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Carbon-Based Nanostructured Materials as Electrode in Lithium-Ion Batteries and Supercapacitors

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Carbon-based Nanostructured Materials as Electrodes in Lithium-Ion Batteries and Supercapacitors

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering

By

Zhuo Yao
B.E., Dalian Jiaotong University, 2010

2013
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Zhuo Yao ENTITLED Carbon-Based Nanostructured Materials as Electrodes in Lithium-ion Batteries and Supercapacitors BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Engineering.

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ABSTRACT

Yao, Zhuo. M.S.Egr, Department of Mechanical and Materials Engineering, Wright State University, 2013

“Carbon-based Nanostructured Materials as Electrodes in Lithium-ion Batteries and Supercapacitors”

Carbon-based nanocomposites attract much attention as electrode materials in electrochemical energy storage systems due to their low-cost, extraordinary high electrical and thermal conductivity, super high surface area etc. In this research, graphene nanosheets (GNS) and their nanocomposites with manganese oxides (GNS/MnO\textsubscript{x}) or silicon nanowires (GNS/SiNWs/CF) are studied for their applications in Li-ion batteries and supercapacitors. GNS powders are synthesized via a chemical oxidation of nature graphite followed by appropriate reduction process. GNS/MnO\textsubscript{x} composites are synthesized rendering MnO\textsubscript{x} nanoparticles embedded on the surfaces of GNS. SiNWs grown in carbon fibers are mechanically mixed with GNS powders. The impacts of the manganese valence and GNS content in the GNS/MnO\textsubscript{x} nanocomposites on the lithium storage characteristics in terms of Coulombic efficiency, capacity, cycle life, and rate capability are investigated experimentally. GNS/MnO\textsubscript{x} hybrid anode material shows a high reversible lithium storage capacity up to 838 mAh/g with a Coulombic efficiency of 65%, good cyclic performance with 0.8% fading per cycle, and high rate capability with 67% at the current density of 800 mA/g. The GNS/SiNWs/CF hybrid exhibits high reversible
discharge capacity of 975 mAh/g with Coulombic efficiency of 85.7%. Further the capacitive charge storage characteristics of both GNS and GNS/MnO$_x$ are studied in ionic liquid electrolytes and aqueous electrolytes, respectively. Supercapacitors consisting of GNS electrodes in EMIMBF$_4$ ionic liquid electrolyte show the high specific capacitance of 109 F/g, good cyclic life of over 1000 cycles, high power density of 44.4 kW/kg, and high energy density of 256 Wh/kg etc. Supercapacitors consisting of GNS/MnO$_2$ nanocomposite electrodes in Na$_2$SO$_4$ aqueous electrolyte deliver specific capacitance up to 164 F/g. This study shows significantly improved electrochemical performances in lithium-ion batteries and supercapacitors by using GNS-based composites.
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Chapter 1: Introduction

Electrochemical energy conversion systems have many advantages in terms of high energy conversion efficiency, high energy density, freedom from noise pollution, and good mobility etc. Lithium ion batteries (LIBs) and supercapacitors are two most common electric energy storage devices based on electrochemical principles. LIBs, having the highest energy density among different kinds of batteries, no environment effect, low self-discharge rate, and excellent long cycle life, etc, are now widely used in consumer electronics such as laptops, cell phones, and personal digital assistants (PDAs) [1] and are also very popular in military, hybrid electrical vehicle (HEV), and aerospace applications. Supercapacitors due to the high power density, and outstanding long cycle life etc., have tremendous application values and market potential in electrical vehicles, communication, and national defense.

1.1 Lithium-ion Batteries and Anode Materials

A battery is made up of one or a group of interconnected electrochemical cells, depending on the specific application it is designed for. An electrochemical cell consists of a cathode (positive electrode), anode (negative electrode) separate with an ionic conducting electrolyte. The electrical energy is generated by the redox reactions between the cathode and anode. Redox is short for reduction-oxidation, and is an electrochemical processing involving electron transfer to or from a molecule or ion changing its oxidation state.
LIBs using the insertion compounds as anode are developed from lithium batteries to tackle the safety problem because of high chemical activity of lithium anode. The discharge/charge process of a LIB is a reversible process of lithium ions insertion/extraction into/from the host electrode materials, with no formation of metallic lithium at the anode side. On charging, lithium ions transport from the cathode to electrolyte and then intercalate into the carbonaceous anode material. Electrons are removed from cathode through an external circuit to the anode. On discharging, the lithium ions which are intercalated in the anode transport back to the cathode, and oxidation reaction occurs at the anode and reduction at the cathode [2]. A schematic of a typical Li ion cell is shown in Fig 1.1 [2].

![Figure 1.1 Schematic illustration of charge-discharge process in a lithium ion cell.](image)

Depends on different requirements and applications, various types of carbons, e.g. graphite, coke, and mesocarbonmicrobeads (MCMB), whose electrical potentials are close to the potential of Li are always chosen as anode materials. Common cathode materials are lithium transition metal compounds LiM_yX_z(M represents the transitional metal like Fe, Co, Ni, Mn, etc, while X represents the anion). Electrolyte
can be either liquid or solid. Liquid electrolyte is usually non-aqueous solution of lithium salt such as LiClO$_4$, LiPF$_6$, and LiBF$_4$ and various solvent including different kinds of ethers, esters and carbonates. The reactions at both electrodes and the whole Li ion cell can be shown as the following:

Cathode: \[ \text{Li}_{1-x}M_yX_z \leftrightarrow \text{Li}_{1-x} \delta M_yX_z + \delta \text{Li}^+ + \delta \text{e} \quad (1-1) \]

Anode: \[ \text{Li}_x \text{C}_n + \delta \text{Li}^+ + \delta \text{e} \leftrightarrow \text{Li}_x + \delta \text{C}_n \quad (1-2) \]

Overall: \[ \text{Li}_{1-x}M_yX_z + \text{Li}_x \text{C}_n \leftrightarrow \text{Li}_{1-x} \delta M_yX_z + \delta \text{C}_n \quad (1-3) \]

Li-ion batteries, compared with the other types of high-performance secondary batteries, have many significant advantages:

- High work voltage. Due to using carbon as the negative electrode which has a relative lower electrical potential (0.01-1.5V vs. Li/Li$^+$), the loss of voltage will be reduced to the minimum level. Li-ion batteries have a high working voltage around 3.6V, which is equivalent to three Ni-Cd or Ni-M$\text{H}_3$ batteries.

- High energy density. Because the high working voltage and capacity, the energy density is high. At present, the specific energy of Li-ion batteries can be as high as 180Wh/kg which is four times higher than Ni-Cd batteries and two times higher than Ni-M$\text{H}_3$.

- The efficiency of charge-discharge can be as high as 100%.

- Low self-discharge rate. When a Li-ion battery is charging at the first time, there will be a layer of solid-electrolyte interface (SEI) film forming on the surface of electrodes. Ions are able to pass through the SEI, but the electrons will not. For this reason, the self-discharge rate of the Li-ion battery is effectively prevented.

- Environmental friendly. The Li-ion battery doesn’t consist of poisonous elementals such as Hg, Pb, and Cd.
Theoretically, all the materials which have a relative low electric potential compared with lithium metal, and the lithium ions are able to insertion and extraction in them can be used as anode materials. In addition, ideal anode materials require the following features: 1) good charge/discharge reversibility and cycling perdurability; 2) low first irreversible capacity; 3) good compatibility with electrolyte solution; 4) relative high specific capacity; 5) safety and environmental friendly; and 6) the cost is low, etc. Different types of anode materials are listed in Table 1.1.

Table 1.1 Different Types of Anode Materials Used in Li-ion Batteries

<table>
<thead>
<tr>
<th>Material</th>
<th>Theoretical capacity (mAh/g)</th>
<th>Practical capacity (mAh/g)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>372</td>
<td>250</td>
<td>Low cost, safe</td>
<td>Low charge capacities</td>
</tr>
<tr>
<td>Hard Carbon</td>
<td>372</td>
<td>418</td>
<td>High specific capacity</td>
<td>High irreversible capacity and poor cyclic performance</td>
</tr>
<tr>
<td>Carbon Nanotubes</td>
<td>782</td>
<td></td>
<td>High charge-discharge capacity and cyclic performance</td>
<td></td>
</tr>
<tr>
<td>Graphene</td>
<td>744</td>
<td>350</td>
<td>Good mechanical properties, High theoretical capacity</td>
<td>irreversible capacity is high and voltage hysteresis</td>
</tr>
<tr>
<td>Metal oxide composites</td>
<td>880</td>
<td>700</td>
<td>High theoretical capacities</td>
<td>Poor cyclic performance</td>
</tr>
<tr>
<td>Tin-based Material</td>
<td>994</td>
<td>400</td>
<td>High theoretical capacities</td>
<td>Poor cyclic performance</td>
</tr>
<tr>
<td>Si</td>
<td>4200</td>
<td>2158</td>
<td>High theoretical capacities, Good cyclic performance, high capacity</td>
<td>Poor cyclic performance</td>
</tr>
<tr>
<td>Si-Carbon composite</td>
<td>850</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.1.1 Carbon Anode Materials:

Since lithium insertion in carbons was reported in 1980s, carbon materials are widely used as the anode material. The insertion and extraction of lithium ions in carbons, during the charge/discharge process, does not cause dramatic volume change. On this account, the cycle life and safety are much better than that of lithium metal batteries. Lithiated carbon has a potential very close of metallic lithium (potential difference between lithiated carbon and lithium metal is \(\leq 0.5V\)) which result in Li-ion batteries a comparable whole cell voltage to the lithium metal batteries [3].
Extensive studies in the past decades revealed that the morphology of different carbonaceous materials plays an important role in the lithium insertion process.

The theoretical capacity of natural flake graphite (NFG) is 372 mAh/g (based on the formation of LiC$_6$), 10 times lower than that lithium metal (3862 mAh/g). Practically, the reversible capacity is only about 300-350 mAh/g because of the impurities and defects existing in graphite powders. NFG is also sensitive to the electrolyte solution resulting in low value of first Coulombic efficiency and poor cycle life performance. Several methods were applied to improve the electrochemical performances of NFG, from mild oxidation[4], polymer coating [5], to metals or metal oxides deposition [5, 6]. For instance, shown in figure 1.2, the NFG anode showed the recharge capacity of 330.7 mAh/g with the Coulombic efficiency of 73.4%. After the mild oxidization and carbon coating process, the first charge capacity increased to 344.7 mAh/g and 359.7 mAh/g with the Coulombic efficiency of 89.7% and 83.2%, respectively.

![Figure 1.2 The first charge-discharge curves of nature flake graphite (NFG), mild oxidized graphite (MGO), and carbon-coated MGO (C/MGO) [7].](image-url)
Hard carbon is formed by interlaced single-layer graphite nanosheets. When lithium ions are intercalated into it, Li ions can be adsorbed on both sides of the single-layer graphite sheet leading to a higher specific lithium storage capacity. Different from NFG, there is no obvious voltage platform in the charge/discharge curves of hard carbons, which is beneficial to estimate the state of charging and discharging in Li-ion batteries. In addition, it is clarified lithium metal deposition does not occur up to 110% over-discharge of the reversible capacity of hard carbons [8]. Whereas in the case of graphite, the lithium metal deposition will occur at 105% over-discharge. So the safety is improved by using the hard carbon as anode material. High irreversible capacity and poor cyclic performance are the main limitations for hard carbons. Some methods are applied to improve the electrochemical performance, such as 1) reducing the impurities of H, so that the specific capacity and cyclic performance will be enhanced [9] and 2) synthesizing the hard carbons under vacuum to reduce the initial irreversible capacity [10]. Figure 1.3 shows the first charge-discharge curves for a hard carbon and two types of porous hard carbons treated by different chemical process methods [11]. The initial discharge and charge capacities of the as-prepared specimen were 802.7 mAh/g and 223.9 mAh/g with the Coulombic efficiency as low as 27.9%. In contrast, the discharge capacities of other two types of porous carbon material were increased to around 1100 mAh/g with the Coulombic efficiency about 40%.
Figure 1.3 First charge-discharge curves for a hard carbon (HC) and two types of porous carbons (PC-1 and PC-2).

Figure 1.1 The discharge-charge curves for graphene sheets [13].

Carbon nanotubes (CNTs) are allotropes of carbon with cylindrical nanostructure. CNTs with nano-sized tube diameter as well as interlaced apertures between the tubes, provide superior intercalation media for high-capacity lithium storage. Lithium ions can not only embed inside the tubes, but also in the apertures between the tubes.
Graphene is another unique carbon allotrope which has a two-dimensional crystal lattice structure. Graphene has outstanding mechanical properties, thermal and electrical conductivities, and large specific surface area, offering great advantages for application in Li-ion batteries. It is reported that graphene nanosheets have theoretical capacity of 744 mAh/g, which corresponds to insertion of one lithium ion per 3 carbon atoms[12]. Figure 1.4 presents the first discharge-charge profiles for graphene nanosheets as anode material at the current density of 100 mA/g. The initial discharge and charge capacities were as high as 2035 and 1264 mAh/g with the Coulombic efficiency of 62.1%. However, some problems, such as high irreversible capacity and large voltage hysteresis etc., need to be solved before it can be partially utilized in Li-ion batteries.

1.1.2 Metal Oxides:

A variety of different metal oxides has been developed as anode materials for LIBS. These metal oxides anodes have many distinguished features, such as high capacity, environmental friendly, and good stability, etc. Typically, there are three sorts of metal oxides, namely tin dioxide (SnO$_2$), titanium dioxide (TiO$_2$), and transition metal oxides, which are categorized by their own distinct lithium storage mechanisms and characteristics.

Tin oxide (SnO$_2$) reacts with lithium through a two-step reaction: firstly, the tin oxide is reversibly reduced to tin which is simultaneously embedded in the matrix of Li$_2$O; and then tin reversibly alloys with lithium. This procedure can be expressed by the following equations:

$$4Li^+ + 4e^- + SnO_2 \leftrightarrow 2Li_2O + Sn$$

$$Sn + xLi^+ + xe^- \rightarrow SnLi_x \ (0 \leq x \leq 4.4)$$
The theoretical lithium storage capacity of SnO$_2$ is as high as ~790mAh g$^{-1}$, which is almost twice higher than that of graphite (~372mAh g$^{-1}$). Figure 1.6 shows the first discharge-charge curves for a nanocrystalline SnO$_2$ anode material. There is a significant horizontal plateau in the 1 V region and a monotonous decrease below the 0.5 V region. The first discharge/charge capacity was 1735 and 665 mAh/g with the Coulombic efficiency of 38.3%. However, the biggest obstacle prevents tin oxide using in practical application is the large volume change during charge and discharge process which leads the pulverization of the electrodes [14].

![Figure 1.2 First galvanostatic discharge-charge curves for SnO$_2$[15].](image)

TiO$_2$ is another kind of metal oxides anode material with distinct electrochemical characteristics. There are eight polymorphs TiO$_2$ well known as rutile, anatase, spinel, TiO$_2$-B, TiO$_2$-R, TiO$_2$-H, TiO$_2$-II and TiO$_2$-III[16]. No matter which types of TiO$_2$ the insertion reaction of Li ions into TiO$_2$ matrix can be generally expressed as the following equation [17]:

$$\text{TiO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{TiO}_2$$
TiO$_2$ has many promising advantages such as good stability, low volume expansion when lithiation, and ease of structure tailoring. However, TiO$_2$ delivers a relative low capacity (~170 mAh g$^{-1}$) which limits its application. Researchers believe that this problem can be overcome through the nanostructure modifications [18, 19]. In addition, with the decreasing of particle size, the ratio of atoms resides near the surface layers have been increased hence increased surface Li storage. The transport length for Li insertion into the bulk of TiO$_x$ will be decreased, and the Li insertion will be more efficiently. As can be seen from figure 1.5, the initial discharge capacities were increased from 110 to 378.4 mAh/g with the particle sizes decreased from 300 nm to 15 nm. Also, about 0.7 Li (264 mAh/g) per unit rutile TiO$_2$ can be reversibly extracted from particles with a size of 15 nm [20].

