCoO\textsubscript{2} (LCO)\textsuperscript{183}, LiMn\textsubscript{2}O\textsubscript{4} (LMO)\textsuperscript{184}, LiFePO\textsubscript{4} (LFP)\textsuperscript{185}, LiNiCoMnO\textsubscript{2}, (NCM)\textsuperscript{186}, and LiNiCoAlO\textsubscript{2} (NCA)\textsuperscript{187}.
Table 5.1 Selected cathode materials for Li-ion battery.

<table>
<thead>
<tr>
<th>Material</th>
<th>LiFeO₄</th>
<th>LiMn₂O₄</th>
<th>LiMnO₂</th>
<th>LiCoO₂</th>
<th>LiNiCoMnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific theoretical energy density [mAh·g⁻¹]</td>
<td>170</td>
<td>148</td>
<td>286</td>
<td>274</td>
<td>278</td>
</tr>
<tr>
<td>Actual specific energy density [mAh·g⁻¹]</td>
<td>130~140</td>
<td>100~120</td>
<td>200</td>
<td>135~140</td>
<td>155~165</td>
</tr>
<tr>
<td>Voltage range [V]</td>
<td>3.2~3.7</td>
<td>3.8~3.9</td>
<td>3.4~4.3</td>
<td>3.6</td>
<td>3.0~4.5</td>
</tr>
<tr>
<td>Cycles</td>
<td>&gt; 2000</td>
<td>&gt;500</td>
<td>Poor</td>
<td>&gt;300</td>
<td>&gt;800</td>
</tr>
<tr>
<td>Transition metal scarcity</td>
<td>Very abundant</td>
<td>Abundant</td>
<td>Abundant</td>
<td>Scarce</td>
<td>Scarce</td>
</tr>
<tr>
<td>Environmental concerns</td>
<td>Friendly</td>
<td>Friendly</td>
<td>Friendly</td>
<td>Co is poisonous</td>
<td>Co and Ni are poisonous</td>
</tr>
<tr>
<td>Safety</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Bad</td>
<td>Satisfactory</td>
</tr>
<tr>
<td>Temperature range [°C]</td>
<td>-20~75</td>
<td>50</td>
<td>Unstable at high temperatures</td>
<td>-20~55</td>
<td>-20~55</td>
</tr>
</tbody>
</table>

* Sourcing from Institute of Scientific and Technological Information of Shanghai (ISTIS).

Table 5.1 shows the different cathode materials for the Li-ion battery. As it could be seen that the ones that contain cobalt and nickel exhibit higher specific energy densities; however, they are also scarce in resources and are baneful for the environment while posing safety concerns at the same time. The iron complex LFP cathode shows extremely good cycle stability and good safety yet the theoretical energy density is too low; therefore, potential improvements and modifications for the iron based cathode are limited and unlikely to prevail in the future. The manganese based LMO cathode shows even lower specific capacity so it is not going to be a good candidate for the Li-ion battery. The LiMnO₂ is relatively more promising in all aspects but there is an issue with the cycle stability and issue with the operating temperature range; nevertheless, it is still potentially
a good candidate to be used in the cathode side due to its high theoretical specific energy density.

Regardless of the type of material that is utilized as the cathode of the Li-ion battery, the electrolyte will undergo reduction at graphite surface, where a passive layer named the solid electrolyte interphase (SEI) is formed due to inorganic/organic decomposition products. This passivation layer is no longer electrochemically active and thus the formation of this layer accounts to the irreversible capacity that could be observed in the first cycle. However, the SEI layer is necessary to prevent further deterioration of the electrolyte, since thermodynamically no solvents are stable with lithium or the Li$_x$C$_6$ near 0 V vs. Li, by blocking the electron from reacting with the electrolyte while allowing Li-ions to pass through. The SEI layer formation is highly dependent on the type of electrolyte that is used; further additives are utilized to provide a good formation of stable SEI layer.

5.1.2 Formation of the lithium dendrite and its implications

A rechargeable Li-metal based battery is one of the most appealing candidates for energy storage devices due to high theoretical storage capacity. Instead of using lithiated graphite which has a theoretical specific capacity of 372 mAh·g$^{-1}$, utilization of pure lithium metal could provide a theoretical specific capacity of approximately 3800 mAh·g$^{-1}$. The high specific capacity accompanies with the phenomenon of lithium dendrite formation during repeated charge and discharge cycles, or simply the formation of random Li electrodeposits.
From scheme 5.1, it could be seen that the electrode is rather smooth initially. As the lithium deposits onto the electrode, since it is practically impossible to deliberately control the uniformity deposition of the lithium onto the electrode, the lithium ions would attach on the electrode in a random fashion, where a topological uneven dendritic growth of lithium would form. Upon reversing the electrochemical reaction, the lithium would dissociate into lithium ions and electrons, in which the SEI layer would to some extent be broken down allowing lithium ions to migrate to the other side of the electrode. In fact, the unevenness of the SEI is one of the reasons that lead to the uneven deposition of the lithium ions on the electrode. After long periods of cycling, the lithium dendrite growth could ultimately span the electrolyte space, and eventually touch the other side of the electrode, in which would result in the short circuit of the battery, and cause thermal runaway overheating that could lead to detrimental disasters.

Many methods were proposed to mitigate the lithium dendrite growth phenomenon; such as alloying Li anodes with other metals\textsuperscript{190-191} or adding additives to enhance a more uniform SEI layer\textsuperscript{192-193}. Despite the reported improvement in alleviating the adverse
effects from the lithium dendritic growths using the above-mentioned methods, the Li-ion battery exhibited other negative impacts in terms of capacity degradation and cycle stability reduction. Therefore, in order to retain the capacity of the anode electrode and also ensure better safety, solid polymer electrolytes (SPEs) are developed to tackle the problematic lithium dendrite growth. It was predicted that SPE with high shear modulus ($G' > 7$ GPa) could suppress the growth of lithium dendrite$^{194}$. Further experimental designs actually demonstrated that with a mechanically rigid microphase-separated polystyrene-b-poly(ethylene oxide) (PS-b-PEO) block copolymers$^{195}$ could develop high resistance to the Li dendrite growth with significantly lower shear modulus of $G' \sim 0.1$ GPa. Another group using cross-linked polyethylene/poly(ethylene oxide)$^{196}$ SPE with even lower modulus of $G' \sim 1.0 \times 10^5$ Pa also reported remarkable dendrite growth suppression as well. In the following section, the SPE would be discussed more in-depth in order to provide a better scope of understanding in the field of SPEs.

