ASYMMETRIC CAPACITORS BASED ON

VANADIUM DIOXIDE/GRAPHENE/NICKLE

AND CARBON NANOTUBE ELECTRODES

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ASYMMETRIC CAPACITORS BASED ON
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AND CARBON NANOTUBE ELECTRODES

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Thesis

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ABSTRACT

A high energy density asymmetric supercapacitor (Vanadium dioxide/ graphene/Nickle (VGN)// Carbon nanotube) was fabricated in this research. Graphene and vanadium dioxide (VO$_2$) were used as the supporting and active materials, respectively, to build the positive electrode of the asymmetric capacitor. Graphene was grown on the porous nickel (Ni) foam in order to supply both large surface area and bi-continuous electron/electrolyte passages. Vanadium dioxide was used to provide large redox based capacitance. Carbon nanotube (CNT) was chosen as the negative electrode due to its stability under reductive condition and its high surface area. Both of the graphene and CNT were synthesized by chemical vapor deposition method. Vanadium dioxide was prepared on graphene/Ni substrate by hydrothermal reaction. In an asymmetric supercapacitor device, CNT was used as anode and VO$_2$/Graphene is used as cathode. The device can be operated at a voltage up 1.6 V in aqueous solution and achieved a remarkable capacitance of 187 F/g at a charge/discharge current density of 5 A/g with an energy density of 16.6 W h/kg and a power density of 2 KW/kg. Moreover, the device showed an excellent cycling performance in 4.0 M KCl electrolyte with a capacitance retention of 98.8% after 1000 cycles and 87.7% after 3000 cycles.
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CHAPTER I

INTRODUCTION

1.1 Carbon-based material (Graphene and CNT)

Graphene is a 2D sheet of carbon atoms arrayed in a hexagonal honeycomb lattice.\(^1,2\)

![Unit Cell]

Figure 1-1: Diagram showing the graphene lattice unit cell.\(^3\)

Graphene has been attracting great interest because of its distinctive physical properties.\(^2,3\) First, it has large specific surface area (SSA) (theoretical SSA: 2630 m\(^2\)/g) with high electrical conductivity (1738 Siemens per meter).\(^4\) In addition, it’s transparent and absorbs only 2.3% of incident light per single graphene sheet.\(^5\) What’s more, the electron mobility of graphene at room temperature is very high, with reported values in
excess of \(15,000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}\). The mechanical properties of graphene are also excellent. It has a breaking strength over 100 times greater than a hypothetical steel film of the same thickness.\(^6\)

Overall, good conductivity, light, transparent, large surface area and mechanical stability make graphene a promising materials in many applications.

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure.\(^7\)

![Figure 1-2: Diagram showing the single wall carbon nanotube.](image)

These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity, mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials. In addition, the high electrical conductivity and specific surface area render them promising for energy storage applications.\(^9\)
1.2 Chemical vapor deposition

Many methods have been developed to produce graphene, such as chemical reduction of graphite oxide\(^{10}\) high temperature annealing of single crystal silicon carbide (SiC)\(^{11}\) and chemical vapor deposition (CVD) on metal substrates.\(^{12}\) CVD is regarded as the most promising method to grow graphene with good quality and large size.

There are two types of growth mechanisms depending on the solubility of carbon in the metal.\(^{13}\) One is the carbon segregation and/or precipitation mechanism as schematically illustrated in Fig. 1-2-a.\(^{14}\) For those catalysts with a 50% high solubility of carbon such as Ni, the hydrocarbon compound cracks at high temperatures to form carbon atoms, which dissolve in the metal.\(^{15}\) Upon cooling, the carbon atoms precipitate out from the metal and then are nucleated on the surface to form graphene. The number of graphene layer is strongly dependent on the cooling rate. The other one is the surface growth mechanism as shown in Fig. 1-2-b.\(^{13}\) Instead of diffusing into the matrix of metal catalysts, carbon precursor layer firstly adsorbs on the surface of copper catalyst, and then nucleates and grows to form graphene island and finally graphene by continuous growth.\(^{16}\)
In this research, copper is used as substrate to grow single layer graphene. Furthermore, a more complicated material, porous Ni is used as the substrate to grow curved graphene. Synthesis of CNT is another job in this research. CVD is used to synthesize vertically aligned carbon nanotube on stainless foil. The mechanism of nanotube formation is hypothesized to be as follows: First the ethylene ($C_2H_4$) was decomposed to produce free radicals, which formed CNTs in presence of the iron catalyst. Once the catalyst deactivates, the formation of CNT will be stopped. Active free radicals are also known to recombine with carbon to form larger molecules. Therefore, on one hand the carbon formed in the gas phase was deposited on the metal surface, at the same time the carbon was consumed to form secondary products. As the residence time along the tube increased, the concentrations of the active species changed, leading to CNTs films with different thickness. The experimental details will be discussed in chapter 2.
1.3 Supercapacitor