![Figure 1.3 First three galvanostatic discharge-charge curves for rutile TiO2 with different particle sizes [21].](image)

Transition-metal oxides (TMO, $TM = Co, Fe, Ni, Cu$ etc) have been reported to have over 700 mAh/g theoretical capacities. The mechanism of Li reactivity differs from the classical Li insertion/de-insertion (like TiO$_2$) or Li-alloying processes (like SnO$_2$). Lithium reacts with such TMO anodes involving reversible formation and decomposition of Li$_2$O, accompanying the reduction and oxidation of metal.
nanoparticles (in the range 1-5 nanometers) [22]. This reaction procedure can be depicted by the following equation [23]:

$$2e^- + 2Li^+ + TMO \leftrightarrow xLi_2O + M$$

The electrical conductivity of transition-metal oxides is relatively low, and the volume change during the charge-discharge process is high, so the discharge rate and the cycling stability are poor. Reducing the material size will promote the secondary reaction on the surface of the material leading to high irreversible capacity and shorten the cycling performance. The micromorphology of the material affects the electrochemical performance greatly. Taking Co$_3$O$_4$ for example, the electrochemical performance of macroporous Co$_3$O$_4$ plates is superior to that of nanoparticles and rod-like nanoclusters [24]. Using the composite material to enhance the stability of the transition-metal oxides also attracts significant research interest. Zhang et al. [25] have successfully synthesized the carbon coated iron oxide nanospindles which enhance the conductivity of the electrode and lead to stabilized SEI films.

![Figure 1.4 First galvanostatic discharge-charge curves for Co$_3$O$_4$][26.](image)

**1.1.3 Alloy-based Materials:**

In 1971, Dey [27] found that lithium can be electrochemically alloyed with some metals, like Sn, Pb, Al, Cu, Mg, Zn, Ag, Cd and Si etc, at room temperature. The
theoretical capacity of tin is 994 mAh/g which is higher than that of graphite. However, the volume change is great during the alloying/dealloying. So the key factor to improve the electrochemical performance of metal-based anodes is to increase the cycling performance. Tin alloys (SnM, M=Cu, Ni, Fe, and Co, etc) materials showed excellent processing performances, good electric conductivity, and not as sensitive to the environment as the graphite anode materials. There is a promising prospect to replace the graphite anode materials. By changing the preparation methods to obtain the nano-sized tin-based anode materials is a direction for the research in the future. However, with reducing the size of the material there are some side effects, such as the oxidation on the surface leading to the increasing of initial irreversible capacity and the trend of aggregation will increase.

Silicon is an attractive alloy-based anode material for its highest theoretical capacity (4200 mAh/g), and it is low cost and environment friendly. Similar to tin, during the lithium ions insertion and extraction process the volume change by 400% which will cause the electrode crushing and capacity fading. To circumvent this problem, several research efforts have been carried out to disperse fine Si particles within a solid, mixed conducting host matrix [28]. Carbonaceous materials are the most common materials which act as both the electrochemically active materials and the structural buffer materials. There are many advantages by using carbonaceous materials as host matrix. First of all, the electric contact can be greatly improved because of the high electric conductivity of carbonaceous materials. Furthermore, carbonaceous host matrix can effectively remit the internal stress during the charge/discharge process so that the volume of electrodes will not change greatly. At last, carbonaceous materials can also contribute to the reversible capacity. Graphite, graphene, mesophasemicrobeads (MCMB), etc. have been used as the host matrix for
silicon. Preparing the nano-sized and micro-organized Si-based materials as negative electrode to overcome the pulverization problem and enhance the cycling life performance is another hot area in recent years. Various types of Si nanomaterial have been studied in the last four years, including Si nanowires, Si nanotubes, and Si hollow nanoparticles [29]. A high specific capacity of ~3500mAh g⁻¹ has been achieved, which almost reached the theoretical capacity of silicon. At the same time, the energy density and power density are increased significantly, and it allows the battery working at high operation rate.

Figure 1.5 SEM images of different nanostructured silicon anodes, (a) Si/carbon composite [30], (b) silicon nanowires [31], (c) silicon nanotubes [32] and (d) silicon hollow particles [33].
1.2 Supercapacitors and Related materials

The structure of supercapacitors is similar to that of batteries in design and manufacturing. As shown in Fig 1.9[34], an supercapacitor consist of two electrodes, an electrolyte, and a separator [35]. When charging/discharging, opposite charges accumulate on the surface of each electrode forming the electrical field that allows the supercapacitor to storage energy. The most important task in supercapacitors is to fabricate nanoscale electrode materials which have high surface area and/or high porosity.

![Diagram of a supercapacitor](image)

Figure 1.6. Principle of a single-cell double-layer capacitor and illustration of the potential drop at the electrode/electrolyte interface [34].

Generally speaking, supercapacitors can be classified into two categories, based on the energy storage mechanism [36]. One is called electrical double layer capacitor (EDLC), and the other is pseudo-capacitor. In the EDLCs, the capacitance comes from the pure electrostatic charge accumulated at the electrode/electrolyte interface. Since there is no transfer of charge between the electrode and electrolyte, there are no
chemical or composition changes associated with non-Faradic processes. Because of these, electrical energy storage in EDLCs is highly reversible and hence very long cycle life. In contrast to EDLCs, the electric energy storage mechanism in pseudo-capacitors involves charge transfer between electrode and electrolyte, which is accomplished through electrosorption, reduction-oxidation reactions, and intercalation processes [37, 38]. Due to this reason, the energy densities and capacitances of pseudo-capacitors may be greater than EDLCs but cycle life will be shorter [39, 40].

There are three common electrode materials used in supercapacitors: carbons, metal oxides, and conducting polymers. Not only the electrode material affects the performance of supercapacitors strongly, but also the electrolyte is an important component. When operating at high voltage, the supercapacitors provide high power density and energy density. However, it is limited by the performance of electrolyte applied, such as electrochemical stability, voltage window, and ionic concentration. In general, the electrolyte applied in supercapacitors can be classified into three categories, aqueous electrolyte, organic electrolyte, and ionic liquids (ILs).

1.2.1 Electrode Materials of Supercapacitors

Carbon Materials:

Carbon based materials are seen as prospective electrode materials in this application. There are many advantages for carbon materials, such as low cost, easy processing, abundance, environmental friendly, good electronic conductivity, higher specific surface area, wide operating temperature range, and high chemical stability [41]. Carbon materials are always used in EDLCs. Lots of porous carbon materials with well-controlled uniform pore size have been synthesized [42], since the porous
carbons were first synthesized by Knox, et al. [43]. Figure 1.10 (a) shows a typical cyclic voltammogram of an activated carbon in aqueous electrolyte.

Activated carbons have a complex structure composed of different size pores to achieve high surface areas. Theoretically, the capacitance of supercapacitors strongly depends on the surface area of electrode materials. However, not all of the high surface area active carbons have higher capacitances. When the surface areas are electrochemically inaccessible to conducting ions in electrolyte, such as closed pores or electrolyte ions are too large to get into the micropores [44], these surface area may be not fully effectively utilized in charge accumulation. As a consequence, the capacitance of various materials does not linearly increase with the increasing of the specific surface area [35]. It was observed that a porous carbon with a surface area as high as 3000 m² g⁻¹ only had a specific capacitance < 10 μF cm⁻², which is much smaller than the theoretical EDL capacitance (15-25 μF cm⁻²) [45].

Recently, nanostructured carbon allotropes like carbon nanotubes and graphene nanosheets have attracted great attention in using as the electrode materials because of their superior electrical properties and highly surface area. The mesopores in carbon nanotube electrodes are interconnected, so the utilizing of surface area is more efficiently to achieve higher capacitances. The electrolyte ions are allowed to transfer freely inside the nanotubes. Details of graphene-based electrode materials in supercapacitors will be addressed in Chapter 4.

**Conducting Polymers:**

Conducting polymers are rendered conductive through a conjugated bond system along the polymer backbone. Typically, they are from either chemical oxidation or electrochemical oxidation reaction of the monomer [46]. There are many advantages for using conducting polymers as electrode materials for supercapacitors such as high
voltage window, high storage capacity, low cost, and adjustable redox activity through chemical modification [47, 48]. It is believed that the n/p-type polymer configuration, with one negatively charged and one positively charged conducting polymer electrode, has the greatest power density and potential energy. However, there are also some disadvantages by using conducting polymers. Firstly, the n-doped conducting polymer materials prevented the pseudo-capacitors from reaching their potential [40, 49]. Secondly, the stability of the pseudo-capacitors is limited by the mechanical stress on conducting polymers during the reduction-oxidation reactions [50]. Figure 1.10 (b) shows a typical cyclic voltammogram of PPy/VCF polymer-carbon fiber composite electrode in aqueous electrolyte.

**Metal Oxides:**

Metal oxides are always used as electrode materials for pseudo-capacitors. In general, metal oxides show higher capacitance than carbon materials, and more stable than conducting polymers. Ruthenium oxide (RuO₂) attracts more attention in aqueous-electrolyte based supercapacitor (see figure 1.10 c ) than other metal oxide materials because of its high proton conductivity, long cycle life, good thermal stability, wide potential window, and high rate capability [51]. Ruthenium oxide achieves its capacitance by the intercalation of protons into its amorphous structure. Furthermore, the resistance of ruthenium oxide is lower than that of other electrode materials. Although it is prospective, the industrialization of it has been limited by its prohibitive cost. Thus, how to lower the cost while maintain the performance is the major area of research subject [39]. In recent years, people tried to use RuO₂ and carbon composited materials as electrode materials. By this method, the quantity of RuO₂ used has been significantly reduced, and at the same time, higher capacitance
has been maintained. Figure 1.10 (c) shows a typical cyclic voltammogram of an hydrous RuO$_2$ in aqueous electrolyte.

### 1.2.2 Electrolyte Materials of Supercapacitors

**Aqueous electrolytes:**

$\text{H}_2\text{SO}_4$, KOH, $\text{Na}_2\text{SO}_4$ etc. based aqueous solutions can provide relatively low resistance and high ionic concentration. Supercapacitor which utilizes the aqueous electrolyte always shows higher capacitances than that with organic electrolyte. Furthermore, the process of preparing and utilizing aqueous electrolytes is not very strict. The main disadvantage of aqueous electrolytes is its low voltage window (about 1.2 V) due to the thermodynamic decomposition of water, which limits the power and energy density.

**Organic electrolytes:**

Organic electrolytes are lithium salts and quaternary ammonium salt, such as LiClO$_4$ and TEABF$_4$, dissolved in some common organic solvent such as polycarbonate (PC), acrylonitrile (ACN), and gamma – butyrolactone (GBL) etc. Organic electrolyte has relatively higher achievable voltage and hence higher energy density because the maximum energy stored is determined by the square of the unit-cell voltage. The voltage of a supercapacitor applied organic electrolyte can be above 2 V. The float voltage is 2.3 V, and it is possible to increase up to 2.7 V for a short time [34]. Water content in the organic electrolyte is the main limitation for the cell voltage. For this reason, extreme purification procedures are necessary before these electrolytes are applied. Additionally, special surface coating on the electrodes is necessary to protect water absorption. Besides the water contamination and high cost,
other considerations on the use of organic electrolytes are their low conductivity, high resistance, and hence low power density.

**Ionic liquids:**

Ionic liquids (ILs) are the molten organic salts at room temperature which are composed of solely cations and anions. ILs can provide a wide voltage window ranging from 2 – 6 V and conductivity about 10 mS/cm [52]. With the increasing of operating voltage, the maximum energy/power density will be greatly increased.

ILs, such as 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄), 1-Ethyl-3-methylimidazoliumhexafluorophosphate(EMIMPF₆), 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) etc, have been widely researched in recent years and regarded as the next generation electrolytes due to their interesting physical properties such as high electrochemical stability over a wide potential window (>3 V), high thermal stability, non-toxicity, and non-flammability, etc. However, because of the high viscosity liquids and low ionic conductivity, the electrochemical performance working as electrolyte in supercapacitors is effected [35]. Figure 1.10 (d-f) compares the typical cyclic voltammograms of graphene-based electrode in the three different electrolytes. The figure clearly shows that the voltage window extending from 1V to around 2.4V and up to 3.5V when the electrolyte is changed from KOH aqueous electrolyte, TEABF₄/AN organic electrolyte, to EMIM-NTF₂ ionic liquid.
Figure 1.7 Cyclic voltammogram profiles of different electrodes in aqueous electrolyte: (a) active carbon, (b) PPy/VGCF [53] and (c) hydrous RuO$_2$ [54]; graphene based electrode supercapacitors in different electrolyte: (d) aqueous electrolyte (KOH), (e) organic electrolyte (TEABF$_4$/AN) [55] and (f) EMIM-NTf$_2$ [56].
1.3 Objective and Scope of This Research

With the rapidly developing of various electronic devices such as electrical vehicles and hybrid electric vehicles, the demand for high energy storage system has significantly increased. Both lithium-ion batteries and supercapacitors are the main electrochemical energy storage devices whose energy density and performance largely depend on the chemical and physical properties of the electrode materials. In this research study, several carbon-based nanomaterials are synthesized and employed as the potential electrode materials in the lithium-ion batteries and supercapacitors towards performance improvements.

Firstly, graphene nanosheets (GNS) and their manganese oxide composite materials were synthesized through a new chemical approach. The material morphological and electrochemical characteristics of the nanocomposite materials synthesized at different conditions are revealed and discussed in chapter 2.

Secondly, silicon nanowires grown on carbon nano-fibers and their composites with GNS were structurally characterized and preliminarily studied as the anode material in lithium-ion batteries, which are presented in chapter 3.

Thirdly, GNS powders, synthesized using Hummers’s approach followed by different reduction treatments were employed as the electrode materials in supercapacitors with two types of ionic liquid (C₈mimBF₄ and EMIMBF₄) electrolytes. In addition, GNS in composites with manganese oxide were tested as the electrode materials in supercapacitors in aqueous (1 M Na₂SO₄) electrolyte. Their electrochemical performances are discussed in chapter 4.

The conclusions of the thesis work are summarized in chapter 5.
Chapter 2: Syntheses and Li-Storage Characteristics of Graphene Nanosheets and Their MnO$_x$ Composites

2.1 Introduction

Nanoparticulate transition-metal oxides (TMO$_x$, where M is Cu, Mn, Fe, Co or Ni etc) have received much attention as alternative anode materials for Li-ion batteries. The mechanism of TMO$_x$ working as anode materials is different from the classical Li insertion or Li-alloying processes which can be described in equation 2-1 [57, 58]

$$2e^- + 2Li^+ + TMO_x \leftrightarrow xLi_2O + TM$$

According to equation 2-1, at the initial lithiation stage metal oxides are converted to metallic state along with Li$_2$O formation and will be reversibly returned to its initial state upon delithiation. Since the oxidation state is fully utilized and more than one electrons are involved in the conversion reaction, the transition metal oxide anode materials always show the high energy densities and reversible capacities. TMO$_x$ shows high reversible electrochemical capacities of 700 - 900 mAh/g, which is over twice of the gravimetric capacity and six times volumetric capacity compared with graphitic carbon anode [22, 59].

Manganese oxide (MnO$_x$) has many advantages over other transition metal oxides, such as high lithiation capacity (theoretical capacity 755.5 mA/g), relative low electrical motivation force (1.032 V vs. Li/Li$^+$), as well as environmental friendly and low cost. However, there are still some limits for using manganese oxide-based anodes in practical Li-ion batteries because of their poor electrical conductivity and large volume change during cycling. It is widely believed that the nanoparticle size of
the MnOₓ may address the volumetric change problems and improve the electrochemical performances. Zhong et al.[23] compared different nanoparticle sizes of MnO powder through mechanical milling, and then coated with 5% carbon. These two approaches effectively increased the cyclic performances. A sponge-like nanosized Mn₃O₄ [58] was synthesized by reducing Mn(OOCCH₃) with ammonium hydroxide and hydrazine at 80°C and then heated at 300°C for 5 hours. The first discharge and charge capacity were 1327 mAh/g and 869 mAh/g, respectively, at the current rate of 0.25 C. The capacity maintained at ~800 mAh/g after 40 cycles which indicated the good cyclic performance. In addition, as the current density increased up to 10 C, this anode material could still deliver a specific capacity as high as 500 mAh/g indicating improved rate capability. Recently, many research groups are working on synthesizing different types of nanostructured manganese oxide-based anode materials, such as Mn₃O₄ nano-fibers, and interconnected MnOₓ nanowires, etc.