5.2 Introduction to solid-state electrolyte

The utilization of liquid-based electrolytes is currently the main trend in the conventional Li-ion batteries since liquid electrolytes could easily be dispersed and diffused into the electrodes and they act as a good medium for the high mobility of the lithium ions. However, risks including volatilization, flammability and explosion$^{197-198}$ arise as the liquid electrolytes are employed into the battery. Since safety, as it is being stressed over and over again throughout this chapter, is the utmost important factor in the battery, strong urge for the development of solid-state electrolytes has taken place due to its potential to eliminate safety concerns; due to the fact that solid-state electrolyte is solid intrinsically$^{199}$. The main advantage of the solid-state electrolyte is that it does not corrode,
leak, combust or cause shortages in comparison to the liquid electrolytes\textsuperscript{200-201}. Perhaps the most intriguing potential from the solid-state electrolyte is the fact that it is inert against metallic lithium, which makes it both as an electrolyte that allows the lithium ion migration and as a separator that separates the anode and cathode to prevent short circuit. Since the solid-state electrolyte itself is rather homogeneous and could be configured to be pore-free, it could be utilized to suppress the lithium dendrite formation\textsuperscript{202}. However, interestingly, despite understanding the implementation of solid-state electrolyte could enhance the safety of the battery, the development of the solid film up to date has not been able to live up to the advancement of the other components in the battery – the cathode and the anode. This stalemate in the development of solid-state electrolyte could be attributed to the following reasons\textsuperscript{199}:

(1) The electrolyte component is much more sensitive to the operating conditions compared to the electrode counterparts, making it difficult to alter from system to system. Especially for solid-state electrolyte, which is more dependent on the operating conditions in comparison to its liquid counterpart.

(2) On the cost basis, the solid-state electrolyte is much more expensive compared to the conventionally used LiPF\textsubscript{6} in carbonate-based electrolytes. In fact, the LiPF\textsubscript{6} and carbonated coupled electrolyte is so cheap that other liquid electrolytes systems with better performance could not change the existing supply chain in the market.

(3) Perhaps the most important reason is that the solid-state electrolytes are generally limited by their ionic conductivity under room-temperature conditions and other electrochemical performance issues including short cycle life, mismatch with cathode and
large interfacial or grain boundary resistance\textsuperscript{203}. These issues would be further discussed in the next section.

In order to understand the mechanism of solid-state electrolyte and thus further tackle the challenges reported, the concept of ionic conductivity would have to be explained. Currently, there are two different types of ionic transport models to quantitatively determine the ion transport and thus calculate the ionic conductivity values of solid-state electrolytes.

1. Arrhenius model

\[
\sigma = A \exp\left(\frac{-E_a}{kT}\right)
\]  

(5.3)

where \(\sigma\) is the ionic conductivity with units of S cm\(^{-1}\), \(E_a\) is the activation energy that could be calculated from linear best-fit of \(\log \sigma\) vs. \(1/T\), \(A\) is the pre-exponential factor by extrapolating curve to infinite temperature, and \(k\) is the Boltzmann constant. The Arrhenius model describes the ion hopping decoupled from long-range motions of matrix\textsuperscript{204}, which is most suitable for inorganic electrolytes that have fixed crystal lattices\textsuperscript{205} amorphous polymer and glass phases below glass transition.

2. Vogel-Tammann-Fulcher (VTF) model

\[
\sigma = \sigma_0 T^{-\frac{3}{2}} \exp\left(\frac{-B}{T-T_0}\right)
\]  

(5.4)

where \(B\) is the pseudo-activation energy for conductivity with units of \(E_a/k\), and \(T_0\) is the reference temperature is usually taken at 10 K - 50 K below experimental glass transition temperature. The VTF model is more relevant for polymer electrolytes that possess hosts with free volume, and the parameters could be obtained by fitting the following relationship\textsuperscript{204}.
\[
\log_{10} \left( \sigma T^{0.5} \right) = \log_{10} \sigma_0 - 0.43 \frac{E_a}{k(T-T_0)}
\]  \hspace{1cm} (5.5)

The conduction of ions from one side of the solid-state electrolyte to the other side for inorganic crystal electrolytes is by the transferring of mobile ions through interstitial sites or vacancies; as for polymeric electrolytes, the transferring of conductive ions is by continuous coordination between mobile ions and polar groups\textsuperscript{197}.

As seen from both the Arrhenius model and the VTF model, the temperature of the environment strongly affects the ionic conductivity of the solid-state electrolyte. Typically, according to the equations from two different models, the ionic conductivity has a direct proportional relationship with the temperature; as the temperature increases, the ionic conductivity increases. Liquid electrolytes typically exhibit an ionic conductivity over 10\textsuperscript{-2} S\textperiodcentered cm\textsuperscript{-1}, whereas the solid electrolytes depending on system could range from 10\textsuperscript{-9} \textendash 10\textsuperscript{-2} S\textperiodcentered cm\textsuperscript{-1} depending on the system.

There are three-types of solid-state electrolytes – solid polymer electrolytes (SPEs), inorganic solid electrolytes (ISEs) and composite solid electrolytes (CSEs), where the CSE is essentially the combination of SPE and ISE mixture. The SPEs could be further categorized into two classes – crystalline and amorphous. The amorphous part of the SPE would be the main focus of this chapter.
Table 5.2 Comparison of different solid-state electrolytes and the performances within an actual Li-ion battery.\(^{205}\)

<table>
<thead>
<tr>
<th>System</th>
<th>ISEs</th>
<th>SPEs</th>
<th>CSEs</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ionic conductivity</strong> ([S \cdot \text{cm}^{-1}])</td>
<td>Oxide</td>
<td>Sulfide</td>
<td>Nitride</td>
<td></td>
</tr>
<tr>
<td>(10^{-4} \sim 10^{-3})</td>
<td>10(^{-2})</td>
<td>(10^{-6} \sim 10^{-3})</td>
<td>(10^{-5})</td>
<td>(10^{3})</td>
</tr>
<tr>
<td><strong>Electrochemical stability range</strong> ([V])</td>
<td>4.5 ~ 12</td>
<td>5</td>
<td>5.5</td>
<td>4.5</td>
</tr>
<tr>
<td><strong>Li(^+) transference number</strong></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(\leq 1)</td>
</tr>
<tr>
<td><strong>Mechanical stability</strong></td>
<td>High</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Thermal stability</strong></td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Flexibility</strong></td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td><strong>Resistance</strong></td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Interfacial property</strong></td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Safety in LIB</strong></td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Energy density</strong> ([\text{Wh} \cdot \text{kg}^{-1}])</td>
<td>150 ~ 400 (Metallic Li anode)</td>
<td></td>
<td></td>
<td>150 ~ 200</td>
</tr>
<tr>
<td><strong>Power density</strong> ([\text{W} \cdot \text{kg}^{-1}])</td>
<td>Low</td>
<td></td>
<td></td>
<td>High</td>
</tr>
<tr>
<td><strong>Configuration</strong></td>
<td>Simple</td>
<td></td>
<td></td>
<td>Complex</td>
</tr>
<tr>
<td><strong>Cost</strong></td>
<td>High</td>
<td></td>
<td></td>
<td>Low</td>
</tr>
</tbody>
</table>
Table 5.2 is a summarization to compare and contrast the fundamental properties of different solid-state electrolytes to their liquid electrolyte counterpart and also the actual performances when employed in a Li-ion battery. As it could be seen, the performance of the solid-state electrolyte could exceed the performance of the liquid electrolyte when pure metallic lithium is used; however, the power density remains to be an issue since the overall migration of lithium ions is much slower compared to liquid. Furthermore, the cost of the solid-state electrolyte remains high, making it difficult to be mass produced and commercialized.

The following characteristics must be fulfilled in order to enable large-scale application of the solid-state electrolytes:

1. High ionic conductivity at room temperature. An ionic conductivity of $10^{-4}$ S·cm$^{-1}$ at room temperature has to be fulfilled in order to achieve a performance similar to the liquid electrolytes.

2. Low electronic conductivity accompanying with low interfacial and grain boundary resistance.

3. Stable electrochemical window over a wide range. Typically, an electrochemical stability domain should range from 0 V to 4 or 5 V.