Supercapacitors as promising energy storage devices have attracted much attention in the past few decades due to their high power density, charge/discharge rates as well as long lifetime cycles. The comparison of various energy-storage devices shown in the following figure 1-3.

![Ragone chart showing energy density vs. power density for various energy-storage devices.](image)

Figure 1-4: Ragone chart showing energy density vs. power density for various energy-storage devices.

Specific capacitance, energy density and power density are three important parameters for the performance of capacitors. The specific capacitance of pseudocapacitors can be obtained by two different methods. It can be calculated from the cyclic voltammetry (CV) curves by using Eq.
\[
CS = \frac{2 \int idV}{m \times \Delta V \times S}
\]  

(1)

where \(Cs\) is the specific capacitance, \(\int idV\) is the integrated area of the CV curve, \(m\) is the mass of active material, \(\Delta V\) is the potential range, and \(S\) is the scan rate.

Alternatively, the specific capacitance can be calculated from the Charge-Discharge (CD) curves by using the Eqs. (2) \(^{19}\)

\[
CS = \frac{4I}{m \times dV/dt}
\]

(2)

where \(I\) is the applied current, \(m\) is the mass of the active material, and \(dV/dt\) is the absolute value of the slope of the discharging curve.

The energy density and power density can be calculated at using Eqs. (3) and (4), respectively\(^{19,20}\).

\[
E = \frac{1}{8} CS \times (\Delta V)^2
\]

(3)

\[
P = \frac{E}{t}
\]

(4)

where \(E\) is the energy density, \(CS\) is the specific capacitance from CD, \(\Delta V\) is the potential range, \(P\) is the power density and \(t\) is the time to discharge. However, the energy density of supercapacitors is still lower compared with conventional batteries, although it has improved a lot than conventional batteries which limits their use in some applications.\(^{21}\)
According to the above equation 3, Energy density is determined by capacitance and chemical window of the device.\textsuperscript{20} In a standard symmetric supercapacitor, the chemical window is limited by the electrochemically reversible potential window of the electrode materials and electrolytes, whichever is smaller. For instance, in an aqueous system, the chemical window of the supercapacitor is limited to \(~1\text{ V}\) due to the redox of solvent water. Asymmetric supercapacitors can make use of the different potential windows of two electrodes to increase the maximum operation voltage in the cell system, resulting in an enhanced specific capacitance and significantly improved energy density.\textsuperscript{22} Electrodes of asymmetric capacitor usually consist of two different types: a battery-type Faradic electrode (as energy source) and an electrostatic double layer capacitor type electrode (as power source).\textsuperscript{22}