Meanwhile, it is believed that graphene nanosheets (GNS) are able to serve as the good matrix for the transition metal oxides for its ultra-high surface area, and good electrical conductivity which will compensate the low conductivity of metal oxides and improve the electrochemical performance as anode materials. In order to further increase the surface area of the GNS and the lithium storage performance, MnOₓ has been added to form 3 D nanostructured MnOₓ-GNS hybrids. There are many approaches to synthesis the graphene/MnOₓ composites around the world.

Kim et al.[60] used chemical reduction method to disperse Mn₃O₄ nanoparticles (20 – 30 nm) GNS. This hybrid material retained a high capacity of ~990 mAh/g after 30 cycles. It was observed that the first discharge curve was quite different from the following ones, which indicated that an irreversible structural change occurred. Through XRD and Raman spectroscopy analysis, they reported that at
discharging to 1.0 V some degree of solid solution Li$_y$Mn$_3$O$_4$ ($1 \leq y$) formed. As the continuing discharge, MnO$_x$ ($x \sim 2$) formed.

Liu et al.[61] synthesized the manganese oxide/GNS using the hydrothermal reduction method. The Mn$_3$O$_4$ and MnO nanoparticles were uniformly dispersed on the surface of graphite nanosheets. This sandwich structure improved the electrochemical performance of barely Mn$_3$O$_4$ and MnO nanoparticles because of the buffering, confining and conducting effects of graphite nanosheets. The Mn$_3$O$_4$/GNS hybrid material maintained 437 mAh/g at the current density of 200 mA/g after 50 cycles. It is needed to mention that the first discharge capacity of this anode material was 1100 mAh/g, and charge capacity was 750 mAh/g, accordingly the Coulombic efficiency was 68%.

Wang et al.[62] hydrolyzed Mn(CH$_3$COO)$_2$ in GO suspension and then did the hydrothermal treatment at 180°C to obtain reduced graphene oxide (RGO) and Mn$_3$O$_4$ nanocomposites. The as-prepared anode material showed high capacity of 810 mAh/g (based on the total mass of the hybrid) and ~900 mA/g (based on the mass of Mn$_3$O$_4$) at the current density of 40 mA/g. Also, the capacity retention was as high as 98% after first five cycles. Even increased the current density to ten times (400 mA/g), the capacity still maintained as high as ~780% mAh/g after 40 cycles. This hybrid anode material greatly increased the electrochemical performance compared with free Mn$_3$O$_4$ nanoparticles whose specific capacity was as low as ~300 mAh/g and decreased to ~115 mAh/g after 10 cycles.

Yu et al.[63] prepared a layer-by-layer RGO-MnO$_2$ nanotube composite (see figure 2.1) as anode material. The composite was composed by 20 layers films (10 layers of RGO nanosheets and 10 layers of MnO$_2$ nanosheets with 1:1 weight ratio). The researchers reported that this composite film exhibited a high reversible capacity
of 686 mAh/g at the current density of 100 mA/g, and 208 mAh/g event at the current density as high as 1600 mA/g.

![Figure 2.1 Schematic view for synthesizing (a) RGO and (b) MnO₂ Nanotubes layer-by-layer thin films [63].](image)

Table 2.1 summarizes the information of MnOₓ nanomaterials and GNS/MnOₓ nanocomposites collected from published literatures including their morphology, synthesis conditions, manganese component phases, GNS contents, and electrochemical performances.

In this research study, we developed a low-cost sol-gel approach to disperse MnOₓ nanoparticles in graphene GNS matrix and employed the nanocomposites as anode materials for lithium-ion batteries. The objective is to experimentally clarify the impacts of the manganese valence and GNS content in the composite on the lithium storage characteristics in terms of Coulombic efficiency, capacity, cycle life and rate capability.
Table 2.1 Summary of synthesis and electrochemical information about MnOₓ-based nanomaterials collected from published literatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphology</th>
<th>Basic synthesis Info</th>
<th>1st d/c capacities (mAh/g), efficiency</th>
<th>Rate capability (mAh/g at mA/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>rodlike 100–150nm in diameter, 1–2 µm in length</td>
<td>MnAC+(NH₄)₂S₇O₇, 140°C 2hrs, then 500°C 10 hrs Ibtd, amorphous MnO₂ 350°C 10 hrs</td>
<td>1146/627, 55%</td>
<td></td>
<td>[23]</td>
</tr>
<tr>
<td>MnO₃</td>
<td>ibid amorphous MnO₂ 280°C 3 hrs in H₂/Ar, 700°C 2 hrs in Ar ibid amorphous MnO₂ 400°C 10 hrs in H₂/Ar, 700°C 2 hrs in Ar</td>
<td></td>
<td></td>
<td></td>
<td>[23]</td>
</tr>
<tr>
<td>MnO</td>
<td>ibid amorphous MnO₂ 280°C 3 hrs in H₂/Ar, 700°C 2 hrs in Ar</td>
<td></td>
<td></td>
<td></td>
<td>[23]</td>
</tr>
<tr>
<td>MnO</td>
<td>agglomerate, 0.5–1.5 µm nanosheets, 0.5–1.5 µm</td>
<td>MnO (commercial) Carbon coated-MnO</td>
<td>1270/690, 53%</td>
<td>300 at 800</td>
<td>[64]</td>
</tr>
<tr>
<td>MnO</td>
<td>Spongelike 30–80 nm</td>
<td>MnO and ammonium hydroxide at 300°C 5 hrs</td>
<td>1327/869, 65%</td>
<td>520 at 500</td>
<td>[65]</td>
</tr>
<tr>
<td>MnO₂/GNS</td>
<td>20–30 nm</td>
<td>GO + MnCl₂ + KMnO₄ + NH₄OH, 80°C 8 hrs, 120°C dried</td>
<td>1789/1100, 62%</td>
<td>400 at 1000</td>
<td>[60]</td>
</tr>
<tr>
<td>MnO₂/GNS</td>
<td>30–50 nm</td>
<td>GO + MnAC + NaOH, hydrothermal 180°C for 12 hrs, 15% GNS</td>
<td>1100/750, 68%</td>
<td>610 at 200</td>
<td>[61]</td>
</tr>
<tr>
<td>MnO/GNS</td>
<td>30–50 nm</td>
<td>ibid, then 400°C 2 hrs in H₂/N₂, 12% GNS</td>
<td>1320/820, 62%</td>
<td>200 at 600</td>
<td>[61]</td>
</tr>
<tr>
<td>MnO₂/GNS</td>
<td>10–20 nm</td>
<td>GO + MnAC, hydrolysis, hydrothermal at 180°C for 10 hrs, 10% RGO</td>
<td>1320/850, 64%</td>
<td>600 at 800</td>
<td>[62]</td>
</tr>
<tr>
<td>MnO₂/GNS</td>
<td>70–80 nm</td>
<td>GO + MnO₂ nanotube hydrothermal</td>
<td>1232/686, 55.7%</td>
<td>300 at 800</td>
<td>[66]</td>
</tr>
</tbody>
</table>

2.2 Experimental Aspects

2.2.1 Chemical Synthesis of GNS Powders

Natural graphite powders (HMP 850) were oxidized to graphite oxide (GO) using the modified hummer’s method. 100 mL 98% sulfuric acid was poured into the mixture of 2 gram graphite (HMP 850) and 2 gram sodium nitrate. Then 10 gram of potassium permanganate (KMnO₄) is gradually added. The mixture was completely stirred for overnight, and diluted with deionized water. 12 mL hydrogen peroxide was added to the solution, and the colour of the mixture was changed to greenish yellow. The obtained solution was put on the hot plate at 150°C until it gets dried. The dried sample was washed with deionized water until its pH value turns to neutral. Then the
sample was placed in ultrasonic wave for 2 hours. GNS powder was obtained after the as prepared sample was dried.

2.2.2 Synthesis of GNS/MnOₙ Hybrid Powders

22 mg as-prepared GNS powders dissolved in water and were ultrasonicated for 3 hours. Then 78 mg manganese acetate (MnAC) dissolved in water and was gradually added to the GNS solution then continuously stirred for 2 hours. Ammonium hydroxide and hydrazine were added to the mixture and stirred for 3 hours at 100°C. The mixture was filtered and dried at 150°C. The different GNS/MnOₙ nano composite anode material with their acronyms and description were listed in Table 2.2.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Acronym</th>
<th>Anode Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GNS/MnOₙ-1</td>
<td>Nano composite heat treated at 150°C in air.</td>
</tr>
<tr>
<td>2</td>
<td>GNS/MnOₙ-2</td>
<td>Nano composite heat treated at 400°C in air.</td>
</tr>
<tr>
<td>3</td>
<td>GNS/MnOₙ-3</td>
<td>Nanocomposite heat treated at 400°C in 5% H₂/Ar atmosphere.</td>
</tr>
</tbody>
</table>

2.2.3 Structure, Morphology and Composition Analyses

Bruker D8 X-ray diffractometer (XRD) was used to identify the crystal structure of the manganese component in the hybrid. The morphologies of the GNS/MnOₙ sample were visualized by the JEOL scanning electron microscopy (SEM). The carbon content was identified by analyzing the weight loss of the powder after heat treatment and energy dispersive spectroscopy (EDX).
2.2.4 Electrode and Electrochemical Characterizations

Below are the steps of preparing Swagelok-type battery cells used for testing in electrochemical working station. The active anode material was mixed with a binder polyvinylidene fluoride (PVDF) in N-Methyl-Pyrrolidone (NMP) at the weight ratio of 9:1 to form viscous slurry. The slurry was uniformly coated on Cu foil with a blade. The as-prepared electrode sheets were dried at 120°C for 12 hours in vacuum oven. Afterwards, the electrode sheet is punched into round specimens with a diameter of 3/8 inch for electrochemical characterizations. The electrode weight is the total weight of the copper, PVDF binder and the active anode material. The net weight of the active anode material, i.e. GNS or GNS/MnOx, is the total weight minus the weight of the copper foil and PVDF binder. The actual weight was used for calculating the performance of the anode material. All the chemicals used in the electrode preparation are purchased from Sigma-Aldrich.

Swagelok cells were assembled in glove box which controlled the oxygen and moisture levels less than 0.5 ppm. The electrolyte was 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC) at 1:1 volumetric ratio. Lithium metal foil was used as counter and reference electrode.

The cells were galvanostatic charge-discharge at the preset current density with the voltage window ranging from 0.01 – 3.0 V on a battery testing station (Land CT). Electrochemical impedance spectra (EIS) was obtained by applying a sine-wave signal with an amplitude of 10 mV in the frequency range of 1 MHz to 0.1 Hz on Camry electrochemical analysis system at the preset capacity interval after relaxation for 2 hours.
2.3 Results and Discussion

2.3.1 Structure and Morphological Material Characterizations

Figure 2.2 shows the XRD profiles of the three samples of GNS/MnO$_x$ hybrid with different processes methods. For comparison, GNS and GNS+MnAC simple mechanically mixing of GNS + MnAC were also included. In the GNS profile, there was only a board peak at 24.6° which is the characteristic XRD spectrum of GNS. This indicated that all graphite were converted into reduced graphene oxide nanosheets. The spectrum of GNS + MnAC shows many crystalline diffraction peaks corroborated well with those of crystalline MnAC. It is reported that crystalline MnAC can only transform to Mn$_3$O$_4$ with the thermal treatment above 400°C in air. However, in GNS/MnO$_x$-1 profile, all the crystalline MnAC related peaks disappeared, which confirms that all in the MnAC had transformed to MnO$_x$. In addition, all the observed peaks in GNS/MnO$_x$-1 corroborated well with the Mn$_3$O$_4$. The nanoparticles size of the Mn$_3$O$_4$ was estimated about 30 nm, based on the width of diffraction peaks. In profiles of GNS/MnO$_x$-2 which was heated at 400°C, the phase of Mn$_3$O$_4$ was not altered but the width of the diffraction peaks was increased indicating the increase of particles size. Thermal treatment at 400°C in the H$_2$/Ar environment, the MnO peaks can be observed and are labeled with stars. Semi-quantitative analyses, from the XRD spectrum, indicated that the atomic ratio of MnO to Mn$_3$O$_4$ was 3:2.
EDX micro elemental composition analysis was employed to determine the carbon and manganese content. Five different regions with different area sizes were selected on each sample compositional analyses to improve the accuracy. The average carbon contents in the three specimens were 44 wt%, 20 wt%, and 42%, respectively. The prepared conditions, manganese component phases, and GNS contents in the samples prepared at the three different conditions are listed in Table 2.3.

The morphologies of the GNS and GNS/MnOₓ hybrids were examined by using SEM. Figures 2.3 (a) and (b) show the SEM images of GNS at low and high magnification, respectively. From the images it can be observed that the GNS synthesized by the modified Hummer’s method shows thin wrinkle flakes indicating high surface area. Atomic force microscopic images also confirmed the existence of single graphene nanosheets [67].

Figure 2.2 XRD spectra of the GNS/MnOₓ nanocomposites in comparison with GNS and GNS+MnAC
During the synthesis process of GNS by modified Hummer’s method, a number of different function groups such as epoxyl, carboxyl and hydroxyl, attached on the surface and edges resulting the wrinkled morphology. These function groups will coordinate with Mn ions which is driven by electrostatic interactions. Mn ion – GNS mixture formed when all the Mn ions absorbed onto GNS. Ammonium hydroxide and hydrazine solution was added to help the precipitation of Mn ion into Mn(OH)$_2$. Mn(OH)$_2$ is a metastable compound that can be easily oxided to Mn$_3$O$_4$ by oxygen. It can be observed from figures 2.4 (a) and (b) that manganese oxide nanoparticles homogeneously bonded onto both sides of the GNS surface. The GNS embedded with the MnO$_x$ nanoparticles, which stacked and cross-linked formed multilayer sandwich structure leading to relatively thick flaky type morphology than GNS. SEM images of GNS/MnO$_x$ – 3 are similar to those of GNS/MnO$_x$ – 1 and hence are not shown again.

Lithium storage electrochemical reaction is anticipated to be benefited from this sandwich structure. Firstly, the GNS working as a strain buffer would accommodate the volume change caused by the insertion/extraction of lithium ions. Secondly, the GNS network provided a short path for electrical conducting and decreased the internal impedance of the electrode. At last, MnO$_x$ nanoparticles served as “spacer”
between the GNS forming the 3-D structure which will effectively prevent the restacking of individual graphene nanosheets.

Figure 2.4 SEM images of GNS/MnO$_x$-1 at low magnification (a) and high magnification (b).

Figure 2.5 SEM images of GNS/MnO$_x$-2 (a) and (b), and MnAC-400 (c) and (d)

Loose fluffy agglomerates can be observed in the GNS/MnO$_x$-400 SEM images, shown in figures 2.5 (a) and (b). Some parts of GNS were burnoff after heated at 400°C, hence, some Mn$_3$O$_4$ nanoparticles existed as free-standing agglomerates. This
is similar with pure manganese acetate heated at 400°C in air for 12 hours, which showed large spherical agglomerates as shown in figure 2.5 (c) and (d). This structure is unfavorable that will decrease the cycle performance and electrical conduction for reversible lithium storage.