4. High chemical stability with presence of electrodes (especially pure metallic lithium anode).

5. High mechanical strength and compatibility of thermal/volumetric expansion coefficients with both electrodes.

6. Low cost, high throughput, simple synthetic route and environmental friendly.
Table 5.3 In 2010, United States Advanced Battery Consortium (USABC) established requirement values for batteries in different criteria under the application of electric vehicles\textsuperscript{208}.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Requirement Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Power density</strong></td>
<td>600</td>
<td>W⋅L\textsuperscript{-1}</td>
</tr>
<tr>
<td><strong>Specific power density</strong></td>
<td>400</td>
<td>W⋅kg\textsuperscript{-1}</td>
</tr>
<tr>
<td><strong>Energy density\textsuperscript{*}</strong></td>
<td>300</td>
<td>Wh⋅L\textsuperscript{-1}</td>
</tr>
<tr>
<td><strong>Specific energy density\textsuperscript{*}</strong></td>
<td>200</td>
<td>Wh⋅kg\textsuperscript{-1}</td>
</tr>
<tr>
<td><strong>Shelf life</strong></td>
<td>10</td>
<td>yr</td>
</tr>
<tr>
<td><strong>Cycle</strong></td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td><strong>Price</strong></td>
<td>&lt; 100</td>
<td>$/kWh</td>
</tr>
<tr>
<td><strong>Recharge time</strong></td>
<td>&lt; 3-6</td>
<td>Hr</td>
</tr>
<tr>
<td><strong>Operating environment</strong></td>
<td>-40 ~ 85</td>
<td>°C</td>
</tr>
</tbody>
</table>

\textsuperscript{*}The requirement values are set to be a C/3 discharge rate.

From table 5.3, the required values for different criteria have to be fulfilled in order to be used in electric vehicle applications. As it could be seen that it is rather challenging to fulfill all of the values provided within different criteria using one particular system of solid-state electrolyte; therefore, many modifications and combinations are undergoing in order to search for the best optimized system for the application.

5.2.1 Solid polymer electrolytes

As mentioned in the previous section, many combinations of solid-state electrolytes are under research, the solid polymer electrolytes (SPEs) are of particular interest due to the flexibility of the polymer structure. The SPEs are basically made by mixing polymers with a lithium salt, where the lithium salt is immobilized in a desired host polymer matrix\textsuperscript{209}. The development and discovery of the SPE initiated when Wright\textsuperscript{210} in 1975 found out use of poly(ethylene oxide) (PEO), having the characteristic oxyethylene (CH\textsubscript{2}-CH\textsubscript{2}-O)
archetype, in combination with alkali metal salt complexes could provide ionic conductivity readings, which spurred up a new direction in pursuit for SPEs. It was in 1979 that the SPE was actually utilized and applied into the Li-ion batteries. As being slightly mentioned in the previous section, there are generally three different types of polymers – the crystalline, the amorphous and the semi-crystalline. Since it is given that salt with lower lattice energy and host polymer with higher dielectric constant could facilitate the dissociation and transport of ions; special salts are selected to preserve ionization, while polar groups existing in polymers creating coordination bonds with the ions are chosen. Therefore, the salt and polymer coupling components are important in providing a higher ionic conductivity. Nevertheless, it is still under discussion and research that whether the crystalline polymer matrix host or the amorphous polymer matrix host would better assist the transport of ions.

In order to act as a suitable host to dissociate the lithium salt, the polymer or the active portion of the copolymer should have at least the following essential characteristics:

1. The donor power of the atoms or groups of atoms must be significant to form coordinated bonds with cations.

2. Segmental motion of the polymer chain has to be taken place easily; therefore, the bond rotation barriers have to be low.

3. The ion bonds formation within the multiple intrapolymer is important thus an optimal distance between the coordinating centers has to be figured out.

Many different polymers in fact satisfy the mentioned criteria for instance poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(dimethylsiloxane) (PDMS), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl
chloride) (PVC), poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) et cetera, yet the most studied and advantageous polymer host is the PEO since the polar group in the repeating oxyethylene unit has the ability to dissolve or complex with the ionic salts. Many derivatives of the PEO were designed to provide functional end groups to further enhance the property of the PEO. Additionally, the PEO host is capable of dissolving various selections of salts, making it appealing for the SPE application.

The addition of salt into the polymer host produces a binary polymer salt system, or also known as the dry SPEs. The polymer host, typically the PEO, PEO\textsubscript{n}-salt complex is governed by the competition between the solvation and lattice energies of the polymer and inorganic salt. Low lattice energy exhibited from both the salt and polymer would increase the stability of the SPE. The \( n \) value could also be presented as the salt/EO ratio, in which the lower the ratio would give a higher ionic conductivity. Furthermore, it might be slightly counter-intuitive that the ionic conductivity and the transference number would decrease as the salt concentration increases\textsuperscript{214}. This could be attributed to the hindrance to the motion of polymer chains in which inhibited ion transport and also decrease in dissociation of the salt (re-formation of the ion-pairs) that reduces the amount of anions\textsuperscript{215}. The optimized ratio for the PEO-salt dry complexes exceeds 1:8, when the concentration of the salt increases up to 1:4, ion aggregation phenomenon would be observed. Combinations include (PEO)\( x \)-LiClO\textsubscript{4}\textsuperscript{216}, PEO-LiN(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}, PEO-LiCF\textsubscript{3}SO\textsubscript{3}\textsuperscript{217}, PEO-LiBF\textsubscript{4}\textsuperscript{218} were being tested near room temperature conditions, but the outcome in terms of the ionic conductivity is unacceptable, not able to exceed the workable value of \( > 5 \times 10^{-4} \) S\,cm\textsuperscript{-1}. Under higher temperatures, the PEO, with a crystallization temperature below 70
°C, would be mostly amorphous state, thus able to support an increment of anion migration that enhances ionic conductivity. Therefore, the binary polymer salt system could be in use when the temperature is at the upper temperature requirements, yet currently not practical under room temperature applications.

The addition of a plasticizer could decrease the crystallinity temperature of polymers, so that the amorphous nature of the polymer could be brought down to room temperature. Mixing liquid plasticizers including low molecular weight poly(ethylene glycol) (PEG) or non-aqueous organic solvents such as dimethylsulfoxide (DMSO) or ethylene carbonate (EC) into the binary system to produce a ternary SPE system could increase the ionic conductivity. The use of these additives at once decreases the crystallinity of the dry SPE matrix and increases segmental motion of the polymer chain. The additive itself could also act as medium to support salt dissociation so that the migration of ions increase to enhance charge transport properties. The ionic conductivity could be greatly improved with addition of plasticizers where could be supported by the following systems: (PEO)$_8$-LiClO$_4$ with EC:PC; (PEO)$_8$-LiClO$_4$ with PC; PEO-LiCF$_3$SO$_3$ with PEG$^{219}$; PEO-LiBF$_4$ with crown ether$^{220}$. The mentioned ternary system could reach ionic conductivity levels of $10^{-4} \sim 10^{-3}$ S·cm$^{-1}$, which are significantly higher than the binary salt counterpart and moreover, exceeding the requirement values that proposed. However, with the enhancement of the ionic conductivities by addition of plasticizers due to the increase in amorphous phase, mechanical integrity of the SPE severely deteriorates and the reactivity against the metal anode increases$^{221}$. Therefore, in order to retain the high ionic conductivity provided by the ternary SPE system, additional methods must be utilized to ameliorate the mechanical integrity of such ternary system.
5.2.2 Mechanism of the solid polymer electrolyte

It has been discussed that the more amorphous the SPE, the better the ionic conductivity. However, it was also reported otherwise that the crystalline phase could assist the ion transport as well.