Transition metal-oxides\textsuperscript{22-24} often exhibit several oxidation states and the electrochemically Faradaic redox reactions between those oxidation states are fast and reversible. As such, they are often used as positive electrode for energy source in asymmetric supercapacitors. Although the transition metal-oxide materials provide large redox capacitance, their conductivity is usually poor and additional conducting fillers are typically required on the positive electrode.\textsuperscript{25} On the negative electrode side, carbon is the most commonly used materials due to its stability under reduced conditions. However, the specific capacitance of electrostatic double layer based carbon materials is typically smaller than that of redox reaction based transition metal oxides, hence the high electrolyte accessible surface is desired for carbon materials in order to balance the capacitance of positive electrode with minimum excess of mass.
Therefore, in an asymmetric supercapacitor consisting of redox cathode and electrostatic double layer anode, the power density is limited by the redox electrode and the energy density is limited by double layer electrode. To build an ideal asymmetric supercapacitor, the redox materials need to be optimized to gain faster ion and electron transport properties, on the other side, the double layer electrode should be optimized in order to achieve large electrochemistry accessible surface area. Here in this work, a novel aqueous electrolyte based asymmetric supercapacitor device with vanadium oxide/graphene positive electrode and carbon nanotube (CNT) negative electrode was developed. Vanadium oxides have attracted much attention for supercapacitor applications\textsuperscript{23,25-32} recently due to the abundance of the material and a broad range of oxidation states. Graphene is a zero bandgap semimetal and has extremely high surface area and conductivity\textsuperscript{3}, which was used to construct three-dimensional bi-continuous substrate for vanadium oxide in this work. Vertically aligned CNT (VACNT) was synthesized on the stainless steel sheet as negative electrode, which provides both large surface area and stability under reductive environment.\textsuperscript{17} The asymmetric capacitors exhibited a stable operational voltage up to 1.6 V in aqueous media and achieved a capacitance of 187 F/g at a current density of 5 A/g. The device showed an energy density of 16.6 Wh/kg at a power density of 1.99 KW/kg.
Figure 1-5. Schematic illustration of the asymmetric supercapacitor device composed of the VO$_2$/graphene/Ni cathode and CNT anode

The scheme of the asymmetric supercapacitor is illustrated in Figure 1-5. The current collector of the positive electrode is nickel foam. Graphene is synthesized on the surface of nickel to provide both high surface area substrate and electron conducting path. The vanadium dioxide (VO$_2$) nanocrystals are synthesized on the surface of graphene by hydrothermal reaction$^{33}$ (see Methods for the detail). In such a design, the structure of the positive electrode is bi-continuous. The thin active material film (VO$_2$) is covered on the porous conducting graphene substrate, the electron transfer distance (from VO$_2$ to graphene) is very short. In addition, graphene provides a fast channel for electron transport to the current collector. On the other hand, the electrolyte can have a continuous channel (the voids of the graphene substrate) to flow, which promotes the ion mobility and electrolyte-oxide materials interaction. Such a design can benefit the high power density of the positive electrode, which is usually the limiting factor of metal oxide
cathode in asymmetric supercapacitor. The negative electrode of the asymmetric supercapacitor in this work is VACNT on stainless steel. Carbon nanotube is widely used as negative electrode material in asymmetric capacitors due to their high surface area and good stability. In this work, VACNT were synthesized by chemical vapor deposition system on stainless steel substrate. Therefore the as prepared sample can be directly used in supercapacitor fabrication without using binder materials. The VACNT has high specific area and high density, which is required for the electrostatic double layer based negative electrode in asymmetric supercapacitor.
CHAPTER II

EXPERIMENTAL SECTION

In this chapter, the materials and instrument for this research are discussed, which include the growth techniques of porous graphene and CNT, the deposition of metal oxide, and the characterization of the materials, the fabrication and evaluation of capacitors.

2.1 Experimental process

In this research, CVD system is used to grow graphene and CNT. The picture of CVD system is shown in figure 2-1.

![Chemical vapor deposition system](image)

Figure 2-1: Chemical vapor deposition system
2.1.1 Synthesis of graphene on Ni foam

Graphene was synthesized by chemical vapor deposition on the pressed Ni foam substrate via modified procedure from literature. The commercial nickel foam is pressed and then transferred into the center of tube furnace. The sample is then annealed at 1000 °C for 20 minutes under argon (Ar) (500 sccm, 1 atm). After annealing, the argon was replaced with growth feed stocks (hydrogen (H₂): 200 sccm and methane (CH₄): 8 sccm). The growth time is 5 minutes.