2.3.2 Electrochemical Characterizations

Electrochemical Characteristics of GNS

Figure 2.6 shows the first, second, fifth and tenth charge-discharge curves of the GNS anode at the current density of 50 mA/g. The first discharge curve rapidly decreased to around 1.2 V and then gradually decreased to 0 V with a midpoint of around 0.5 V. While charging, the curve gradually increased with a midpoint of around 1.5 V. The charge-discharge curves showed large voltage hysteresis and no distinguishable plateau, which are the characteristics of lithium storage in GNS. The first discharge and charge specific capacity were 1248 mAh/g and 843 mAh/g, respectively, with a Coulombic efficiency of 68%. The irreversible capacity is the results of SEI formation, irreversible lithium absorption, and electrolyte reaction with the function groups of GNS. The reversible capacity of GNS was as high as around 800 mAh/g which is almost twice of commercially used graphite (372 mAh/g) anode. This is because lithium ions are able to embed on the both sides of the graphene nanosheet and also on some function groups of GNS. In the following ten cycles, Coulombic efficiency significantly increased and stabilized over 95%. This indicates the good cycle performance of GNS anode material. The general lithium storage reaction in GNS can be expressed in the following equation:

$$\text{GNS} + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x\text{GNS} \quad (1)$$
The shapes of GNS charge-discharge curves significantly changed while Mn$_3$O$_4$ nanoparticles are embedded on GNS (shown in Figure 2.7 (a) – (c)). The first discharge/charge capacities for the three GNS/MnO$_x$ hybrid samples were 1430/850, 1504/578, and 1344/838 mAh/g with the Coulombic efficiency of 59%, 40% and 65%, respectively. The initial discharge plot can be divided into 3 regions. The first region was from 3.0 V to 0.5 V which is correlated with the insertion of lithium ions into Mn$_3$O$_4$ forming LiMn$_3$O$_4$ as follows:

$$Mn_3O_4 + xLi^+ + xe^- \rightarrow Li_xMn_3O_4$$  \hspace{1cm} (2)

The plateau between 0.5 V to 0.3 V is correlated with the formation of SEI and the phase transformation from Li$_x$Mn$_3$O$_4$ to MnO as follows:

$$LiMn_3O_4 + Li^+ + e^- \rightarrow 3MnO + Li_2O$$ \hspace{1cm} (3)

Because the SEI formation and reaction (2) and (3) are irreversible, the first discharge plot is always different from the following ones. Comparing figure 2.7 (a) and (b), the GNS/MnO$_x$-2 exhibited insignificant high-voltage slop. This is because the less content of GNS decreased the electronic conductivity, which resulted in the large internal impedance and overvoltage.

Electrochemical Characteristics of GNS/MnO$_x$

The shapes of GNS charge-discharge curves significantly changed while Mn$_3$O$_4$ nanoparticles are embedded on GNS (shown in Figure 2.7 (a) – (c)). The first discharge/charge capacities for the three GNS/MnO$_x$ hybrid samples were 1430/850, 1504/578, and 1344/838 mAh/g with the Coulombic efficiency of 59%, 40% and 65%, respectively. The initial discharge plot can be divided into 3 regions. The first region was from 3.0 V to 0.5 V which is correlated with the insertion of lithium ions into Mn$_3$O$_4$ forming LiMn$_3$O$_4$ as follows:

$$Mn_3O_4 + xLi^+ + xe^- \rightarrow Li_xMn_3O_4$$  \hspace{1cm} (2)

The plateau between 0.5 V to 0.3 V is correlated with the formation of SEI and the phase transformation from Li$_x$Mn$_3$O$_4$ to MnO as follows:

$$LiMn_3O_4 + Li^+ + e^- \rightarrow 3MnO + Li_2O$$ \hspace{1cm} (3)

Because the SEI formation and reaction (2) and (3) are irreversible, the first discharge plot is always different from the following ones. Comparing figure 2.7 (a) and (b), the GNS/MnO$_x$-2 exhibited insignificant high-voltage slop. This is because the less content of GNS decreased the electronic conductivity, which resulted in the large internal impedance and overvoltage.
The reaction of lithium ion with manganese oxide can be observed at the long plateau at around 0.4V as well as in the region below 0.4 V in the initial discharge plot and expressed as follows [60, 61]:

$$MnO + 2Li^+ + 2e \leftrightarrow Mn + Li_2O \quad (4)$$

Comparing with the initial discharge plot of GNS (see figure 2.6 and equation (1)), it can be concluded that in the low-voltage region, GNS also contributes a portion of the capacity.

Among the three reaction equations between lithium and manganese oxides, reactions (2) and (3) are irreversible and mainly contributes to the irreversible capacity during the first discharge process while only the reaction (4) is reversible. According to previous studies [60, 68] based on XRD and Raman analyses, no matter the phase of the starting material is MnO, Mn$_3$O$_4$, or MnO$_2$, manganese would be oxidized to nanosized MnO once fully charged to 3.0 V. Hence the high valency manganese oxide will lead to form extra Li$_2$O which produce extra irreversible capacity in the initial discharge process. The formation of extra Li$_2$O is in the order of MnO$_2$ (1 • Li$_2$O) > Mn$_2$O$_3$ (1/2 • Li$_2$O) > Mn3O4 (1/3 • Li$_2$O).

The 2$^{nd}$, 5$^{th}$, and 10$^{th}$ cycles charge-discharge profiles are also shown in figures 2.7 (a) to (d). The shapes of the plot from the 2$^{nd}$ cycle didn't change significantly which indicated the stable cycle performance. Both of GNS/MnO$_x$-1 and GNS/MnO$_x$-3 showed the Coulombic efficiency as high as over 92%. However, the Coulombic efficiency of GNS/MnO$_x$-2 was only about 80% in the following nine cycles.
Figure 2.7 Galvanostatic discharge-charge profiles of GNS and GNS/MnO$_x$ obtained at the current density of 50 mA/g
Table 2.3 Summary of GNS and GNS/MnO\textsubscript{x} hybrid anode materials with their prepared conditions, manganese component phases, GNS contents, and electrochemical performances.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GNS</th>
<th>GNS/MnO\textsubscript{x}-1</th>
<th>GNS/MnO\textsubscript{x}-2</th>
<th>GNS/MnO\textsubscript{x}-3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Synthesis info</strong></td>
<td>As-prepared</td>
<td>As-prepared</td>
<td>400°C 12 h in air</td>
<td>400°C 12 h in 5% H\textsubscript{2}/Ar</td>
</tr>
<tr>
<td><strong>GNS content</strong></td>
<td>100%</td>
<td>44%</td>
<td>20%</td>
<td>42%</td>
</tr>
<tr>
<td><strong>MnO\textsubscript{x} phase</strong></td>
<td>N/A</td>
<td>Mn\textsubscript{3}O\textsubscript{4}</td>
<td>Mn\textsubscript{3}O\textsubscript{4}</td>
<td>Mn\textsubscript{3}O\textsubscript{4}+MnO (40 : 60)</td>
</tr>
<tr>
<td><strong>1\textsuperscript{st} capacity</strong></td>
<td>1248/843</td>
<td>1430/850</td>
<td>1433/578</td>
<td>1279/838</td>
</tr>
<tr>
<td><strong>1\textsuperscript{st} efficiency</strong></td>
<td>68%</td>
<td>59%</td>
<td>40%</td>
<td>65%</td>
</tr>
<tr>
<td><strong>2\textsuperscript{nd} capacity</strong></td>
<td>810</td>
<td>806</td>
<td>494</td>
<td>772</td>
</tr>
<tr>
<td><strong>10\textsuperscript{th} capacity</strong></td>
<td>790</td>
<td>619</td>
<td>233</td>
<td>719</td>
</tr>
<tr>
<td><strong>Capacity fading</strong></td>
<td>0.3%</td>
<td>2.6%</td>
<td>5.9%</td>
<td>0.8%</td>
</tr>
</tbody>
</table>

Table 2.3 summarizes the GNS and GNS/MnO\textsubscript{x} hybrid anode materials with their prepared conditions, manganese component phases, GNS contents, and electrochemical performances. As shown in Table 2.3, the capacity fading of GNS/MnO\textsubscript{x}-2 is the highest of 5.9% compared the other two GNS/MnO\textsubscript{x} hybrid materials, because the GNS content in the former sample is the lowest of 20%. This means the presence of sufficient GNS can provide good buffer to accommodate the volume change during the lithium ions insertion/extraction process, and also good electronic conductive path. Comparing GNS/MnO\textsubscript{x} – 1 with GNS/MnO\textsubscript{x} – 2, it can be concluded that the more Mn\textsubscript{3}O\textsubscript{4} in the starting materials the less Coulombic efficiency. Comparing with GNS/MnO\textsubscript{x}-1 and GNS/MnO\textsubscript{x}-3, the GNS contents are almost same, but there is more MnO in GNS/MnO\textsubscript{x}-3 and the efficiency is higher than GNS/MnO\textsubscript{x}-1. The difference of the cyclic performance is due to the presence of MnO in GNS/MnO\textsubscript{x}-3. However, the sample with the best cyclic performance of GNS/MnO\textsubscript{x}-3 still displayed slightly inferior to pure GNS, indicating the limited reversibility of the displacement reaction of MnO\textsubscript{x}.

Figures 2.8 (a) to (d) show the charge-discharge profiles of the four samples at different discharge current rates from 25 mA/g to 800 mA/g. Also, the capacity as a
function of discharge current rate is shown in figure 2.8 (e). GNS/MnO$_x$-3 showed best rate capability for its content of GNS and MnO is high and even better than that of GNS. At the current density increased from 50 mA/g to 800 mA/g, the capacity decreased from 810 mAh/g to 425 mAh/g (52.4%) for GNS. In contrast, for GNS/MnO$_x$-3, there was still 67% of full capacity maintained at the current density of 800 mA/g.

The metallic lithium formation was avoided by presetting the cutoff potential to 10 mV. So the polarization caused by increasing the discharge current density is equivalent to shift the cutoff voltage upwards. From figure 2.8 (a) it can be observed that the main capacity was contributed from the voltage region below 0.3 V. When increasing the discharge current density, it is equal to up-shifting the voltage baseline and decreasing the capacity. For GNS anode, when increasing the discharge current from 25 mA/g to 800 mA/g, the overvoltage potential was around 300 mV. The capacity read from the discharge curve in 2.8 (a) at 300 mV and 25 mA/g is 410 mAh/g which is consistent with the discharge capacity at 800 mA/g (425 mAh/g). However, in figure GNS/MnO$_x$-3, the capacity was mainly contributed above 300 mV. Therefore, at 300 mV polarization, there was less impact on it, and 475 mAh/g was still maintained.
Figure 2.8 The discharge-charge profiles of (a) GNS, (b) GNS/MnOx-1, (c) GNS/MnOx-2 and (d) GNS/MnOx-3 at different discharge rates from 25 mA/g to 50 mA/g (the charge rate is set up at 50 mA/g), and (e) capacity as a function of the discharge rate.
2.4 Summary

In this study, GNS/MnO\text{x} hybrid anode materials with different content of GNS and MnO\text{x} were chemically synthesized. Their structures, morphology as well as the electrochemical characteristics were analyzed. MnO\text{x} nanoparticles worked as “spacer” between graphene nanosheets and formed a 3-D structure, which greatly improved the lithium storage performance. In addition, GNS worked as a “buffer” which accommodated the volume change caused by the manganese oxide displacement reaction, and shorten the electronic conductivity path.

It was verified that the lower manganese valency would deliver higher reversible capacity. GNS/MnO\text{x}-3, consisting of GNS 42% wt, Mn\text{3}O\text{4} 23% wt%, and MnO 35% which is the one with highest GNS and MnO contents delivered better performances than the other specimens. Specifically, the reversible capacity up to 838 mAh/g has been obtained, with a Coulombic efficiency of 65%. In addition, the specimen exhibited good cyclic performance with 0.8% fading per cycle and high rate capability with 67% at the current density of 800 mA/g. GNS/MnO\text{x} has a relatively high lithium storage potential versus Li (0.5 V) which is helpful to increase the high rate capability and reduce the risk of metallic lithium formation and safety hazard.
Chapter 3: Morphological and Li-Storage Characteristics of Silicon Nanowires in Compositing with Carbon Fibers and Graphene Nanosheets

3.1 Introduction

Silicon is an alternative promising anode materials for Li-ion batteries. It was reported that the alloying process in silicon anodes results in formation of Li_{12}Si_{7}, Li_{14}Si_{6}, Li_{13}Si_{4}, and Li_{22}Si_{5}, alloys [69]. Table 3.1 shows the crystal structure, unit cell volume, and volume per silicon atom of different Li-Sn alloys. When the Li_{22}Si_{5} alloy forms, each silicon atom accommodates 4.4 lithium atoms corresponding the specific capacity is 4200 mAh/g, which is the highest value known so far. However, the progressively large volume expansion occurs simultaneously. The volume of Li_{4.4}Si is four times higher than that of the parent silicon. Such high volume change will cause disintegration of the electrode and the dramatically fade of cycling performance.

Table 3.1 Crystal structure, unit cell volume and volume per Si atom for the Li-Si system [69]

<table>
<thead>
<tr>
<th>Compound</th>
<th>crystal structure</th>
<th>Unit cell Volume (Å³)</th>
<th>Volume per silicon atom (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>Cubic</td>
<td>160.2</td>
<td>20.0</td>
</tr>
<tr>
<td>Li_{12}Si_{7}, (Li_{1.7}Si)</td>
<td>Orthorhombic</td>
<td>243.6</td>
<td>58.0</td>
</tr>
<tr>
<td>Li_{14}Si_{6}, (Li_{1.7}Si)</td>
<td>Rhombohedral</td>
<td>308.9</td>
<td>51.5</td>
</tr>
<tr>
<td>Li_{13}Si_{4}, (Li_{1.25}Si)</td>
<td>Orthorhombic</td>
<td>538.4</td>
<td>67.3</td>
</tr>
<tr>
<td>Li_{22}Si_{5}, (Li_{4.4}Si)</td>
<td>Cubic</td>
<td>659.2</td>
<td>82.4</td>
</tr>
</tbody>
</table>
Various methods have been employed to improve the electronic contact between particles to mediate the volume change impacts. One is mixing conductive additives, for instance, graphite flakes or nano-scale carbon black to increase the electrical contact between components in the electrode[70]. The conductive additives suppress the Si volume change on some extent, and improve the Li de-alloying kinetics, also relieving mechanical stresses. Reducing the Si particles size to nano-size and developing nanostructured Si is another very effective method.

3.1.1 Si - Carbon Matrix Composites

Carbon has been used as the matrix because of its softness, good electronic conductivity, relative low mas, reasonable Li-insertion ability, and small volume expansion [71]. Therefore, Si dispersed in carbon and its allotrope tested as anode material aroused great interest.

Si- Active Carbon Composites:

Z. Luo et al. [72] reported Si-carbon composites by mixing Si nanoparticles (30nm to 50nm) with active carbon. In order to find the best amount of silicon carbon composites for the best electrochemical performance, several different samples were made by different silicon powder content ranged from 1% to 7%. It was found that the reversible capacity increased and the first efficiency decreased correspondingly. The highest first discharge capacity of 579 mAh/g was obtained at 7% silicon content. The reversible capacity increased from 358 mAh/g to 478 mAh/g when the silicon content ranged from 1% to 7%, and the first Coulombic efficiency decreased from 85.2% to 82.6%.

Q. Si, et al. [73] showed that the electrochemical performance of the Si-carbon composite depended on the particle size and the content of Si. They found the best
result was obtained from the specimen with silicon particle size of 50 nm composite with 48% carbon. Coulombic efficiency in the first cycle of 69.2% and the second cycle reversible discharge capacity of 970 mAh/g were obtained. Meanwhile, the capacity fading was 0.24% per cycle in the first 40 cycles. Also, 10-20 nm nano-Si deposited on the graphite by thermal vapor deposition of silane [74] were studied. The initial charge and discharge capacity were 1350 mAh/g and 1000 mAh/g, respectively. After 100 cycles, the reversible capacity was maintained over 900 mAh/g.

**Si- Carbon Nanotube Composites:**

L. Hu, et al.[29] prepared Si-carbon nanotube (Si-CNT) made of amorphous Si on porous embedded in 3D CNT sponges through chemical vapor deposition (CVD) which is shown as Fig.3.1. CNT functions as both mechanical support and electrical conductor. Excellent contact between the electrolyte and silicon was obtained because the porous structure of the CNT provided sufficient channels for the flow of electrolyte. The discharge and charge capacities in the first cycle were 3200 mAh/g and 2750 mAh/g, respectively, with a Coulombic efficiency of 86%. They pointed that the cycling performance could be greatly enhanced with the adjustment of the cutoff voltage although the capacity will decrease a bit.