![Figure 5.2 Mechanism of the amorphous solid polymer electrolytes.](image)

It could be seen from figure 5.2 that within a polymer matrix, the lithium ion could form a complex by interacting with the suitable coordination sites, which is the polar groups within the PEO, the oxygen in the ethylene oxide repeating unit. The lithium ions and the corresponding negatively charged ion dissociate and recombine to another coordination site by hopping from the local segments. For instance, in $t = 0$, the lithium ion is coordinated within the one at the bottom area interacting with the surrounding polar groups. In $t = 1$, the lithium ion hops to the upper area with another polymer segment, where the polar groups from the top polymer segment readily interacts with the lithium ion. At $t = 2$, the polar groups from the bottom polymer segment loses its interaction with the
lithium ion while the top polymer segment completely form the coordination interaction. The process continues on in a certain direction under the application of an external field, the process is so called the ion conductive process\textsuperscript{212}. Based on the understanding of ion conductive process, most researchers reported that ion transport occurs in the amorphous phase and consider the crystalline region of the polymer as a hindrance for the migration of anions\textsuperscript{222}. However, the ion conductive process is not able to explain several cases where high ionic conductivities are achievable by ceramics, in which it is completely crystalline compared to the SPE. Another viewpoint was provided and reported regarding the different conduction mechanism of the crystalline polymer electrolytes\textsuperscript{223}.

![Diagram of mechanism](image)

**Figure 5.3** Mechanism of the crystalline solid polymer electrolytes.

From figure 5.3, the mechanism in ionic conductivity of the crystalline region of the SPE was depicted. Instead of confining in the concept of anions movement within the chain segments, it was proposed that the anions movements are hopping over the spiral channels that were constructed by the local polymer segments since it is known that the crystalline polymer chains fold to form unmovable interlocks. So essentially, at $t = 0$, the lithium ion is coordinated within the polar groups of the spiral polymer segments. At $t = 1$, 
upon an application of external force, the lithium ion was driven to hop in a certain direction and thus enforces the formation of another coordination interaction. At $t = 2$, the same process goes on that eventually move the lithium ion to migrate from one side to the other side.

5.3 Experimental

The following subsections would be on the experimental section in preparing the solid polymer electrolyte film and the methods in measuring the intrinsic properties.

5.3.1 Materials preparation and the synthesis of the solid polymer electrolyte film

Poly(ethylene glycol) diacrylate (PEGDA, Sigma Aldrich, 99%) with molecular weight of 700 g·mol$^{-1}$, succinonitrile ($\text{C}_4\text{N}_2\text{H}_4$ or SCN, Alfa Aesar, 99%), glutaronitrile ($\text{C}_5\text{N}_2\text{H}_6$, Alfa Aesar, 99%), and photoinitiator bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Irgacure® 819, Sigma Aldrich, 97%) were purchased without further purification. LiTFSI salt (Matrix Scientific, 99%), and electrode materials including LiFePO$_4$ (LFP, MTi Corp.) were placed in the oven at 100°C overnight to remove residual moisture before use. Battery fabrication components: aluminum current collector was purchased from MTi Corp., carbon black (Super P, MTi Corp.), poly (vinylidene fluoride) (PVDF, Sigma Aldrich, 99.5%), anhydrous 1-methyl-2-pyrrolidinone (NMP, Alfa Aesar, 99%), round punched lithium metal pieces (Li, MTi Corp.) were used as purchased.

In a typical fabrication process in making the SPE film, the LiTFSI salt, the polymer host PEGDA and the succinonitrile plasticizer were kept and stored in an argon filled glovebox ($\text{O}_2 < 0.5$ ppm, $\text{H}_2\text{O} < 0.5$ ppm). The ratio of the ternary mixture of LiTFSI:PEGDA:succinonitrile is 35:25:40, which was slightly modified accordingly from
the previously reported to enhance the ionic conductivity. PEGDA and succinonitrile were mixed at the given ratio prior to the addition of the LiTFSI salt. The ternary-component blend was vigorously stirred for half an hour at room temperature with a vortex mixer (120V, VWR International) to obtain a transparent homogeneous solution. 2 wt% of photoinitiator in respect to the PEGDA was introduced into the transparent homogeneous blend, and then the mixture is further stirred for another 5 minutes allowing the photoinitiator to dissolve. The transparent mixture was left to rest for 10 minutes in order to allow the bubbles to defoam. Subsequently, the mixture was poured into a mold with desired depths of thickness with a glass cover on top to obtain a smooth surface and a controlled thickness. An UV light source with a wavelength of 350 nm was exposed to the sample for 1 minute to obtain a transparent, solvent-free, free-standing SPE film.

5.3.2 Characterization of the solid polymer electrolyte film

The solid polymer electrolyte film could be mainly separated into two large subsections, one is the thermal/mechanical measurements, and another one is the electrochemical measurements.

5.3.2.1 Thermal and mechanical measurements

Glass transition temperature and crystallinity of the SPE film was determined by the utilization of differential scanning calorimetry (DSC, TA Q200, TA Instruments Inc.), where the temperature range was scanned from -90 °C to 70 °C at a temperature ramping rate of 10 °C·min⁻¹. The SPE film samples for the DSC were pre-dried overnight in a dry box prior to the measurements. Thermal gravimetric analysis (TGA, TA Q50, TA Instruments Inc.) was to determine the weight percentage component of the ternary system
and also the thermal stability of the SPE. The temperature was measured from room temperature to 500 °C at a rate of 10 °C·min⁻¹ under nitrogen atmosphere to determine the weight percentages of different components. Tensile test SPE test specimens were prepared by a mold with dent dimensions of 30.0 mm × 5.0 mm × 0.6 mm. The specimen strips was then peeled off from the mold and placed in a dynamic mechanical analyzer (DMA, TA Q800, TA Instruments Inc.). The SPE strips were stretched at a constant strain rate of 1 mm·min⁻¹ under air environment until the film breaks.