2.1.2 Synthesis of CNT/stainless Composites

A layer of CNT catalyst (Fe/Al₂O₃: 1 nm/10 nm) was coated on stainless steel sheet (TBI) by E-beam evaporator. VACNT were grown on the stainless steel sheets by chemical vapor deposition method. The process is similar to graphene growth except the following changes: The reaction gas feedstock are H₂ (100 sccm), C₂H₄ (8 sccm) and H₂O (50 sccm, delivered by bubbling H₂ through a water bath). The growth temperature is 750 °C and growth time is 10 min.

2.1.3 Hydrothermal reaction

VO₂ was prepared by hydrothermal method. Briefly, V₂O₅ (CACROS, 0.225 g) was dissolved in 10 mL of deionized water with stirring. The solution was heated to 80 °C and 0.375 mL of H₂SO₄ (J.T.Baker) was added to the yellow suspension and stirred for a while. Subsequently, 0.125 mL of hydrazine hydrate (Alfa Aesar, 99%) was added to the solution. The color of the solution changed to green and then to blue. The PH of the solution was then adjusted to 4 by 1 mol/L NaOH solution. At the end of the addition,
gray to brown precipitates were formed. The whole procedure was carried out under the solution temperature of 80 ºC. The precipitate was filtered and washed with water, then it was redispersed in 10 mL of water in a Teflon-lined autoclave. Graphene covered nickel foam samples was added to the solution. The hydrothermal reaction was carried out at 220 ºC for 1h. After the reaction, the samples were taken out and washed gently then dried in vacuum oven. The black precipitates from the solution (the free-standing VO$_2$ nanocrystal) were also collected for XRD experiments.

![Synthesis of Vanadium dioxide](image)

**Figure 2-2:** Synthesis of Vanadium dioxide.

2.1.4 Fabrication of supercapacitors

In order to obtain the capacitance of individual electrode, the three electrode system are used. The active materials is used as working electrode, potassium chloride (4 M) was
used as electrolyte. Platinum wire and SCE electrodes were used as counter and reference electrodes, respectively (shown figure 2-3). To construct an asymmetric supercapacitor, the loading mass ratio of active materials was estimated by the specific capacitance from CV results in the three-electrode system. The asymmetric supercapacitor was built by stacking anode, fibrous separator (cellgard 3501) and cathode in series in a swagelock cell. The electrolyte is degased 4 M KCl aqueous electrolyte solution. The impedance spectroscopy was measured in the frequency range of 100 kHz-0.1 Hz at open circuit potential with an alternative current perturbation of 5 mV. The following figure is the system used in the experiment. (figure 2-4), the method of assessment is shown in figure 2-5. All electrochemical measurements were carried out on a CHI 660 electrochemical workstation.

![Figure 2-3: Scheme of the setup of the electrochemical workstation](image-url)
2.2 Characterization

Graphene and CNT were characterized by Raman (HORIBA Labman, wave length: 532 nm). The crystallographic structures of the vanadium dioxide were determined by a powder XRD system (Bruker AXS Dimension D8) equipped with Cu Kα radiation (λ = 0.15406 nm). The microstructure of the samples was investigated by SEM (JEOL JSM-7401) and TEM (JEOL JEM2010). The high resolution TEM was obtained on a FEI Tecnai G2 F20 ST TEM.
2.2.1 The characters of carbon nanotube/stainless steel composite

Carbon nanotube is widely used as negative electrode material in asymmetric capacitors due to their high surface area, good stability and low cost. In this work, carbon nanotubes were synthesized by chemical vapor deposition system on stainless steel. Figure 2-5 is SEM images for CNT, the length of the CNT is about 500 microns. Figure 2-6 is Raman spectroscopy for CNTs. The ratio of the D peak and G peak means it is multi-wall carbon nanotubes.

Figure 2-6: SEM for CNT on stainless steel.
2.2.2 The characters of VO$_2$/Graphene/Ni composite and VO$_2$ powders.