![Figure 3.1 Schematics of a) CNT sponge used in CVD; b) Conformal CVD deposition of amorphous Si onto CNT surface to form Si-CNT coaxial nanostructure, and c) Pressed nanostructured Si-CNT for battery test [29].](image)
Si- Carbon Nano-fibers Anode:

Ji and Zhang [75] reported a high performance Si and carbon nano-fibers (CNF) composite with porous structure which was simply synthesized by electrospinning and subsequent carbonization of the mixture of polyacrylonitrile (PAN), poly-L-lactic acid (PLLA) and nano-Si. This composite exhibited the initial reversible capacity as high as 1100 mAh/g, with the Coulombic efficiency of 82.1%. However, the reversible capacity retention was not that good. After 30 cycles, the capacity decreased from 1100 mAh/g to 600 mAh/g.

Similarly, Q. Si et al. [76] prepared a composite of nano-Si powder with a pyrolytic carbon and carbon nano-fibers (CNF). The sample was prepared by two approaches. One was directly mixing of CNF with the nano-Si powder coated with carbon produced by pyrolysis of polyvinylchloride (PVC). The other is mixing of CNF, nano-Si powder and PVC with subsequent firing. Both of the samples exhibited promising cycling performances. A capacity of more than 900 mAh/g was maintained after 30 cycles for the first sample, and the Coulombic efficiency of the first cycle was only 53%. The second sample had a higher Coulombic efficiency of 73%. In this experiment, 20 mg GO, 10 mg SiNWs/CF composite (146% weight increase) 5% SBR and 5% CMC were mechanically mixed. The mixture was then pressed into pellet for using as the working electrode.

Si- Graphene Anode:

Si-graphene has attracted a lot interest recently because Si has the highest lithium insertion capacity and graphene acts as the buffering to accommodate the large volume change during the insertion and excretion of lithium. Compared with carbon nanotube, carbon black and graphite, graphene can provide better ability to prevent the agglomeration of Si particles because of its sheet structure [73].
Lee et al. [77] prepared composites of Si nanoparticles dispersed between graphene sheets, and supported by a 3-D network of graphite. This composite showed high specific capacity and excellent cycling life. The capacity was as high as 2200 mAh/h after 50 cycles and 1500 mAh/g after 200 cycles, corresponding to the capacity fade less than 0.5% per cycle. Ji et al. [78] synthetized Si-graphene multiple layer structured anodes. Initial charge and discharge capacities of 2499 mAh/g and 2217 mAh/g were obtained, respectively, with the Coulombic efficiency of 88.71%. From the second cycle, this composite delivered a reversible capacity of 2163 mAh/g, with the capacity retention of 97.6%. The Coulombic efficiency was as high as 96% after the second cycle.

3.1.2 Nano-Structured Silicon Anodes

Nanoparticle Si Anodes:

It was reported that reducing the particle size could obtain high Li storage capacity and enhance the cycling performance. For instance, a discharge capacity of 2775 mAh/g and a charge capacity of 2097 mAh/g were obtained by a nano-Si anode in the first cycle. Also its cycle life was much better than that of bulk Si anode. The reversible capacity on the first 10th cycle was 1729 mAh/g [79].

Three-Dimensional Porous Si:

Porous Si is a new type of nano-structured material with the three dimensional (3-D) structure [80]. Because of its 3-D structure, the available volume of the active material can be much more effectively utilized. Moreover, the energy density will increase significantly while still stay with high power density. Shin et al. [80] fabricated porous Si using an electrochemical etching process. The micropores consisted of one-dimensional channels with pore diameter varying from 1 to 1.5 μm.
and depth extending up to 15 \( \mu m \) [6]. Electrolyte can flow inside of the channels, facilitating a process producing high energy and power density. Fig 3.2 [81] shows the morphological of porous Silicon. It was found that with the increasing channel depth of the porous Si the capacity increased. Electrochemical test on 3-D porous Si reported by Cho et al [82] showed the capacity of 2820 mAh/g to 2780 mAh/g after 100 cycles at 0.2C rate. Furthermore, the Coulombic efficiency is about 98%. It can be seen that the capacity retention and initial Coulombic efficiency of the 3-D porous Si represent a significant improvement over that of the nanosize Si.

![Image](image.png)

Figure 3.2 Top (a, c, e) and cross-sectional views (b, d, f) of as prepared porous Si sample at different magnifications [6].
Si Nanowires:

Si nanowires (SiNWs) are another promising nanostructured anode materials which can accommodate large strain without pulverization, and provide good conduction and electronic contact. Firstly, the nanowires allow for better accommodation of the large volume changes and relax mechanism strain inside [83, 84]. Secondly, all the nanowires can be utilized to contribute to the capacity because each Si nanowire is electrically connected to the metallic current collector [85]. Thirdly, efficient charge transport is allowed by the one-dimensional (1-D) nanowires structure.

Chan et al. successfully grew Si nanowires by employing a vapor-liquid-solid (VLS) method. Initial discharge capacity of 4277 mAh/g, and charge capacity of 3124 mAh/g were reported, corresponding to a Coulombic efficiency of 73%. Figure 3.3 (a) shows the pristine, unreacted SiNWs have a crystalline structure with the diameter about 89 nm. After electrochemical cycling reacted with Li, seen figure 3.3 (b), the diameter of NWs significantly increased to around 141 nm. During the cycling process, crystalline silicon reacted with Li to form Li₅Si alloy, and at 10 mV, all of silicon changed to amorphous Li₄.₄Si. Later, Cui’s group [86] reported a Si crystalline – amorphous core – shell with hierarchical structure anode. Figure 3.4 shows the SEM images of the Si crystalline – amorphous specimen grown on stainless steel substrate at 485°C. The as-prepared Si nanowires delivered a high reversible discharge capacity of ~ 1000 mAh/g, good cyclic performance with high Coulombic efficiency of over 90% after 100 cycles. Also good electrochemical performance at high discharging – charging rate was observed (6.8 A/g, 20 times of carbon at 1 h rate).
Figure 3.3 SEM image of pristine SiNWs before (a) and after (b) electrochemical cycling [85].

Figure 3.4 SEM images of Si Crystalline – amorphous on stainless steel substrate at 485 °C for (a) 10 min, (b) 20 min and (c) 40 min [86].

Recently, Hu, L et al. [87] deposited Si nanoparticles on the substrate of vertically grown Si nanowires from an aqueous, binder-free Si nanoparticle ink. The Si nanowires function as the conductive path to the collector for Si nanoparticles and the active anode material. Such Si nanoparticles decorated Si nanowires network anode exhibited excellent electrochemical performance. The reversible discharge capacity was ~1800 mAh/g, and the areal capacity was greatly increased from ~0.6 mAh/cm² (pure Si nanowires) to ~2.5 mAh/cm², and the Coulombic efficiency maintained about 98% after 50 cycles.

Si Nanotubes:
Song et al [88] successfully synthesized silicon nanotubes (SiNTs), shown in figure 3.5. The special property of the SiNTs is that they have axial void spaces which provide enough free surfaces to benefit the mechanics, without creating additional surfaces for accelerated SEI formation. This particular structure makes the electrode available to endure great mechanics stresses and volume change during the intercalation of lithium ions. The SiNTs were obtained three-step processes: 1) using hydrothermal process to grow dense ZnO nanorods on the surface of stainless steel; 2) chemical vapor deposition (CVD) Si onto the nanorods; and 3) selective removing ZnO via a high temperature reduction process. The first discharge and charge capacity is as high as 3860 mAh/g and 3360 mAh/g, respectively, at a rate of 0.05C. The capacity decreases from 3360 to 1490 when increasing the rate from 0.05C to 2C. It can be explained by the intrinsic property of Si which is low electron conductivity and lithium ion diffusivity.

![Figure 3.5 SEM image of a vertically aligned SiNTs. [88]](image)

Silicon nanowires (SiNWs) based nanostructured materials, as discussed previously, are attractive anode candidates for Li-ion batteries because of the high
specific surface area and short ion diffusion length. The nanowire structure can be more adaptable for volume change during charge-discharge. In this part of research study, in collaboration with University of Dayton, SiNWs were grown on the surface of carbon nano-fibers utilizing the chemical-vapor-deposition (CVD) method. On the other hand, graphene can improve the electric contact of the composite material due to the good electrical conductivity of the carbonaceous materials. Furthermore, graphene is also a good alternative candidate of anode material, and will contribute to the overall reversible capacity. In order to further improve the cyclic performance of the SiNWs/CF composite anode, GO was added working as a buffer to accommodate the volume change during the lithiation and de-lithiation process. In this study, graphene is mechanically mixed with SiNW/CF in an attempt to enhance the cycle performance. The experiments and preliminary characterizations will be presented in this chapter.

3.2 Experimental Aspects

3.2.1 Silicon Nanowires Growth

The growth of SiNWs on carbon fibers was conducted by Q. Jiang at University of Dayton [89]. Figure 3.6 schematically shows the CVD of directly growing SiNWs on carbon nano-fiber with the help of nanoparticle Au catalyst. Hydrogen tetrachloroaurate (III) hydrate was dissolved in ethanol with the ratio of 1:5 to form Au solution. The catalyst solution was dipped on the carbon nano-fibers and then dried at 60℃ for 2 hours. The as-prepared sample was placed in the middle of the quartz tube which was heated by the three-zone furnace. Argon was firstly purged at the flow rate of 800 sccm for 30 minutes in order to get rid of air. As the temperature
of the furnace reached 700°C, high-purity hydrogen gas and silane gas were supplied into the tube at the ratio of 1:2. The growth time was set as 10 minutes.

![Diagram of furnace](image)

Figure 3.6 Schematic of synthesis SiNWs through CVD method.

### 3.2.2 Electrode Preparation and Electrochemical Characterizations

For electrochemical test, the substrate with the deposited SiNWs was cut into 0.5 × 0.5 cm square. For GO/SiNW/CF electrode, GO and SiNW (146wt%) /CF were mechanically mixed with the binder (5% SBR and 5% CMC) and pressed into pellet.

Swagelok cell was then prepared in the argon-filled glove box, and contain an SiNWs as anode, a Li foil cathode, a microporous polyethylene separator and an electrolyte solution of 1M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 vol.%). The cells were galvanostatic charge-discharge at the preset current density with the voltage window ranging from 0.01 – 3.0 V on a battery testing station (Land CT).

### 3.3 Results and Discussion

Jiang [89] has reported the growth mechanism and structural characterization elsewhere. In short, it was founded that 1) the droplets of Au-Si alloy formed on the surface of carbon nano-fibers at the initial stage with an average droplet diameter of ~100 nm; 2) both length and diameter of SiNWs gradually increase with prolonging
the growth time. (~300 nm at 10 min growth time); 3) initially the fine crystalline structure SiNWs formed but with the time increased amorphous Si deposited on the outside of the crystalline which results the diameter and length growth.

**Morphology and Element Distribution**

Figures 3.7 (a-e) show the morphology and the element distribution of SiNWs/CF samples characterized by using scanning electron microscope (SEM) integrated with electron dispersive spectroscopic (EDS) analyses. Si, O, Au, and C elemental mapping were performed on the samples.

Figure 3.7 (a) shows the SEM image of SiNWs/CF sample. From which, it can be observed that the relative thinner SiNWs with a diameter of ~100 nm homogeneously grown on the surface of carbon nano-fiber. Figure 3.7 (b) shows the distribution of carbon element in the same region of the SiNW/CF sample. It confirms the carbon element dominant in fibers. The randomly distributed carbon element signals distributed outside the carbon fibers in the image is the effect of the carbon sticker used for holding the samples for SEM imaging. From figure 3.7 (c) it can be observed that silicon mainly distributes on the surface of carbon nano-fiber and the nanowires are basically pure silicon. Because gold is used as the catalyst, the gold widely distribute on the surface of carbon nano-fiber, as can be seen in Fig. 3.7 (e). In addition, insignificant amount of oxygen was found due to subsequent exposure the samples in the air after growth (see figure 3.7 (d)).
Figure 3.7 SEM and EDX mapping images showing morphology and element distribution of SiNWs/CF.

**Electrochemical Characterizations**

Figures 3.8 (a) and (b) show the charge-discharge profiles of carbon nano-fiber (CF) and carbon nano-fiber supported silicon nanowires (SiNWs/CF), respectively. CF was tested as the baseline for the calculation of the net lithium storage in SiNWs.
The first discharge capacity on bare CF was close to 390 mAh/g and the first charge capacity was 191 mAh/g with the Coulombic efficiency of 48.6%. Seen from figure 3.8 (b), the first discharge capacity (including both CF and SiNWs) of SiNWs/CF specimen significantly increased to 1540 mAh/g and the first charge capacity was 980 mAh/g giving the Coulombic efficiency of 64%.

It is believed that during the first discharge, crystal Si reacted with Li to form Li$_x$Si. Large irreversible capacity occurred mainly above 0.3 V during the first discharge. Compare figure 3.8 (a) and (b), the irreversible slop centered around 1.3 V is the consequence of irreversible lithium reaction and electrolyte reaction with the functional groups of carbon fiber and native silicon oxide layer on SiNWs. The following dramatically decreased voltage between 1 V to 0.3 V is due to the formation of SEI layer formation.
Figure 3.8 Galvanostatic discharge-charge profiles of (a) carbon nano-fibers (CF) and (b) SiNWs (28wt%)/CF

Based on the capacity results, the galvanostatic discharge and charge capacity of SiNWs can be calculated leading to the value of 4500 mAh/g and 3800 mAh/g for Si, respectively. Hatchard et al [90] reported that they employed pure SiNWs as anode and Li$_{4.4}$Si was formed at room temperature giving the first discharge capacity of 3579 mAh/g. The obtained reversible charge capacity is very close to the reported theoretical value. From the second cycle, the capacity dramatically dropped which is because of the brittle property of the sample and the problem of pulverization. The capacity fading was also caused by the volume change after 1 cycle performance. The capacity still maintained over 820 mAh/ after 5 cycles.

Figure 3.9 Galvanostatic discharge-charge profiles of GO/SiNWs/CF (67%/13%/17%) composite anode at the current density of 50 µA/cm$^2$.

Figure 3.9 shows the discharge-charge profiles of SiNWs/CF in composite with GO powders. This mixed composite anode showed the first discharge and charge capacity of 1367 and 780 mAh/g, respectively, with a Coulombic efficiency of 77%. From the 2$^{nd}$ cycle, the Coulombic efficiency increased up to 86%. The discharge capacity of SiNWs in this composite can be calculated leading to the value of 2555
mAh/g and 2300 mAh/g, which is well consistent with the theoretical capacity value of Si. However the cycle performance is not as good as that of SiNWs/CF, after cycling for 5 cycles the capacity decreased from 1367 mAh/g to 600 mAh/g, correspondingly the capacity fading per cycle was 11%. Apparently, this experiment is not optimized resulting in unsatisfactory cycling performance. In the future work, the weight content of GO and SiNWs/CF as well as binder should be finely adjusted to achieve better performance.

3.4 Summary

Table 3.2 summarized the galvanostatic charge-discharge results of the CF and SiNWs/CF as anode. The SiNWs (28wt%) /CF specimen can deliver the discharge capacity 1540 mAh/g and charge capacity 980 mAh/g in the first cycle, corresponding to values of 4500 mAh/g and 3800 mAh/g for Si, respectively. The capacity still maintained over 820 mAh/g after 5 cycles. The sample of SiNWs/CF combined with GO (weight 67%) showed the first discharge and charge capacity of 1367 and 780 mAh/g, respectively, with the first Coulombic efficiency of 77%. However, the optimal composition in both cases is yet optimized to achieve better cycling performances.