5.3.2.2 Electrochemical measurements

Ionic conductivity measurements were carried out by using the stainless steel (SS)/SPE/SS configuration. The thickness of the SPE was controlled to 1 mm by using a mold. The thickness of the SPE film was further validated through the use of a thickness gauge (547S-401, Mitutoyo) and SEM. AC impedance was carried out by using the electrochemical workstation (CHI608E Electrochemical Analyzer, CH Instrument), where the electrochemical impedance spectroscopy (EIS) test was scanned from the range of 1 MHz to 0.1 Hz with a perturbation voltage of 10 mV. Ionic conductivity at different temperatures was carried out under the same cell configuration yet placed in a self-designed thermal chamber that is linked with a thermal couple (Omron E5AK). Several data points were collected within the temperature range of 25 °C to 120 °C. For instance, at 30 °C, the cell was placed in the thermal chamber and allowed to rest for at least 30 minutes prior to conduct the AC impedance. Linear sweep voltammetry (LSV) was tested under the SS/SPE/Li block cell configuration using the same electrochemical workstation under room temperature conditions. The thickness of the SPE film is 1 mm with a diameter of 7/16". In the LSV, the potential ranges from 0 V to 10 V at a sweeping rate of 0.5 mV·s⁻¹.
The same block cell configuration was used for the cyclic voltammetry (CV) measurements, where the voltage range was selected to be from -0.5 V to 5 V at a scanning rate of 0.5 mV\cdot s^{-1}. Lithium transference number (t_{Li^+}) was tested using the Li/SPE/Li configured coin cell. The thickness of SPE was controlled to a thickness of 250 μm. The initial AC impedance value and the final value of the AC impedance were obtained using the EIS. The second step polarization was done by chronoamperometry technique with a polarization voltage of 10 mV. Cell lifetime and stability were studied by using a symmetric coin cell with the Li/SPE/Li configuration. The thickness of the SPE film was controlled to 250 μm with a diameter of 1/2”. This cell configuration was used to test the lithium plating/stripping and the short circuit. The cells were tested out and carried out using 8 Channel Battery Analyzer BST-8A with the self-designed thermal chamber that is controlled to 30 °C. In the plating/stripping test, typically the cells were charged and discharged under a desired current density for duration of 1 to 2 hours, which is strongly dependent on the value of the current utilized. The test terminates when the cell short circuits or starts exhibit drastic unstable voltage fluctuations. The failure and short circuit of the battery could be observed as the time dependence on the voltage profile commenced to be irregular or an observation of a sudden drop in voltage profile.

5.3.3 Fabrication of the battery

The fabrication of the battery is of paramount importance in order to obtain good performances.
5.3.3.1 Lithium-ion battery

LiFePO$_4$, carbon black and PVDF was first measured at weight ratios of 80, 10, and 10, respectively. The powders were placed in a Teflon container with ceramic balls and NMP solvent to form the slurry. The container is then placed on a ball milling machine (MTi Corp.) to allow vigorous mixing and form a homogeneous thick mixture. The slurry is then casted on an Al foil using a doctor blade to form a thin layer of coating with mass loading around 0.3 mg·cm$^{-2}$. This pre-coated LFP electrode was subsequently dried at 80 °C overnight in an oven to allow the removal of solvents.

The composite electrode material was synthesized first prior to casting on the pre-coated LFP electrode. The composite electrode material was prepared in the Ar glovebox by mixing the previously mentioned LFP slurry with LiTFSI/PEGDA/succinonitrile ternary SPE electrolyte transparent liquid mixture using pestle and mortar at a weight ratio of 60 to 20, respectively. The SPE/electrode slurry mixture was casted on the pre-coated LFP electrode inside the glovebox and left to dry on a hotplate at 40 °C for over 24 hours. The composite LFP electrode typically has a mass loading of 4~5 mg·cm$^{-2}$ was placed into the previously utilized mold. The SPE liquid mixture was then casted on top of the LFP composite electrode and then exposed to UV light to further polymerize the SPE. A Li foil was then placed on top of SPE to have the configuration of Li/SPE/composite-LFP.

5.3.3.2 Lithium-sulfur battery

For the fabrication of the Li-S battery, the same electrode material was used from chapter III, where the cZIF-8/S electrode was implemented as the cathode of the Li-S
battery. The electrode preparation method could be seen in the experimental section of chapter II. Ternary mixtures of PEGDA, succinonitrile and LiTFSI salt were mixed under 20, 40 and 40 weight ratios, respectively. 2 wt% of the Irgacure® 819 in respect to the PEGDA was added into the transparent liquid and then vigorously mixed again to ensure homogeneity. The mixture liquid was casted on glass microslides with tape as the spacer framework mold. The photo-polymerization took place upon exposure to UV light at 350 nm with an intensity of 5 mW·cm⁻². The photo-polymerization process was in a nitrogen filled glovebox for 15 minutes to allow complete polymerization. The cZIF-8/S electrode was used as the cathode together with the Li metal to sandwich the SPE-membrane. The cZIF-8/S electrode, SPE membrane, and Li metal have diameters of 5/16”, 1/2”, and 7/16”, respectively.

5.3.3.3 Battery electrochemical measurements

Both the fabrication method of the Li-ion battery and the Li-S battery electrodes were described in the previous sub-sections. For the Li-ion battery, the galvanostatic charge/discharge cycling test of the fabricated battery cells was carried out in the chemical window range of 2.5 V to 3.9 V using the same 8 Channel battery Analyzer BST-8A (1mA) from MTi. The current density was initially applied at a rate of 30 mA·g⁻¹ for 10 cycles then subsequently ramped to 50 mA·g⁻¹ in the following cycles. For the Li-S battery, the galvanostatic charge/discharge cycling test was conducted from the chemical window range of 1.6 V to 3.0 V. For the long cycle testing, the current density was set to be 0.05 C for all cycles. As for the C-rate testing, increments of current densities were applied to test the power density stability. 0.05 C, 0.1 C, 0.2 C, and 0.5 C were charged and discharged for 10 cycles prior to switching back to the initial 0.05 C.
5.4 Results and discussions

The following subsections would be focusing on the results that were obtained from the data.

5.4.1 The SPE film

Figure 5.4 The phase diagram for the PEGDA, SCN and LiTFSI salt SPE\textsuperscript{224}.

From figure 5.4, the phase diagram of the ternary system between PEGDA, SCN and LITFSI salt could be seen. The figure was adapted from a previous collaboration\textsuperscript{224}, where it was mentioned that a wide isotropic region could be observed allowing possibility of a melt polymer phase without any assistance from the solvent. The non-shaded blank
region is the areas where transparent homogeneous slurry could be formed. Whereas the shaded black areas are the regions where individual components could not be completed dissolved within the ternary system. Therefore, in order to achieve homogeneous slurry, the ratios were deliberately selected from the isotropic regions. As for the glutaronitrile plasticizer, the ratio was directly adapted from the succinonitrile counterpart since there is only one carbon difference in the structure of the molecule.

Figure 5.5 (a) The mold that was used to fabricate the different thicknesses of SPE film. (b) Image of a free-standing SPE that was punched out using a punch size with a diameter of 1/2”.

As it is shown in figure 5.5a, different depths of grooves were machined into the micro-level to provide desired SPE thicknesses. In figure 5.5b, free-standing SPE film was punched off from the mold and then subsequently utilized for further characterizations. The thicknesses of the SPE membranes were mainly controlled by the depth of the grooves; however, dealing with thicknesses that are in the micrometer scale could be tricky at times; therefore, the use of the thickness gauge from Mitutoyo that has a resolution up to 0.001
mm or 1 μm could assist in the validation of the thickness of the SPE. The SEM was also used to further confirm the SPE thickness as shown in figure 5.6. The SPE membrane was peeled off from the mold with a groove depth of 250 μm, under SEM the thickness was slightly off from the desired thickness yet within the range of the error.