Figure 2-7(a) is the photo of nickel foam sample, sample after graphene growth and after VO$_2$ deposition. The detailed experiments are described in the Methods part. The sample became darker after each step. The graphene grown on the nickel foam has been investigated by Raman spectroscopy (Figure 2-7(b)). From the Raman spectrum, the two characteristic G (1575 cm$^{-1}$) and 2D (2740 cm$^{-1}$) are very clear. The spectrum indicated a monolayer or double layer graphene based on the ratio of G/2D.$^{35}$ However, recent research indicates that the graphene grown on the nickel surface are usually multilayered due to the segregation mechanism. In this case, it is difficult to perform Raman mapping as the substrate is curved. Nevertheless, the suppression of the D (~1380 cm$^{-1}$) indicated that the quality of the graphene grown here is good.
A series SEM images has been shown in Figure 2-7(c) – (f), which provide the microscopic information of untreated nickel foam 2-7(c), graphene covered nickel foam 2(d) and VO$_2$ covered graphene on nickel foam 2-7(e) and 2-7(f). The insets of 2-7(c) – (e) are same sample under higher magnification. It is clear that after graphene growth, the morphology of the nickel foam didn’t change. The surface of the nickel foam is covered by graphene with different domain size. The wrinkles in the inset of Figure 2-7(d) are possible domain boundaries which can be found in CVD graphene very often$^{22}$. After hydrothermal treatment, a layer of vanadium oxide is covered on the graphene surface homogeneously. (Figure 2-7 e) The EDAX experiments (Figure 2-8) also confirmed this uniform coverage. Figure 2-7(f) is the high-resolution SEM image on the indicated area of the inset of Figure 2-7(e). It is obvious that the vanadium oxide is nanowhisker shaped and has much larger surface area compared with the substrate.
Figure 2-8: Images of the electrode material. (a) Photos of (i) pure Ni foam, (ii) graphene/Ni foam and (iii) VO$_2$/graphene/Ni foam. (b) Raman spectroscopy for graphene on Ni foam. (c) SEM images for pure Ni foam. (d) graphene/Ni foam. (e) VO$_2$/graphene/Ni. Insert is high magnification. Scar bars in (c), (d) and (e) are 100 μm, (f) is 100 nm. Insert scar bar is 10 μm.
Figure 2-9: EDAX mapping for VO$_2$/graphene/Ni
Figure 2-10: TEM for VO₂ powder.
The vanadium oxide formed on the graphene surface is further characterized by XRD and TEM. Fig. 2-9 shows the XRD patterns of the VO$_2$ powder after hydrothermal reaction. The XRD pattern of vanadium oxide matches very well with the standard spectrum of VO$_2$ (B) (JCPDS PDF#31-1438). The TEM image of a typical VO$_2$ (B) nanowire is shown in Figure 2-7c. High resolution TEM images indicated and electron diffraction of VO$_2$ (B) shows a single-crystalline structure, which is consistent with XRD results.
CHAPTER III

RESULT AND DISCUSSION

3.1 The electrochemical characterization of symmetric capacitors

Symmetric capacitors (VGN//VGN and CNT//CNT) were assembled first. (Figure 3-2). The specific capacitance of pseudocapacitors can be obtained by two different methods. It can be calculated from the cyclic voltammetry (CV) curves by using Eq.

\[
Cs = \frac{2 \int idV}{m \times \Delta V \times S}
\]  

(1)

where Cs is the specific capacitance, \( \int idV \) is the integrated area of the CV curve, m is the mass of active material, \( \Delta V \) is the potential range, and S is the scan rate.

Alternatively, the specific capacitance can be calculated from the Charge-Discharge (CD) curves by using the Eqs. (2) \(^9\)

\[
Cs = \frac{4I}{m \times dV/dt}
\]  