Table 3.2 Galvanostatic charge-discharge results of CF, SiNWs/CF, and GNS/SiNWs/CF anodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight Content (%)</th>
<th>1st D/C Capacity (mAh/g) for total</th>
<th>2nd D/C Capacity (mAh/g) for total</th>
<th>1st D/C Capacity (mAh/g) for Si</th>
<th>1st Cycle Coulombic Efficiency</th>
<th>2nd Cycle Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>393/191</td>
<td>223/206</td>
<td></td>
<td>48.6%</td>
<td>92.3%</td>
<td></td>
</tr>
<tr>
<td>SiNWs/CF</td>
<td>28/72</td>
<td>1540/985</td>
<td>975/836</td>
<td>4200</td>
<td>64%</td>
<td>85.7%</td>
</tr>
<tr>
<td>GO/SiNWs/CF</td>
<td>67/20/13</td>
<td>1367/780</td>
<td>898/818</td>
<td>2555</td>
<td>77%</td>
<td>86%</td>
</tr>
</tbody>
</table>
Nano structured silicon is a promising candidate anode material which provide high reversible capacity and at the same time maintain the good cyclic performance. In the future work, graphene can be added to the SiNWs forming the SiNWs/Graphene composite. In this composite graphene can provide short conductive path and worked as a good “buffer” to accommodate the volume change during the lithiation and de-lithiation. Furthermore, more elaborate electrochemical impedance studies are needed to understand the chemical reactions and kinetics of electrode process occurred on the charge – discharge process.
Chapter 4: Graphene-based Supercapacitors

4.1 Introduction

In capacitors, different from batteries, charges will accumulate on the interface of the electrode and the electrolyte. The capacitance of a capacitor is directly related with the interface, and can be expressed as the following:

\[ C = \frac{A\varepsilon}{4\pi d} \]  \hspace{1cm} 4-1

where A is the area of the electrode surface, d is the distance between the electrodes. In the supercapacitors A represents the active surface of the electrode porous layer, \( \varepsilon \) is the medium dielectric constant, d is the thickness of the electrical double layer [35]. From this point of view, choosing a material with high surface area and good electrical conductivity as the electrode material is especially important for a supercapacitor. Graphene, a two-dimension nanostructure material, in addition to the amazing properties above, can provide a large active surface area for fast transport of ions to achieve high double-layer capacitance. On the other hand, MnO\(_x\) is considered as one of the promising electrode materials for aqueous electrolyte supercapacitors owing to is low-cost, abundant on earth, and environmental friendly. However, due to the low specific surface area of MnO\(_2\), the specific capacitance is very low. Furthermore, although by preparing nanostructured MnO\(_x\) powders to increase the specific surface area, the structure is not stable and will be easily changed resulting in the poor cyclic performance. In addition, the low electrical conductivity will severe
affect their specific capacitance [91]. Given this situation, the MnO\textsubscript{x} is combined with graphene which will both provide the large specific surface area high electrical conductivity, and the supercapacitors using graphene-MnO\textsubscript{x} as electrode material can be benefited from EDL mechanism and the pseudo-mechanism. In this part of research study, three different types of graphene, synthesized utilizing different methods and their composites with MnO\textsubscript{x} are employed as electrodes of electrical double-layer supercapacitors (EDLS).

Supercapacitors are suffering the main limitation that the power density is significantly lower than that of the other energy storage devices. How to increase the power density of supercapacitors is another important issue should be taken into consideration. The max power of a supercapacitor can be expressed in equation 4-2:

\[
P = \frac{V^2}{4RM}\]

where \(V\) is the operating voltage of the supercapacitor; \(R\) is the equivalent series resistance, which is composed from the internal components of the supercapacitor, for example electrodes, current collector, and electrolytes; \(M\) is the total mass of the electrodes. From equation (4 - 2) it can be easily deduced that the max power of a supercapacitor is primarily limited by the operating voltage \(V\) and ESR. Electrolyte is the mainly limitation of the operating voltage. Compared with aqueous electrolyte (voltage window is about 1.2 V), ionic liquids (ILs) can provide a wide voltage window ranging from 2 – 6 V and conductivity about 10 mS/cm [52] which is an effective method to overcome its main drawback. In this research study, two types of ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF\textsubscript{4}) and 1-methyl-3-octylimidazolium tetrafluoroborate (C\textsubscript{8}mimBF\textsubscript{4}) and their mixtures at various volumetric ratios are tested as electrolytes, and their electrochemical characteristics are compared.
4.2 Research Status of Graphene-Based Electrodes

4.2.1 Graphene Nanosheets:

Graphene oxide suspension reduced by hydrazine hydrate is the simplest but useful method to prepare reduced graphene materials. Stoller and co-workers [55] prepared the reduced graphene electrodes materials through this method firstly. After the reduction procedure, the graphene sheets agglomerated into particles which was around 15 – 25 μm in diameter, and the specific surface area measured by N₂ absorption Brunauer—Emmett—Teller (BET) method was 705 m²/g. The specific capacitances of 135 F/g and 99 F/g were obtained with KOH and TEABF₄ in acetonitrile as electrolyte, respectively. It is pointed that while the graphene oxide dispersed in aqueous solution, irreversibly agglomerates will occur [57]. Chen and co-works [92] employed the gas-based hydrazine to reduce the solid-state graphene oxide instead of dispersing the graphene oxide in aqueous solutions. The agglomeration of the graphene sheets was effectively reduced. The accessibility of the ions into the reduced graphene electrodes was enhanced, not only the outer region of the solids but also the inner region compared the convention reduced by the hydrazine solution. Thus the large specific capacitance of 205 F/g with the power density of 10 kW/kg was achieved in an aqueous electrolyte.

Graphene also can be obtained through the thermal reduction of graphene oxide method. Rao et al. [93] reduced the graphene oxide at 1050°C, and the specific surface area was as high as 925 m²/g. Accordingly the specific capacitance was 117 F/g in H₂SO₄ electrolyte and 75 F/g in PYR₁₄TFSI electrolyte. The drawback of this method is that the high-temperature exfoliation process is energy consuming and difficult to control.
Yang et al. [94] introduced a high vacuum environment thus lower the reduction temperature of graphene oxide to around 200°C. The vacuum environment offered an outward driving force which will promote the fast exfoliation of graphene layers, and results in an effectively exfoliation of graphene layers. With the discharge current density of 100 mA/g, the capacitance for aqueous and organic electrolyte system were 264 F/g and 122 F/g, respectively. These values are much higher than that of high temperature reduced samples [93].

Cao and co-works [95] reported that the graphene oxide was reduced in air similar as the low-temperature thermal exfoliation approach. At the current density up to 1 A/g with KOH electrolyte, the specific capacitance was 232 F/g. This high capacitance was attributed from both the electrical double layer mechanisms from graphene sheets and pseudo-capacitance from the oxygen groups on the surface of graphene sheets. According to the authors, although the capacitance can be a little bit increased, the pseudo-capacitance is still unwanted because this will have a negative effect on the stability of the capacitors.

Ruoff et al. [56] reported that graphene oxide could be exfoliated and well dispersed in propylene carbonate (PC) solvent with the sonication treatment. The suspension was heated at 150°C to remove oxygen function group on the surface of graphene oxide. The conductivity of the reduced graphene prepared through this method was as high as 5230 S/m. Supercapacitor with this kind of reduced graphene as electrode material and EMIM-NTF₂ as electrolyte showed the capacitance of 187 F/g, energy density 6.5 Wh/kg, and power density 2.4 kW/kg with the voltage window of 3 V.
4.2.2 **Graphene-based Composites:**

After reducing the graphene oxide, due to the loss of oxygen-group between the graphene sheets, the electrostatic repulsions would decrease which will cause the reduced graphene sheets to agglomerate. Thus this will greatly limit the accessibility of ions into the surface of reduced graphene sheets, and lower the electrochemical performance of supercapacitors. From this point of view, many reports have introduced the so called “stabilizer” or “spacers” into the graphene layers to inhibit the agglomeration of reduced graphene sheets.

Si et al. [96, 97] prepared a platinum nanoparticles intercalated graphene electrode material which effectively inhibited the agglomeration of graphene sheets yielding a high specific surface area about 862 m$^2$/g. While compared with the dried graphene with the capacitance of 14 F/g, the Pt-graphene hybrid significantly increased the capacitance up to 269 F/g. Figure 4.1 shows graphene sheets and nanoparticle-modified graphene sheets in its dispersion and dry state.

![Figure 4.1 Schematics of a) graphene sheets and b) nanoparticle-modified graphene sheets in its dispersion and dry state [96].](image)
Fan and co-workers [98] employed carbon black as “spacers” to inhibit the agglomeration of graphene sheets and thus the accessibility of ions into the graphene layers. The carbon black particles were deposited on the edge of graphene sheets that help the diffusion and migration of electrolyte ions easier. Correspondingly, the obtained specific capacitance was 175 F/g at the scan rate of 10 mV/s in 6 M KOH electrolyte. Even the scan rate increased up to 500 mV/s, the capacitance still remained at 118 F/g.

Zhang et al. [99] prepared a series of surfactant-stabilized graphene materials by intercalating graphene oxide with different surfactants including tetrabutylammonium hydroxide (TBAOH), cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzenesulfonate (SDBS), then reduced by hydrazine. The researchers pointed that the wettability of such graphene materials was greatly enhanced, thus the performance as electrode of supercapacitor was improved. Among these three electrode materials, the one intercalated by the TBAOH had the best performance. The specific capacitance of that was 194 F/g in 2 M H$_2$SO$_4$ electrolyte at the current density of 1 A/g.

Recently, Wei et al.[92] successfully synthesized graphene through chemical vapor deposition method. They grew nanomeshes morphology graphene on the template porous MnO layers. By this method, only one or two layers graphene sheets was produced and with the specific surface area as high as 1654 m$^2$/g. Unlike many other methods the graphene was produced by only a small amount at one time, they could synthesis nanomesh graphene at gram-scale one time. Correspondingly, the specific capacitance tested by cyclic voltammetry was 255 F/g at the scan rate of 10 mV/s in 6 M KOH electrolyte solution. In addition, with the increasing of scan rate from 10 mV/s to 500 mV/s, only 21% specific capacitance lose.
Jang and co-workers [100] reported that they had successfully synthesized a mesoporous graphene which has very good accessibility for the ions of ionic liquids electrolytes. They first synthesized the graphene oxide using the modified Hummer’s method, and then they injected the suspension into a forced conventional oven providing a fluidized-bed situation to obtain the curved graphene sheets. This method effectively avoided the agglomeration and prevented the restacking of the graphene sheets with one another when packed or compressed into an electrode structure. With this curved-graphene as electrode and ionic liquid as electrolyte, the capacitance of 100 – 250 F/g with a voltage window of 4.0 V as high current density of 1 A/g was achieved, and the energy density was as high as 85 Wh/kg at room temperature.

4.2.3 Graphene Oxide -MnOx Nanocomposites:

Wang et al. [101] prepared GO – MnO₂ nanocomposite via a straightforward approach to deposit MnO₂ nanoparticles on the surface of the graphene oxide sheets in water/isopropanol solution. The formation mechanism that Mn ions intercalated and adsorbed onto the surface of GO sheets, followed by the nucleation and growth of the crystal species in the double solvent system which in turn exfoliated the graphene oxide sheets. It was confirmed that the α-MnO₂ could successfully attached to both sides of the GO sheets due to the function groups, such as hydroxyl and epoxy groups attached on both sides of the GO sheets. The specific capacitance of GO – MnO₂ nanocomposite was 216, 197.2, 141.5 and 111.1 F/g calculated at the current density of 150, 200, 500 and 1000 mA/g. The specific capacitance of nano – MnO₂ was 211.2 F/g calculated at a current density of 200 mA/g. However, the specific capacitance retention of nano – MnO₂ was only 69% (145.7 F/g) which was lower than that of GO – MnO₂ of 84.1% (165.9 F/g). Compared GO – MnO₂ and nano – MnO₂ electrodes, it
was confirmed that the specific capacitance of GO – MnO₂ was contributed from both electrical double layer mechanism and pseudo-capacitive mechanism. Although the specific capacitance of GO – MnO₂ was slightly lower than that of nano – MnO₂, the electrochemical stability was obviously enhanced.

Fan and co-workers [91] also synthesized graphene – MnO₂ nanocomposite by an easy deposition of nanoscale MnO₂ on the surface of graphene sheets under microwave irradiation. According to their report, the highest specific capacitance of 310 F/g was achieved with 78% wt MnO₂ content at 2 mV/s scan rate in 1 M Na₂SO₄ electrolyte. As the scan rate increased to 100 and 500 mV/s, the specific capacitance retention ratio still maintained 88% and 74%, respectively. Such promising electrochemical performance was attributed to the following reasons. First of all, the coated MnO₂ piled up to form porous which significantly improved the Na ions diffusion rate in the bulk materials. Furthermore, the nanoscale MnO₂ reduced the diffusion length of Na ions and enhanced the utilization of MnO₂. In addition, graphene in the nanocomposite not only acted as the supporters for the deposition of MnO₂ nanoparticles but also provided short electrical conductive channels for Na ions diffusion.

Li et al. [102] reported that flexible graphene– MnO₂ composite papers were fabricated through a simple chemical method. According to their report, the supercapacitor with 24% wt MnO₂ showed higher specific capacitance (256 F/g, at current density of 500 mA/g) and better cycle stability (74% after 400 cycles) than the one with 12% wt MnO₂ component (141 F/g at the current density of 500 mA/g and 52% after 400 cycles). This was ascribed to the fact that high content MnO₂ contributed more capacitance, the graphene – MnO₂ with a wall-packed layered structure not only prevents the agglomeration of the GS but also provided an easy
access of the surface to the electrolyte. Table 4.1 summarized the current research status on various graphene based electrode materials for supercapacitors.

Table 4.1 Summary of Current Research Status on Various Graphene Based Electrode Materials for Supercapacitors

<table>
<thead>
<tr>
<th>Sample</th>
<th>Basic Synthesis info</th>
<th>Specific Capacitance (F/g)</th>
<th>Electrolyte</th>
<th>Calculate method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO</td>
<td>GO reduced by hydrazine</td>
<td>135</td>
<td>KOH</td>
<td>GDC 10 mA</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>GO reduced by gas-based hydrazine</td>
<td>99</td>
<td>TEABF$_4$ in acetone</td>
<td>CV 20 mV/s</td>
<td>[92]</td>
</tr>
<tr>
<td></td>
<td>GO reduced at 1050°C</td>
<td>205</td>
<td>Aqueous electrolyte</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>GO reduced at 200°C in vacuum</td>
<td>117</td>
<td>H$_2$SO$_4$</td>
<td>CV 5 mV/s</td>
<td>[93]</td>
</tr>
<tr>
<td></td>
<td>GO reduced at 200°C in air</td>
<td>75</td>
<td>PYR$_4$</td>
<td>TFSI</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GO in PC, reduced at 150°C</td>
<td>264</td>
<td>Aqueous electrolyte</td>
<td>GCD 0 – 1V</td>
<td>[94]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>122</td>
<td>Organic electrolyte</td>
<td>100 mA/g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>232</td>
<td>KOH</td>
<td>CV 5 mV/s</td>
<td>[95]</td>
</tr>
<tr>
<td>Pt-Graphene</td>
<td>Platinum intercalate in graphene sheet</td>
<td>187</td>
<td>EMIM-NTF$_2$</td>
<td>GCD 0-3V 1 A/g</td>
<td>[56]</td>
</tr>
<tr>
<td>Carbon black-Graphene</td>
<td>Carbon black deposit on graphene sheets</td>
<td>269</td>
<td>Aqueous electrolyte</td>
<td>CV 5 mV/s</td>
<td>[96]</td>
</tr>
<tr>
<td>Surfactant-Stabilized</td>
<td>TBAOH intercalate in graphene, reduced by</td>
<td>175</td>
<td>6 M KOH</td>
<td>CV 10 mV/s</td>
<td>[98]</td>
</tr>
<tr>
<td>Graphene</td>
<td>hydrazine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Curved-Graphene</td>
<td>Apply compressed airstream</td>
<td>194</td>
<td>2 M H$_2$SO$_4$</td>
<td>GCD 1 A/g</td>
<td>[99]</td>
</tr>
<tr>
<td>GO-MnO$_x$</td>
<td>deposit MnO$_x$ nanoparticles in water</td>
<td>154</td>
<td>EMIMBF$_4$</td>
<td>GCD 1 A/g</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>Deposite MnO$_x$ under microwave irradiation</td>
<td>216</td>
<td>1 M Na$_2$SO$_4$</td>
<td>GCD 0.15 A/g</td>
<td>[101]</td>
</tr>
<tr>
<td></td>
<td>Fabricate GO-MnO$_x$ paper layer by layer</td>
<td>310</td>
<td>1 M Na$_2$SO$_4$</td>
<td>CV 2 mV/s</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>256</td>
<td>1 M Na$_2$SO$_4$</td>
<td>GCD 0.5 A/g</td>
<td>[102]</td>
</tr>
</tbody>
</table>

4.3 Experimental Aspects

4.3.1 Synthesis of Active Electrode Materials

GO is synthesized by Modified Hummer’s method, and then RG is obtained by a series of chemical reduction process. Details have been described in chapter 2.4.1. Reduced graphene oxide (RGO) is obtained from GO followed by several reduction steps. Firstly, 2 M sodium hydroxide solution was added into the 1 L GO suspension (1 g/L) until the pH value reached to 10. Then 0.2 mL hydrazine monohydrate was
added, and the mixture was heated at 95°C for 2 hours. Then the sample was filtered and dried in the vacuum oven, and RGO was obtained.