![SEM image of SPE thickness](image)

Figure 5.6 SEM images on the thickness of the SPE.
5.4.2 Thermal and mechanical stability

The thermal stability is considered as one of the important parameters to be considered, in which the degree of crystallinity is a parameter of interest that could be obtained by means of thermo-analytic methods. Typically, the thermal analyses that are conducted on the SPE are the differential scanning calorimetry (DSC) and the thermogravimetry (TGA). The DSC thermogram for the SPE was demonstrated in figure 5.7. The DSC was to determine the amorphous and crystalline content of the SPE. If the

Figure 5.7 DSC thermogram for the SPE-succinonitrile.
SPE film was not homogeneously mixed, regions of crystalline areas would develop and thus result in spikes and peaks on the DSC thermogram. It is clearly seen in figure 5.7 that no sharp peaks are observable from the graph, indicating the amorphous nature of the SPE.

![DSC thermogram for the comparison between SPE-succinonitrile and SPE-glutaronitrile.](image)

In figure 5.8, the two different plasticizers (succinonitrile and glutaronitrile) were used for the ternary SPE film. It could be seen that both plasticizers exhibited no peaks or spikes, which indicated the amorphous of the fabricated SPE membrane.
Figure 5.9 TGA thermogram for the SPE-succinonitrile.

The TGA thermogram was carried out to validate the composition of the SPE. The individual amount of the ternary SPE system could be determined by the weight loss percentage. As it could be seen that there are three major deterioration slopes shown in the figure 5.8, where the first weight loss is approximately 40%, which could be attributed to decomposition of the succinonitrile. The succinonitrile would be firstly removed since it has a relatively lower sublimation temperature in proximity to 100 °C. The second weight loss and the third weight loss slope could be attributed to the rest of the two components,
in which the PEGDA would decompose prior to the Li salt as shown from previously reported\textsuperscript{224}.

![Figure 5.10 TGA thermogram for the comparison between SPE-succinonitrile and SPE-glutaronitrile.](image)

In figure 5.10, the TGA comparison between the different plasticizers was shown. It could be seen that both plasticizers exhibited similar curves indicating that the length of the plasticizer does not have a huge impact on the thermal stability of the SPE film. The pure polymerized PEGDA showed large deterioration upon 400 °C, which is corresponding
to the deterioration observed from the other two SPEs. The SPEs’ PEGDA polymer host deteriorates faster since it was kept in the amorphous state; yet the pure PEGDA polymer host is mostly crystalline thus having a higher deterioration temperature.

Figure 5.11 Pictorial illustration of the SPE membrane undergoing the bending test.

Figure 5.11 shows the series of bending and mechanical abuse of the film, where it could be seen from a1 to a4 the film was bent upwards and b1 to b4 the film was bent downwards. The bend ability of the SPE film suggested the highly flexible nature, which could provide some improvements to the inhibition of lithium dendritic growth. Additionally, the flexible nature of the SPE film could perchance be utilized in wearable technology that requires bendable energy sources.

5.4.3 Electrochemical performances

Ionic transport number, or also named the lithium transference number when the desired subject is the lithium ion. The relationship below holds when the single salt is a monovalent ion,
\[ t^{+/-} = \frac{\mu^{+/-}}{\mu^+ + \mu^-} \]  

(5.6)

where \( \mu \) on the numerator is the mobility, it could be either \( \mu^+ \) or \( \mu^- \) depending on the desired testing subject, the cation or the anion, respectively. The transference number is conventionally being determined by the Hittorf method\textsuperscript{226}; however, it is difficult to be applied for the SPEs. The transference number value could be determined by the utilization of DC polarization and AC impedance, also called the AC/DC method, which was proposed by Bruce et al.\textsuperscript{227} The equation is listed as following,

\[ t^+ = \frac{I_{ss} \cdot (\Delta V - I_0 R_0)}{I_0 \cdot (\Delta V - I_{ss} R_{ss})} \]  

(5.7)

where initially the \( R_o \) value was obtained by the Li/SPE/Li cell configuration by the utilization of AC impedance. Then an application of a small DC pulse of \( \Delta V \) to measure the initial current value of \( I_0 \), and then the steady state current of \( I_{ss} \) after extended period of current passing through was carried out. Eventually, the AC impedance was applied to obtain the final resistance after steady state, \( R_{ss} \). By obtaining all the values, the transference number could be calculated. As shown in figure 5.12, where AC impedance was taken before and after the application of DC polarization, the DC polarization was run for 1000 seconds for the stability of the current; however, it must be noted that the steady state current could take up to three or four times the duration depending on the thickness of the SPE film.
Figure 5.12 The results obtained from the (a) DC polarization and the (b) AC impedance.
From the results obtained by the AC impedance and DC polarization, the value of the transference number was calculated to be around 0.82, which is higher than the liquid based electrolytes yet lower than the ceramic based counterparts. The liquid electrolyte has lower transference number since it contains highly-mobile solvated cations and anions. The ceramic-based solid state electrolytes usually exhibit a lithium transference number in proximity to unity, in which indicates the ion transport is dominated by the lithium ions. The high lithium transference number obtained is due to the entrapment of TFSI\(^{-}\) in the polymer host.

Another important parameter that governs the performance of the SPE film is the ionic conductivity. The ionic conductivity is calculated from the bulk electrolyte resistance that is obtained from the intercept of the AC impedance with the real axis, following the equation below:

\[
\sigma = \frac{1}{A \cdot R_b} \tag{5.8}
\]

where the \(\sigma\) is the ionic conductivity with units of \(S \cdot cm^{-1}\), \(l\) is the thickness of the film with units of \(cm\), \(A\) is the area of the SPE film with units of \(cm^2\), and \(R_b\) is the bulk resistance from the electrolyte that could be measured and calculated by the Nyquist plot from AC impedance with units of \(\Omega\).
Figure 5.13 The relationship between the ionic conductivity and the temperature for the SPE film.

From figure 5.13, it was calculated that the ionic conductivity of the SPE film is approximately $1.1 \times 10^{-3}$ S·cm$^{-1}$ at 25 °C. The top figure shows the ionic conductivity plotted against the reciprocal temperature; whereas the bottom figure simply shows the linear-like relationship between the ionic conductivity and temperature. The extraordinary ionic conductivity has fulfilled several requirements that have been established by governmental agencies. Moreover, as the temperature increases, the ionic conductivity also
increases, which is as expected since the increase in temperature also increases the mobility in the transference of lithium ions. In addition, the polymer host itself at elevated temperature could also be relatively more amorphous, thus resulting in the better ionic conductivity.

Figure 5.14 Electrochemical stability measurements for the SPE film by linear sweep voltammetry.

Linear sweep voltammetry (LSV) result is shown in figure 5.14. The cell configuration to run the LSV is Li/SPE/SS. It could be seen that the initiation of the
electrochemical instability commenced near 5 V, which is associated to the decomposition limit of the SPE film. The SPE film also exhibited excellent performances in the electrochemical stability in comparison to the liquid counterparts, where they typically start to deteriorate over 4 V; the deterioration of the liquid electrolyte highly depends on the type of system that is tested. The decomposition could be caused by the reaction with the metallic lithium that was implemented, or it could also be ascribed to the SPE film itself being activated under high voltages. The stability window for the SPE film is ~5.0 V, ranging from 0 V to 5.0V vs. Li/Li\(^+\), which satisfies many different cathode/anode materials’ operating potential window.

Figure 5.15 Cyclic voltammetry results for the SPE film.
In figure 5.15, the cyclic voltammetry (CV) was utilized to also determine the electrochemical stability of the SPE film. Other than scanning the chemical potential at a constant rate to a higher potential, the CV was used to scan back and forth in a known stable potential window range in order to observe the reversible redox reactions. The larger peaks that are observed on the far left of the plot from the range -0.5 V to 0.5 V correspond to the lithium stripping and lithium plating process.