(2)

where I is the applied current, m is the mass of the active material, and \( dV/dt \) is the absolute value of the slope of the discharging curve.
The energy density and power density can be calculated at using Eqs. (3) and (4), respectively:

\[ E = \frac{1}{8} C_s \times (\Delta V)^2 \]  \hspace{1cm} (3)

\[ P = \frac{E}{t} \]  \hspace{1cm} (4)

where \( E \) is the energy density, \( C_s \) is the specific capacitance from CD, \( \Delta V \) is the potential range, \( P \) is the power density and \( t \) is the time to discharge. Thus, based on the above equations, for VGN//VGN, the specific capacitance at a scan rate of 10mv/s was calculated to be 140 F/g, which was in agreement with the result from the charge and discharge (119.7 F/g at a current density of 1 A/g). And it shows a good performance with an energy density of 2.03 W h/kg at 175 W/kg. As for the CNT//CNT, it got a specific capacitance of 90 F/g at a scan rate of 10 mv/s, which is correspond to the charge and discharge curves (53.4 F/g at a current density of 1 A/g).
Figure 3-1: Characterization of symmetric capacitor based on (a) and (b) VO$_2$/graphene/Ni and (c), (d) CNT as the electrodes, respectively. (a) and (c) CV curves with different scan rate. (b) and (d) Charge and discharge at a current density of 1 A/g.

3.2 The electrochemical characterization of the three-electrode system

The energy density of the device is limited by the chemical window. Electrochemical tests of the electrodes were performed in a three-electrode cell in 4M KCl aqueous
electrolyte with a Pt counter electrode and a SCE reference electrode. Figure 5a shows the cyclic voltammograms (CVs) collected for carbon nanotube deposited on a stainless steel substrate. Figure 5b shows the cyclic voltammograms (CVs) collected for vanadium dioxide with graphene on Ni foam. The specific capacitance of the electrode can be calculated according to the following equation.\(^{22}\)

\[
C = \frac{\int i\,dV}{S \times m \times \Delta V}
\]

Where \(\int i\,dV\) is the integrated area of the CV curve, \(m\) is the mass of active material, \(\Delta V\) is the potential range, and \(S\) is the scan rate. The CVs collected for the CNT electrode at different scan rates showed rectangular shapes, suggesting that the electrode has excellent electrochemical double layer capacitance (Fig. 5a). The specific capacitance at a scan rate of 100 mv/s, 30 mv/s, 10 mv/s and 5 mv/s were calculated to be 40 F/g, 59 F/g, 71 F/g and 84 F/g, respectively. As for the positive electrode (VGN), it shows a redox peak during the reaction, indicating that the electrode has good pseudocapacitance. The specific capacitance at a scan rate of 100 mv/s, 30 mv/s, 10 mv/s and 5 mv/s were calculated to be 80 F/g, 189.5 F/g, 343.2 F/g and 547.4 F/g, respectively.
Figure 3-2: (a) CV curves of VO$_2$/graphene/Ni electrode collected at a different scan rate in a three-electrode system. (b) CV curves of the CNT electrode collected at a different scan rate in a three-electrode system (vs. SCE). (c) CV curves of a VO$_2$/graphene/Ni//CNT asymmetric supercapacitor measured at different potential windows at a scan rate of 100 mV/s.

As shown in Figure 3-2, charge can be stored in a chemical window between +1.0 V and -0.8 V vs. SCE by combining the vanadium oxide/graphene cathode and VACNT anode. Therefore, the asymmetric device could achieve a maximum working voltage about 1.6 V. In order to obtain the maximum device capacitance, it is necessary to balance the charge on the positive and negative electrodes. The following equation was used to determine the active material mass loading of the two electrodes:

$$\frac{m_+}{m_-} = \frac{C_+ \times \Delta V_+}{C_- \times \Delta V_-}$$

(5)

where $m$ is the mass of the electrode, $C$ is the specific capacitance and $\Delta V$ is the potential windows obtained in the three-electrode measurement. (+) refers cathode and (-) refers
anode.\textsuperscript{36} Based on the different scan rate, the different mass ratio of positive and negative electrodes are determined. Asymmetric capacitors based on different mass ratio were fabricated and tested. The chemical window of the asymmetric capacitor was investigated firstly. Figure 5c shows the CV results of the asymmetric capacitor device (with $m_+ : m_- = 1:2$) under different operating potential windows varying from 0.8 to 1.6 V at a scan rate of 100 mv/s. Repeated cycles indicated that the device can be operated up to 1.6 V with aqueous electrolyte, which is much larger compared with the aqueous electrolyte based symmetric capacitor. Further experiments were conducted in order to explore a wide range a mass ratio based asymmetric capacitors and their electrochemical behavior. The results are shown in Figure 3-3. Fig.3-3 shows electrochemical characterization for those asymmetric capacitors, the optimal mass ratio between the electrodes (VGN: CNT) should be 0.5 in the present ASC device (based on data from 100 mv/s). Table 1 summarized the device mass ratio and capacitance of the devices obtained. The mass ratio based on the CV with 5 mv/s scan rate ($m_+ : m_- = 1:6.5$) is not used due to the difficulty for preparing the CNT electrode with large enough mass.