Restacking of graphene nanosheets has hampered the performance of supercapacitors using graphene materials as electrodes. The key issue of increasing the performance of graphene-based materials electrodes is to prevent the restacking and agglomeration of graphene sheets during the electrodes fabrication [92, 100]. During the process of synthesis GO, a concentrate air stream has been employed to obtain curved graphene (CRG) sheets with improved surface area.

In addition, graphene-MnOₓ nanocomposites with different types of graphene (GO, RG, CRG) and different phases of MnOₓ (Mn₃O₄ and MnO₂) were synthesized and employed as electrode materials for supercapacitors. Synthesis procedure of GO-Mn₃O₄ was described in chapter 2. GO-MnO₂ composites were obtained through the following steps. Firstly, 40 mg GO (or CRG) were placed in the 2 mL KMnO₄ (0.05 M) aqueous solution and added 10 mL deionized water. The suspension solution was under ultrasonic treatment for 30 min. Then 2 mL citric acid (0.05 M) was added and continuously stirred for 15 min. The dispersion was refluxed at 80°C for 7 hours and dried in air. Finally, the as prepared nanocomposite was annealed at 400°C for 2 hours in H₂/Ar (5%-95%) atmosphere. Figure 4.2 presents the fabrication process of GNS/MnO₂. The MnO₂ nanoparticles were homogeneously dispersed on the GNS surface, and the oxygen function groups on the surface of GO were reduced by the thermal reduction at 400°C. Hence, a 3-D sandwich-like nanostructure supported by MnO₂ nanoparticles was formed. The sample RG/MnO₂ (CRG/MnO₂) was obtained and tested as the electrode material. The electrode samples with their acronym and description are listed in Table 4.2.
Figure 4.2 Schematic illustration of fabrication process of RG/MnO2.

<table>
<thead>
<tr>
<th>S. NO</th>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GO</td>
<td>Graphene Oxide synthesized by modified hummer’s method.</td>
</tr>
<tr>
<td>2</td>
<td>RG</td>
<td>Reduced Graphene Oxide with hydrazine solution.</td>
</tr>
<tr>
<td>3</td>
<td>CRG</td>
<td>Dried in fluidized-bed to form “Curved” graphene.</td>
</tr>
<tr>
<td>4</td>
<td>CRG-Mn$_3$O$_4$</td>
<td>Curved graphene and Mn$_3$O$_4$ nanocomposite</td>
</tr>
<tr>
<td>5</td>
<td>CRG-MnO$_2$</td>
<td>Curved graphene and MnO$_2$ nanocomposite</td>
</tr>
<tr>
<td>6</td>
<td>GO-Mn$_3$O$_4$</td>
<td>Graphene oxide and Mn$_3$O$_4$ nanocomposite</td>
</tr>
<tr>
<td>7</td>
<td>RG-MnO$_2$</td>
<td>Reduced graphene and MnO$_2$ nanocomposite</td>
</tr>
</tbody>
</table>

4.3.2 Electrode Preparation

The mass of the active material and the thickness of the electrode influence significantly on the testing results [103]. In order to increase the credibility of the experiment data the electrodes were prepared by pellet pressing instead of coating. The electrode material was composed of 80% active electrode materials (listed in table 4.2), 5% styrene butadiene rubber (SBR), 5% carboxymethylcellulose (CMC), and 10% acetylene black. The SBR and CMC were working together as the binder, and the acetylene black was used to enhance the conductivity of the electrodes materials. The electrode materials was completely dried in the oven for 12 hours at 120˚C, and pressed at 1000 psi in a special model. The geometrical area of the
pelleted electrode is around 0.8 cm², correspondingly, the specific surface area of the electrode is 400 cm²/g. However, due to the porous structure existed in the electrode sample, the active surface area didn’t decrease much compared with the original specific surface area of the sample about 1200 cm²/g.

### 4.3.3 Electrolytes

The two ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) and 1-methyl-3-octylimidazolium tetrafluoroborate(C₈mimBF₄) were selected in this study. There structure schematics are shown in Fig 4.3, and the physical properties are summarized in Table 4.3. The two types ILs were also mixed at different volumetric ratio and their correlation with electrochemical performances were studied. The two ILs were placed in the glove box, and used two different syringes with the same size to take the ILs in volume. At last, the two ILs were mixed in one baker and stirred thoroughly with a glass stick.

![Figure 4.3](image)

Figure 4.3 Figure 4.3 Structure schematics of (a) [EMIM] +, (b) [C₈mim] +, (c) [BF₄].

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Cation Diameter (nm)</th>
<th>Anion Diameter (nm)</th>
<th>Viscosity (mPas)</th>
<th>Conductivity (mS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EMIM]⁺[BF₄]⁻</td>
<td>0.79</td>
<td>0.132</td>
<td>9.78</td>
<td>31.1</td>
</tr>
<tr>
<td>[C₈mim]⁺[BF₄]⁻</td>
<td>1.08</td>
<td>0.132</td>
<td>336</td>
<td>10</td>
</tr>
</tbody>
</table>
For aqueous electrolyte, 0.1 mole NaOH was gradually added to 0.05 M (50 mL) H₂SO₄ solution, and 1 M Na₂SO₄ aqueous solution was obtained after the reaction completed. The as-prepared aqueous electrolyte was used with GO-MnOₓ electrode for electrochemical characterizations.

4.3.4 Electrochemical Characterizations

Swagelok cells, consisting of two same electrodes sandwiched a separator soaked with the electrolyte, were assembled in the argon-filled glove box. After assembling the cells in the glove box, they were laid up for 24 hours before tested. The main purpose was to make sure the electrolytes will penetrate through the separator and completely soak in the electrodes materials.

Cyclic voltammetry was obtained at the preset scan rate ranging from 5 mV/s to 500 mV/s with the voltage window varying with different electrolytes on Camry electrochemical analysis system. The cells were also galvanostatically charged/discharged at the preset current density with the voltage window ranging from 0V up to 4.0 V on a battery testing station (Land CT). Electrochemical impedance spectra (EIS) was obtained by applying a sine-wave signal with an amplitude of 10 mV in the frequency range of 500kHz to 0.1 Hz on Camry electrochemical analysis system after the cell was assembled and stood for 24 hours.

For the CV tests, the specific capacitance values were calculated using the formula:

\[ C_{sp} = \frac{4}{uM} \int_{\text{initial}}^{\text{final}} \frac{idV}{uV} \]

where u, V, M are the scan rate (V/s), operating voltage (V), total mass of the active material in both of the electrodes (g), respectively. For the galvanostatic charge-discharge tests, the specific capacitance values were calculated from the formula:
\[ C_{sp} = \frac{4I\Delta t}{m\Delta V} \]

Where \( C_{sp} \), \( I \), \( \Delta t \), \( \Delta V \), \( m \) are the specific capacitance (F/g), the current loaded (A), the discharge time (s), the operating voltage (V) and the mass of active material in the electrodes (g), respectively.

### 4.4 Results and Discussion

#### 4.4.1 Cyclic Voltammetric Characteristics of GO and RGO in EMIMBF\(_4\) Electrolyte

![Cyclic Voltammograms](image)

Figure 4.4 Cyclic voltammetric characteristics of GO (a) and RGO (b) electrode in EMIMBF\(_4\) electrolyte at the scan rate of 20 mV/s with the voltage upper window ranging from 2.5 V to 3.5 V.

Figure 4.4 (a) and (b) shows the CV curves for GO and RGO as electrode material in EMIMBF\(_4\) electrolyte, respectively. For GO, as the voltage window ran from 2.5 V up to 3.5 V, the corresponding capacitance increased from 5 F/g to 13 F/g. Both of the CV curves show the relative rectangular shape which indicates the EDL mechanism of the capacitor. While the GO was chemically reduced to RGO it seems didn’t improve too much. The specific capacitance of RGO was only about 2 F/g to 5 F/g. This phenomenon can be explained from two aspects. Firstly, during the
synthesizing process of the GO and RGO, the nanosheets re-stacked dramatically which caused the specific surface area of these materials was very low. Secondly, in this experiment, EMIMBF$_4$ was employed as the electrolyte. The diameter of the cations and anions are much larger than the other types of electrolytes. Also the relative high viscosity and low conductivity further prohibited the ions from infiltrating into the electrode materials.

4.4.2 Cyclic Voltammetric Characteristics of CRG in EMIMBF$_4$ Electrolyte

Figure 4.5 (a) and (b) show the CV curves of CRG electrode in EMIMBF$_4$ at the scan rate of 20 mV/s and 50 mV/s with the potential window ranging from 2.5 V to 4 V. Both of the CV curves exhibits approximately rectangular shape, which indicates the CRG electrode in EMIMBF$_4$ as electrolyte mainly possess electrical double layer mechanism [55]. At the scan rate of 20 mV/s, the specific capacitance increased from 67 F/g to 143 F/g as the voltage window increasing from 2.5 V to 4 V. Even when the scan rate raise up to 50 mV/s, the specific capacitance still increased from 55 F/g to 109 F/g with the voltage window increasing from 2.5 V to 4 V. As the voltage run up to 4 V, an obvious sharp peak occurs, and also another peak appeared around the voltage of 1.5 V. This means with the increasing voltage window, the specific capacitance was not only contributed by the EDL mechanism, but also the pseudo capacitance.

Although the pseudo capacitance will slightly increase the specific capacitance of the supercapacitor, it is still unwanted because this may be the “unstable” factor in the capacitor and will decrease the cycle life.
Figure 4.5 Cyclic voltammetric characteristics of CRG electrode in EMIMBF4 electrolyte at the scan rate of (a) 20 mV/s and (b) 50 mV/s with the voltage upper window from 2.5 V to 4 V.

Figure 4.6 shows that even at relative high scanning rate (e.g. 500 mV/s), in the voltage window of 0 – 4 V, the CV curves still remained relative close to the rectangular shape suggesting the fast switching behavior of the ions at the CRG electrode /EMIMBF₄ electrolyte interfacial contacts. The specific capacitance decreased dramatically from 101.3 F/g to 31.6 F/g. It is noteworthy that CV curves became distorted gradually with increasing the scanning rate to 500 mV/s. This can be
attributed to the time constant of the system where the transient response falls off exponentially with the RC time constant [104]. When increasing the scan rate, the concentration gradient at the electrode/electrolyte interface will increase and the time constant will become larger. As a consequence, the transient response is pronounced leading to a lag between charging and discharging of the capacitor causing distortion of the CV[105].

![Cyclic voltammetric characteristics](image)

Figure 4.6 Cyclic voltammetric characteristics of CRG electrode in EMIMBF4 electrolyte at the different scan rates, i.e., 20 mV/s, 50 mV/s, 100 mV/s, 250 mV/s, and 500 mV/s, with the voltage window of 0 – 4 V.

The galvanostatic charge-discharge tests were also performed to further investigate the supercapacitive performance of the CRG electrode. Figure 4.7 shows the galvanostatic charge-discharge curves for at the same current density (0.5 A/g) but with different high voltage window ranging from 2.5 V – 3.5 V. Figure 4.8 shows the galvanostatic charge-discharge curve for CRG electrode in EMIMBF4 electrolyte within the same voltage window range (0-3.5V) at two different current densities, i.e. 0.5 A/g and 1 A/g.
Figure 4.7 Galvanostatic charge-discharge curves of CRG electrode in EMIMBF4 electrolyte at the current density of 0.5 A/g with the upper voltage window ranging from 2.5 V – 3.5 V.

Figure 4.8 Galvanostatic charge-discharge curve of CRG electrode in EMIMBF4 electrolyte at the current densities of 0.5 A/g and 1 A/g between 0 and 3.5V.

Both the discharge curves and the charge curves exhibit high symmetry which indicates the good capacitive behavior. The initial portions of the discharge curves show the “IR drop”, which represents the internal resistance of the supercapacitor. It is well known that the internal resistance is the sum of the resistance of the electrolyte
solution, the contact resistance of the interface active material and current collector, and the intrinsic resistance of the active material. The resistance of the electrolyte solution is always the predominate factor [22]. The conductivity and the viscosity are two important parameters of electrolytes, and will affect the resistance of the electrolyte a lot. From figure 4.7 it can be seen that with the increasing of voltage window, the “IR drop” also increased. Thus minimal additional energy can be stored at higher voltages compared with lower voltages. Seen from figure 4.8, the specific capacitance of the supercapacitor was 109 F/g at the current density of 0.5 A/g within the voltage window of 0 – 3.5 V. Even at the high current density of 1 A/g, the supercapacitor still maintained the specific capacitance as high as 89 F/g.

Figure 4.9 Coulombic efficiency and cyclic performance of CRG electrode in EMIMBF₄ electrolyte at current density of 1 A/g.

Cycle life test experiment of CRG electrode in EMIMBF₄ electrolyte was measured by the galvanostatic charge-discharge at the current density as high as 1 A/g with the voltage window 0 – 3.5 V for 1000 cycles. After 1000 cycles, the coloumbic
efficiency calculated from its charge time and discharge time still remained 95% as shown in Fig 4.9. At the first 10 cycles the capacity retention increased from 89% to 96%. This might because of the activation of the electrode material, and the electrode material soaked in the EMIMBF$_4$ electrolyte thoroughly. The specific capacitance of CRG electrode was found to gradually decrease from 80 F/g to 54 F/g, and the specific capacitance fade per cycle was only 2.6%. All these above indicate the good cyclic performance of this supercapacitor.

4.4.3 Cyclic Voltammetric Characteristics of CRG in C$_8$mimBF$_4$

Similar to those in EMIMBF$_4$ electrolyte, CV curves of CRG electrode in C$_8$mimBF$_4$ are rectangular shape at the scan rate of 20 mV/s and 50 mV/s as shown in figure 4.10 (a) and (b). This indicates the EDL mechanism. However, it can be clearly observed that as the voltage window runs up to 3.0 V and above, sharp peaks occur during charge and a corresponding discharge peak emerges around 0.5 V. This phenomenon indicates that although the stable potential window with C$_8$mimBF$_4$ electrolyte is claimed to reach up to 4 V, there is still some processes (may be involved in some redox reactions) occurred at the interface between CRG electrode and C$_8$mimBF$_4$ electrolyte. Firstly, the “ionic absent effect” is usually observed when the local voltage is raised too high even though the voltage window still doesn’t reach the decomposition voltage of the electrolyte [56, 106]. Secondly, the ionic liquid has strong polarity and it is very difficult to completely remove the water in it which may also cause the partial decomposition of the ionic liquid electrolyte and affect the upper voltage window [99]. Since this process is partially reversible, the capacitance of the capacitor is not only contributed by the electrical double-layer mechanism but also the
pseudo mechanism. It is worthy to note that this redox process will reduce the capacitance upon charge/discharge cycling.

Figure 4.10 Cyclic voltammetric characteristics of CRG electrode in C8mimBF4 at the scan rate of (a) 20 mV/s and (b) 50 mV/s with the upper voltage window ranging from 2.5 V – 4 V.

Figure 4.11 shows the galvanostatic charge-discharge curves for CRG electrode in C8mimBF4 electrolyte at the current density of 0.5 A/g and 1 A/g with the voltage
window ranging from 0 – 3.5 V. Compared with figure 4.8, the discharge and charge profile becomes asymmetrical and the “IR” drop is much higher.

![Graph showing voltage vs. time for CRG electrode in C8mimBF4 electrolyte at different current densities.](image)

Figure 4.11 Galvanostatic charge-discharge curves of CRG electrode in C8mimBF4 electrolyte at the current density of 0.5 A/g and 1 A/g with the voltage window of 0 – 3.5 V.