![Graph of Voltage vs Time](chart.png)

Figure 5.16 Lithium-stripping and lithium-plating measurements for the SPE film.

In figure 5.16, the lithium stripping and plating analysis was carried out to demonstrate the stability of the SPE film. The testing method has the following cell configuration: Li/SPE/Li. The cell was applied an alternating external current to induce the growth of metallic dendritic lithium upon mimicking the charge/discharge protocols. Therefore, if the voltage could be kept in a reasonable and stable range upon the application of the current at an extended amount of time, it suggests that the SPE film is capable of
suppressing the growth of the lithium dendrites. In figure 5.16, it could be seen that the film has been cycled for more than 600 hours under an external current of 0.06 mA; while the voltage range has yet to expand to a larger voltage range (typical failure of the cell as the voltage differences increase and eventually short-circuits), indicating the electrochemical stability of the SPE film.

5.4.4 Battery performances

As mentioned in the experimental section that two different systems of batteries were tested using the SPE film – the Li-ion battery and the Li-S battery.

![Figure 5.17 Li-ion battery half cell with composite LFP as the electrode.](image)
In figure 5.17, the performance of the Li-ion battery is shown; the composite LFP is used as the electrode material. The half cell configuration is Li/SPE/composite-LFP. The Li-ion battery was carried out with a current density of 30 mA·g⁻¹ initially for 10 cycles and then 50 mA·g⁻¹ in the following cycles. The initial capacity is low yet as the charge and discharge of the battery proceeds, the battery reaches a stable specific capacity of approximately 145 mAh·g⁻¹, the phenomenon was also observed in several all-solid-state electrolyte literatures²³⁴. The theoretical energy density of the LFP is 170 mAh·g⁻¹ according to table 5.1, and the SPE film was designed to be capable of achieving similar values to the liquid electrolyte counterparts. Additionally, in comparison to the previously reported work²²⁴, the LFP composite electrode contains a higher mass loading due to the processing technique, which enables better cycle stability with higher specific capacities. The Coulombic efficiency of the LFP composite electrode exceeds 99.5%, so that the fading issue would not pose as a huge problem for extended numbers of cycles.

The SPE film was also tested for the Li-S battery system. The Li-S battery utilized the same electrode described in chapter III with a current density of 0.05 C (corresponding to 83.75 mA·g⁻¹) to test the cycle stability of the cell. In figure 5.18, it could be seen that the initial discharge capacity was nearly 1400 mAh·g⁻¹, while the following cycles remained at a discharge capacity of nearly 600 mAh·g⁻¹ for more than 100 cycles. S1 and S2 are the discharge capacities for two different samples under the same conditions, where both of the battery exhibited similar capacities demonstrating the repeatability of the performance. The Coulombic efficiency of the Li-S battery was also in proximity to 100%, suggesting the good cycle stability of the battery.
5.5 Conclusions

The SPE film was fabricated at the ratio of 25:35:40 for the LiTFSI salt, PEGDA polymer host and succinonitrile plasticizer, respectively. It was shown by various characterization techniques that the SPE film is thermally, mechanically and electrochemically stable under the testing conditions. The SPE film was then further utilized in two different battery systems including the Li-ion and the Li-S. The Li-ion battery could achieve good cycle stability up to 80 cycles with a specific capacity of approximately 145 mAh·g⁻¹ at room temperature condition and current density of 50 mA·g⁻¹ with the utilization of composite LFP electrode. The Li-S battery could achieve up to 100 cycles with a specific capacity of nearly 600 mAh·g⁻¹ at a current density of 0.05 C. This work demonstrated that with the integration of a highly ionic conductive SPE film, the
battery system could still retain satisfactory energy densities that are comparable to literature reports while enhancing the safety of the battery.
CHAPTER VI
SUMMARY AND CONCLUSION

In summary, in order to fabricate a battery that has higher energy density in comparison to the current prevailing Li-ion battery, advanced electrochemical energy storage devices or namely, next-generation batteries were made to couple with ordered carbonaceous nanomaterials including the VACNTs in attempt to increase the energy density and cycle stability. Initially, the carbon nanomaterials such as graphene and VACNTs were fabricated through the use of the CVD. The VACNTs were chosen and further grown under a series of trial and error testing to provide the optimized length for the subsequent application. The VACNTs were then characterized by many instruments for instance, Raman spectroscopy, SEM and TEM to further validate the successful growth of the VACNTs. The VACNTs were then made into a Li-O$_2$ battery with the LiTFSI and NMP electrolyte. The Li-O$_2$ battery exhibited reversible specific capacity of 1200 mAh·g$^{-1}$ for 50 cycles under the safe charge and discharge protocol; while under full discharge and charge protocol, the Li-O$_2$ battery shows a high specific capacity of around 6000 mAh·g$^{-1}$. The safe charge and discharge protocol was utilized in order to prevent the build-up of reversible yet non-conductive Li$_2$O$_2$ discharge product, which could result in the deterioration of the battery. Finally, post-electrochemical characterizations were conducted to identify the discharge product of Li$_2$O$_2$ by XRD, Raman spectroscopy and SEM.
Another order nanomaterial that was fabricated was the MOF. The ZIF-8 was selected from the MOF due to the high surface area and thermal/chemical stability. The ZIF-8 was synthesized by simple mixing of Zn(NO$_3$)$_2$·6H$_2$O and 2-MeIm in methanolic solutions. Then, the as-prepared ZIF-8 crystals were further carbonized to produce the cZIF-8 ordered carbonaceous nanomaterial. The cZIF-8 was melt-infiltrated with sulfur to obtain the composite cZIF-8/S electrode. The cZIF-8/S electrode was combined with the advanced electrochemical energy storage system of Na-S in attempt to provide high energy density. The Na-S battery was carried out at room temperature in order to give a safer battery. The cZIF-8 and cZIF-8/S were characterized to both qualitatively and quantitatively determine the amount of nitrogen-doping and the amount of sulfur infiltrated. The RT-Na-S battery was capable of exhibiting a specific capacity of 500 mAh·g$^{-1}$ at a current density of 0.2 C up to 250 cycles, which was comparable to state-of-art RT-Na-S batteries. Ratability of the RT-Na-S battery was also tested to demonstrate the capability of performing at higher rates. Post-electrochemical characterizations such as SEM and XPS were conducted to illustrate the structural morphology of the cZIF-8/S electrode, where the single crystal particle remained intact after cycling for a hundred times. It was speculated that the microporous/mesoporous structure of the cZIF-8 and the high nitrogen doping content synergistically contributed the excellent performance of the RT-Na-S battery.

N,S-HPC was also utilized as the order carbonaceous nanomaterial host to encapsulate the sulfur for RT-Na-S battery. The N,S-HPC was synthesized and then carbonized using a tube furnace prior to sulfur melt-infiltration process. The as-obtained N,S-HPC/S along with its precursor N,S-HPC material were characterized to demonstrate the uniformity of the structure, nitrogen/sulfur doping content, and the amount of sulfur
infiltrated within the carbonaceous matrix. The N,S-HPC/S composite electrode was fabricated to test for the electrochemical performance. The N,S-HPC/S based composite electrode exhibited a long cycle performance of over 10,000 cycles running under a current density of 4.6 A·g⁻¹ while providing an energy density of nearly 100 mAh·g⁻¹. Subsequent characterizations were carried out in attempt to support the phenomenon of nitrogen doping being the chief factor in inhibiting the sodium polysulfide from shuttling; which is the reason of such extraordinary performance.