### 4.4.4 Electrochemical Impedance Spectroscopy Analys

The EIS Nyquist plots were utilized to analyze the electrolyte resistance, electrode impedance and the diffusion procedure of the electrolyte ions. The more vertical of the tail at low frequency the more cell responds closely to an ideal capacitor [55]. Figure 4.12 (a) and (b) shows the Nyquist plot of CRG electrode in EMIMBF4 electrolyte and C8mimBF4 electrolyte, respectively. It can be seen that the tail at low frequency region exhibits a 45° slope line instead of ideal capacitive vertical line. This 45° portion of curve is referred to Warburg resistance correlating with the ion diffusion in the electrode [55]. The dominant Warburg resistance is because of the relative low conductivity and high viscosity of the ionic liquid electrolytes.
At the high frequency region, electrolyte resistance can be determined from the x-intercept of the spectra. The equivalent series resistances of the capacitor in EMIMBF$_4$ electrolyte and C$_8$mimBF$_4$ electrolyte are 15 $\Omega$ and 25 $\Omega$, respectively. This analysis corroborated well with the IR drop observed in the charge/discharge profiles. The conductivity and the viscosity are two important parameters of electrolytes and will affect the resistance of the electrolyte. Because the [C$_8$mim]$^+$ cation has a much longer molecular chain than [EMIM]$^+$ cation, the former one offers the higher electrostatic attraction and hampered the mobility of ions. As a result, the resistance and the “IR drop” of the supercapacitor with C$_8$mimBF$_4$ electrolyte is much higher than that with EMIMBF$_4$.

![Figure 4.12 Nyquist plots of CRG electrode in EMIMBF$_4$ electrolyte (a) and C$_8$mimBF$_4$ electrolyte (b) before charge/discharge process.](image-url)
4.4.5 Ionic Liquid Electrolytes Mixed at Different Ratio

The two types of ionic liquids, EMIMBF$_4$ and C$_8$mimBF$_4$, are mixed together to test the effects of different ratio of two ionic liquids on the electrochemical performance of the capacitor. Figure 4.13 shows the CV curves of the CRG in mixed with a different ratio at the scan rate of 20 mV/s with the upper voltage windows set to 2.5 V, 3.0 V or 3.5 V.
Figure 4.13 Cyclic voltammetric characteristics of CRG electrode in the mixing EMIMBF4 and C8mimBF4 electrolyte with different volumetric ratio at the scan rate of 20 mV/s with the upper voltage window at 2.5 V (a,b), 3.0V(c,d) and 3.5 V (e,f).

Figure 4.13 compiles the specific capacitances of supercapacitors made up of electrolyte with different volumetric ratio of the two ionic liquids. When the capacitor was totally in EMIMBF4 as electrolyte, the capacitance is the highest (116 F/g) between the voltage window of 0 – 3.5 V. Then the specific capacitance gradually decrease with the increasing volumetric ratio of C8mimBF4 to 40% (80 F/g). Subsequently with the increasing of C8mimBF4, the specific capacitance changes less significantly within the range of 80 F/g to 92 F/g with a second peak at 80% C8mimBF4 and 20% EMIMBF4.

Figure 4.14 Specific capacitances of CRG electrode changing with the volumetric ratio of the mixing EMIMBF4 and C8mimBF4 electrolyte.
We attempt to propose a model to explain the observed phenomenon. Because the specific capacitance of supercapacitor is directly correlated with the charges accumulated on the surface of active electrode materials, the more charges on the surface the higher specific capacitance it will be. If there were only one size of ions on the surface, the utilization of the ions would not be sufficient. Mixing the different sizes of ions together is helpful to increase the charges accumulating. Figure 4.15 is the schematic illustration of this model.

In the current research, two types of ionic liquids electrolytes, C$_8$ mimBF$_4$ and EMIMBF$_4$ are tested. It is an effective method to increase the power density and energy density which are also the main limits for the applications of supercapacitors. In the future work, more types of ionic liquids with different anion and cation structures should be experimentally tested. Also mixing two or more types of ionic liquids may be able to decrease the viscosity and increase the conductivity of the mixture.

Figure 4.15 Schematic of the specific capacitance versus size of anions.
4.4.6 GNS/MnO\textsubscript{x} in Aqueous Electrolyte

4.4.6.1 Effects of GNS content:

Figure 4.16 shows the CV curves of CRG/Mn\textsubscript{3}O\textsubscript{4} nanocomposite electrode with different CRG content in 1 M Na\textsubscript{2}SO\textsubscript{4} electrolyte. It can be observed that all the CV curves show relative rectangular shape indicating its electric double layer capacitance. With the increasing of scan rate from 5 to 50 mV/s, the curves exhibit slightly distortion. At the scan rate of 5 mV/s, the specific capacitance of the supercapacitor was 29 F/g, as the scan rate increasing up to 50 mV/s, a specific capacitance of 13 F/g maintains. The decrease in capacitance at higher scan rates is assigned to the presence of inner active sites that cannot sustain the redox transitions, which is possibly due to the diffusion effect of ions within the electrode. The decreasing trend of the capacitance indicates that parts of the surface of the electrode are inaccessible at high charging–discharging rates[107].

Obviously, the shape of the CV curves, shown in figures 4.16 (a) – (c), changed from ideal rectangular to oval with the increasing of scan rate. According to Li et al. [108], this phenomenon can be caused by the following reasons: firstly, the internal resistance of the electrode inhibited the charge collection; secondly, the relative low conductivity of the 1 M Na\textsubscript{2}SO\textsubscript{4} electrolyte solution; finally, the diffusion limitation of Na\textsuperscript{+} in the electrode.

By comparing figure 4.16 (a) – (c), it can be easily concluded that with the increasing of Mn\textsubscript{3}O\textsubscript{4} weight content ratio in the hybrid electrodes the specific capacities are gradually decreasing. For example, at the Mn\textsubscript{3}O\textsubscript{4} weight ratio of 50%, 66% and 75%, the specific capacities are 31, 23, and 19 F/g, respectively. This phenomenon can be contributed by the decreasing of GNS content in the hybrid material which reduces the electrical conductivity.
4.4.6.2 Effects of different MnOx phase

CV and galvanostatic charge-discharge electrochemical tests were also performed to investigate the electrochemical performance of the CRG/MnO₂ electrode sample (see figure 4.17). The specific capacitance of CRG/MnO₂ was calculated to be 109.6, 74, and 62 F/g at the scan rate of 5, 20, 50 mV/s, respectively. Compare CRG/MnO₂ (figure 4.17) and CRG/Mn₃O₄ (figure 4.16), the specific capacitance of the former one (109.6 F/g) is much higher than the latter one (30 F/g). This implies that the MnOₓ phase affects the electrochemical properties significantly and MnO₂ is more suitable than Mn₃O₄ in working as electrode material for supercapacitors.

4.4.6.3 Effect of different types of GNS

Since the RG/MnO₂ and CRG/MnO₂ were all synthesized with the same procedure, both of the samples have the same weight ratio of MnO₂ and the same phase of manganese oxide, the only difference is the graphene nanosheets. The CV profiles of RG/MnO₂ were presented in figure 4.18. The specific capacitance of RG/MnO₂ hybrid material calculated by the CV profiles was 164, 121 and 80 F/g at the scan rate of 5, 20, 50 mV/s, respectively.

Compare figure 4.18 to figure 4.17, the former one shows more ideal rectangular shape even at high scan rate of 50 mV/s, which indicates the CRG/MnO₂ has a lower internal resistance. However, the specific capacitance of CRG/MnO₂ was slightly lower than that of RG/MnO₂. This might because the specific surface area of CRG is much higher than that of RG, and during the preparing procedure, not all the MnO₂ was able to attach on the surface of graphene nanosheets.
Figure 4.16 Cyclic voltammetric characteristics of (a) CRG/Mn3O4-50, (b) CRG/Mn3O4-66, and (c) CRG/Mn3O4-75 electrodes in 1 M Na2SO4 electrolyte at different scan rates from 5 to 50 mV/s.
Figure 4.17 Cyclic voltammetric curves of CRG/MnO₂ electrode: at the scan rate of 5 to 50 mV/s

Figure 4.18 Cyclic voltammetric curves of RG/MnO₂ electrode: at the scan rate of 5 to 50 mV/s
4.5 Summary

The GO and RG made by the modified Hummer’s method had relative low surface area. When working as electrode materials in EMIMBF$_4$ electrolyte, the specific capacitance were as low as 13 F/g and 5 F/g, respectively, due to the “re-stack” during the preparation of the samples. The CRG electrode in EMIMBF$_4$ electrolyte shows a high specific capacitance of 143 F/g at the scan rate of 20 mV/s with the voltage window of 0 – 4 V, and good cycle performance with 2.6% decreasing per cycle after 1000 cycles. The curved shape graphene sheets (CRG) effectively inhibit the agglomeration and highly increase the specific surface area. This makes it an extremely promising candidate electrode material for the electrical double-layer capacitors.

The electrochemical characteristics of CRG in two different types of ionic liquid electrolytes, i.e. EMIMBF$_4$ and C$_8$mimBF$_4$, are compared and summarized in Table 4.4. This study shows that EMIMBF$_4$ can provide a higher specific capacitance, a wider stable voltage window, leading to higher energy and higher power density. Since the two ionic liquids has the same anion, [BF$_4$]$^+$, and the same structure of cations. The only different is the length of chain group on the imidazole ring. C$_8$mimBF$_4$ with the relative longer chain group has higher van der Walls’s force than that of EMIMBF$_4$. Therefore, C$_8$mimBF$_4$ has a lower conductivity and higher viscosity, and the electrochemical performance of the supercapacitor in C$_8$mimBF$_4$ is not as good as the one in EMIMBF$_4$.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Voltage Window (V)</th>
<th>Specific Capacitance (F/g)</th>
<th>Power Density (kW/kg)</th>
<th>Energy Density (Wh/kg)</th>
<th>Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRG</td>
<td>EMIMBF$_4$</td>
<td>0 – 3.5</td>
<td>116</td>
<td>34</td>
<td>197</td>
<td>15</td>
</tr>
<tr>
<td>CRG</td>
<td>C$_8$mimBF$_4$</td>
<td>0 – 3</td>
<td>66</td>
<td>13</td>
<td>82.5</td>
<td>25</td>
</tr>
</tbody>
</table>
Two types of ionic liquids, EMIMBF$_4$ and C$_8$mimBF$_4$, which have the same anions and different cation chains were mixed together, in order to find out the effects of the length of cation chains to the electrochemical performance of ionic liquids. When the electrolyte was solely EMIMBF$_4$, the supercapacitor had the highest specific capacitance of 116 F/g (0 – 3.5 V, 20 mV/s). With the increasing of C$_8$mimBF$_4$ to 40% mass ratio, the specific capacitance continued decreasing, and roughly kept the same as the mass ratio of C$_8$mimBF$_4$ from 60% - 100%.

Different types of GNS/MnO$_x$ hybrid nanocomposites were synthesized and compared as electrode materials for supercapacitors. The specific capacitance and weight ratio of MnO$_x$ content for each sample are summarized in Table 4.5. It was found that the phase of GNS and MnO$_x$ both affect the electrochemical performance significantly. In the nanocomposites RG is more suitable than CRG, and MnO$_2$ is better than Mn$_3$O$_4$ obviously.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Capacitance of Total (F/g)</th>
<th>Specific Capacitance of MnO$_x$ (F/g)</th>
<th>Weight Percentage of MnO$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PureRG</td>
<td>2.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RG/Mn$_3$O$_4$</td>
<td>29</td>
<td>32.5</td>
<td>89%</td>
</tr>
<tr>
<td>RG/MnO$_2$</td>
<td>102 96 164 71 50</td>
<td>637 342 482 173 106</td>
<td>16% 28.8% 34% 41% 47%</td>
</tr>
<tr>
<td>CRG/Mn$_3$O$_4$</td>
<td>38 23 20</td>
<td>76 35 27</td>
<td>50% 66% 75%</td>
</tr>
<tr>
<td>CRG/MnO$_2$</td>
<td>109.6</td>
<td>363</td>
<td>30%</td>
</tr>
</tbody>
</table>

The RG/MnO$_2$ with 34% MnO$_2$ content reached the highest specific capacities of 164 F/g at the scan rate of 20 mV/s. In the hybrid materials, MnO$_x$ contributes a lot on
the specific capacitance by the pseudo-capacitive mechanism. However, when the weight ratio of MnO$_x$ in the hybrid material is too much the specific capacitance will be decreased. This is because MnO$_x$ will reduce the conductivity of the electrode material.
Chapter 5: Conclusion

Carbon-based electrode materials have showed great potential in alternative energy technologies. Electrochemical characteristics of carbon-based electrode materials graphene nanosheets (GNS), reduced graphene (RG), GNS/MnOₓ hybrid materials employed in both lithium-ion batteries and supercapacitors were studied. In addition, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) and 1-methyl-3-octylimidazolium tetrafluoroborate (C₈mimBF₄) are tested as electrolytes for supercapacitors, and their electrochemical characteristics are compared. Furthermore, silicon nanowires (SiNWs) were directly deposited on the substrate of carbon nano-fibers (CF) through the chemical vapor deposition with Au catalyst, and the SiNWs/CF composite were tested as anode material for lithium-ion batteries.

GO/MnOₓ is a priority anode in Li-ion battery, and the lower manganese valency would deliver higher reversible capacity. GNS/MnOₓ—150 (synthesized at 150°C in air) delivered a reversible discharge capacity of 619 mAh/g with an average Coulombic efficiency of 92% and low capacity fade per cycle of 2.6%. GNS/MnOₓ—400 (synthesized at 400°C in air) delivered a reversible discharge capacity of 213 mAh/g with an Coulombic efficiency of 80% and capacity fade per cycle of 5.9%. The decreased electrochemical performance is caused by the higher thermal treatment temperature which greatly increased the particle size of MnOₓ. GNS/MnOₓ—400 inert (synthesized at 400°C in 5% H₂/Ar atmosphere) showed a reversible discharge
capacity of 719 mAh/g with the Coulombic efficiency of 92% and low capacity fade per cycle of 0.8%. On the one hand, MnO$_x$ nanoparticles working as “spacer” between the GNS formed a 3 – D structure which greatly increased the accessibility of lithium ions. On the other hand, GNS worked as a “buffer” accommodated the great volume change caused by the manganese oxide displacement reaction, and provided short conductivity path for lithium ions.

SiNWs grown on carbon fibers (28wt% of SiNWs) delivered a high reversible discharge capacity of 975 mAh/g with an average Coulombic efficiency of 85.7% and capacity fade per cycle of 9.3%. The sample combined with GO and SiNWs/CF showed a reversible discharge capacity of 890 mAh/g equivalent to the capacity of 2490 mAh/g based on Si with the Coulombic efficiency of 77%, and the capacity fade per cycle was 11% after 5 cycles. This promising result indicates that utilizing an effective buffer (GO) to accommodate will greatly promote the cyclic performance.

For supercapacitors three different types of GNS were tested as the electrode material in two types of ionic liquids electrolytes, C$_8$mimBF$_4$ and EMIMBF$_4$. Both of the ionic liquids have the same anions $[$BF$_4]$⁻, and the only difference is the length of the branch chains of the cations. It was experimentally verified that the longer branch chain will decreased the conductivity and charge accumulated on electrode surface resulting in low capacitance. The curved GNS, which has the highest specific surface area, delivered a high specific capacitance of 116 F/g in EMIMBF$_4$ electrolyte at the scan rate of 20 mV/s with the power density of 34 kW/kg and energy density of 197 Wh/kg.

GNS/MnO$_x$ (CRG/Mn$_3$O$_4$, RG/Mn$_3$O$_4$, CRG/MnO$_2$ and RG/MnO$_2$) specimens were tested as the electrode material for supercapacitor in 1 M Na$_2$SO$_4$ electrolyte. RG/ MnO$_2$ composite showed highest specific capacities of 164 F/g at the scan rate of
20 mV/s with the voltage window ranging from 0 – 4 V. In the hybrid material, MnO$_x$
contribute a lot by the pseudo – capacitive mechanism.
REFERENCES


A. Anani and R. A. Huggins, "Multinary alloy electrodes for solid state batteries I. A phase diagram approach for the selection and storage properties


[78] L. Ji, *et al.*, "Graphene/Si multilayer structure anodes for advanced half and full lithium-ion cells," *Nano Energy*.