Due to the advancement in technology, many electronic devices and heavy machinery require battery that could last longer, in other words, a battery with higher energy density is highly desirable. Amongst all the cathode materials for Li-ion battery or the anode materials for next-generation batteries, the metal lithium or metal sodium possess the highest energy density; however, due to the highly reactive nature of these metallic electrodes, they could not be directly utilized in commercial products due to safety concerns. The introduction of the SPE could be the resolution to enable the utilization of these metallic electrodes. SPE film was synthesized by combining LiTFSI salt, succinonitrile or glutaronitrile and the PEGDA polymer host at an optimized ratio as the replacement for the liquid electrolyte. The SPE film was characterized to determine the thermal stability, mechanical properties and the electrochemical stability. Among a myriad of characterizations, the ionic conductivity is one of the most important parameter to determine the usefulness of the film. The prepared SPE exhibited an ionic conductivity of 1.1 \times 10^{-3} \text{S} \cdot \text{cm}^{-1}, which is comparable to lower end liquid electrolytes. The SPE was integrated into a composite LFP electrode to demonstrate the superior performance of all-solid-state Li-ion battery. The Li-ion battery exhibited specific capacity of around 145
mAh·g⁻¹ at a current density of 50 mA·g⁻¹ for more than 50 cycles. The integration of the SPE film into next-generation battery systems including the Li-S battery also showed excellent performances, where a specific capacity of nearly 600 mAh·g⁻¹ was observed under a current density of 0.05 C for more than 100 cycles. The compatibility of the SPE film in both conventional Li-ion battery and the advanced Li-S battery demonstrated the promising future of the SPE system proposed.

It was mentioned in both the abstract and introduction that the main incentive and the objective of the work were to enhance the performance of the advanced ordered electrodes in different battery systems. Both the Li-O₂ battery and the Na-S batteries exhibited commensurate or better performance compared to the current state-of-art Li-O₂ battery and Na-S batteries. In addition, preliminary results regarding the utilization of a pure metal indicate that the SPE system is a promising candidate to at once provide more safe batteries and enable the usage of pure metal electrodes. Despite the fact that the designed ordered advanced electrodes were not able to drastically change the field of energy storage devices, and thus unable to live up to the motivation in reducing the global warming effect caused by the emission of green-house gases. It is anticipated that the designed electrodes and the SPEs could give an insight and be used as a stepping-stone for future developments.
CHAPTER VII

FINAL REMARKS AND SUGGESTIONS FOR FUTURE STUDY

The dissertation was supported by the start-up funding from the University of Akron, National Science Foundation (NSF) through NSF-CBET 1505943 and 1336057, ACS Petroleum Research Fund (PRF#53560-DNI 10) and DOE STTR (DE-SC0013831) through pH Matter LLC.

The dissertation has covered three large topics on the fabrication of the Li-O₂ battery, the fabrication of the RT Na-S battery, and the development of a SPE membrane. In order to fabricate an energy storage device that shows extremely high energy density while providing high safety reliability, it is essential to employ SPE membranes that are compatible into the next-generation batteries. It was demonstrated in Chapter V that the ternary SPE system is capable to deliver good cycle stability while exhibiting satisfactory energy density. The cathode of the lithium-ion battery was based on LFP, which is an active material designed to provide higher stability whereby sacrificing the maximum energy density. The utilization of other higher energy density containing active cathode materials could be utilized to substitute the LFP, for instance the NCM and NCA. Both the NCM and NCA have been commonly implemented into liquid electrolyte based lithium-ion batteries; but not much has been reported with the combination of solid-state electrolytes, which could be perchance attributed to compatibility or contact issues. Therefore, the
energy density could be enhanced as higher theoretical energy density active materials are employed. In fact, preliminary results using the NCM turned out to be positive.

Figure 7.1 The integration of SPE with the NCM cathode materials.

It was could be seen that the first two cycles of the NCM cathode coupled with the SPE membrane with 2wt% LiBOB salt could exhibit excellent specific capacity that is commensurable to the liquid based electrolyte; however, subsequent cycle stability would have to be ameliorated in order to be put into actual use.

Based on the understanding with the currently developed SPE membrane, despite showing high ionic conductivity at room temperature conditions, the mechanical properties of the film could be an issue if being considered for future commercialization. The addition of the plasticizer in the SPE could enhance the amorphousness yet the trade-off is the reduction in the strength of the membrane. To improve the mechanical strength of the membrane, many possible enhancements could be integrated to increase the strength and
toughness of the film while not sacrificing the high ionic conductivity. The first method is to integrate ionic conductive ceramic (or metal oxides) particles or fibers into the SPE. The particles could act as fillers to further increase the amorphousness of the SPE membrane and thus theoretically increase the ionic conductivity; moreover, the ceramic particle itself could also act as local crystalline points for the improvement in mechanical property. The ceramic fibers could achieve similar effects while providing even better matrices to enhance the mechanical properties. The second method is to simply introduce an inert non-electric conductive porous polymer membrane in combination with the SPE. Porous polymeric membrane for instance Celgard® separators or polymer aerogels shown in figure 7.2 with high porosity could be infused with the SPE, thus with the porous polymer membrane acting as the matrix, the mechanical integrity could be assumed. The third method could be the combination of the first and second method, where the inert filler filled SPE is infused in the inert polymer membrane could induce a synergy in giving better mechanical strength and better ionic conductivity.

Figure 7.2 (a) Conventional Celgard® membranes (b) syndiotatic polystyrene membrane aerogel with high porosity.
These modified SPE membranes could further be utilized in the next generation battery systems. In Chapter V, Li-S batteries using SPE were demonstrated to exhibit excellent performance at a relatively lower current density rate compared to its liquid based electrolytes. Similar studies could be tested for the Li-O₂ battery systems, where the VACNT could be used as the cathode. However, instead of the free-standing VACNT utilized in Chapter I, VACNT directly grown on stainless steel mesh (shown in figure 7.3) as the cathode could be more feasible due to the better contact with the current collector.

Figure 7.3 (a) SEM images of the VACNT grown on stainless steel mesh, (b) a zoom in at the edges of the VACNT growth site and bare stainless steel mesh.

As it could be seen in Chapter I, the free-standing VACNTs are very dense and thus the integration of the SPE precursor liquid could be a difficult task in penetrating and accessing the active material. Whereas, specially designed pattern grown VACNTs are more sparsely dispersed in which enables better penetration of the SPE precursor liquid and thus more active materials could be more readily accessible. The use of the SPE
membrane could reduce the potential O$_2$ side reactions directly with the Li metal, so the Li metal could remain more active as reactions proceed. However, the issue regarding the use of the SPE membrane with the Li-O$_2$ battery would arise with the capability of the O$_2$ being introduced into the reaction and also the possible deterioration of the SPE upon long term exposure to O$_2$ or moisture. Regardless, with the integration of the SPE with Li-O$_2$ battery systems, safer battery configuration could be ensured and thus potentially enables the possibility to commercialization.

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