3.3 The electrochemical characterization of the asymmetric capacitor
Asymmetric capacitors have been fabricated based on different mass ratio (the results from 3 electrode system). Figure 3-3 is the characterization of the asymmetric capacitors and the results are shown in Table 1.
Figure 3-3: Asymmetric capacitors based on different mass ratio of VO\textsubscript{2}/CNT. (a) CV curves collected with a scan rate of 30 mv/s. (b) Charge and discharge curves collected at a current density of 2 A/g.
Table 3-1: The capacitance of the electrode based on the three-electrode CV results in Figure 3-2(a) and 3-2(b). The capacitance of the capacitor is based on the two-electrode CV results in Figure 3-1(a), (c), Figure 3-3(a) and Figure 3-4(a) and two-electrode charge-discharge results in Figure 3-1(b), (d), Figure 3-3(b) and Figure 3-4(b) and (e).

<table>
<thead>
<tr>
<th>$m_+ : m_-$</th>
<th>$1:2$</th>
<th>$1:3.2$</th>
<th>$1:4.8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitance of cathode (F/g)</td>
<td>80 (100 mV/s)</td>
<td>189.5 (30 mV/s)</td>
<td>343.2 (10 mV/s)</td>
</tr>
<tr>
<td>Capacitance of anode (F/g)</td>
<td>40 (100 mV/s)</td>
<td>59 (30 mV/s)</td>
<td>71 (10 mV/s)</td>
</tr>
<tr>
<td>Capacitance of the Asymmetric capacitor (F/g) (Scan rate 100 mV/s)</td>
<td>70.3</td>
<td>56.1</td>
<td>52.4</td>
</tr>
<tr>
<td>Capacitance of the Asymmetric capacitor (F/g) (Scan rate 30 mV/s)</td>
<td>112.3</td>
<td>80.7</td>
<td>62.2</td>
</tr>
<tr>
<td>Capacitance of the Asymmetric capacitor (F/g) (Scan rate 10 mV/s)</td>
<td>176.6</td>
<td>117.9</td>
<td>88.4</td>
</tr>
<tr>
<td>Capacitance of the Asymmetric capacitor (F/g) (Scan rate 5 mV/s)</td>
<td>224</td>
<td>121.2</td>
<td>97.2</td>
</tr>
<tr>
<td>Capacitance of the Asymmetric capacitor (F/g) (discharge current 2 A/g)</td>
<td>200</td>
<td>72.5</td>
<td>67.5</td>
</tr>
<tr>
<td>Capacitance of the Asymmetric capacitor (F/g) (discharge current 5 A/g)</td>
<td>187</td>
<td>60.5</td>
<td>60.3</td>
</tr>
</tbody>
</table>

Figure 3-4(a) shows the CV curves of the ASC device with different operating potential windows varying from 0.8 to 1.8 V at a scan rate of 100 mV/s. Figure 8b shows the CV curves of the ASC device at different scan rate, the results were displayed in Figure 8c, the highest capacitance was 224 F/g at a scan rate of 5 mV/s. The superior performance of the ASC device was further confirmed by Galvanostatic charge/discharge measurements. As shown in Figure 3-4(c) the charging and discharge curves remained good shape at different voltage at a current density of 5 A/g, and the specific capacitance of the ASC device with an increase of the cell voltage were displayed in Figure 3-4(d), It is found that the capacitance of ASC increases significantly from 61.7 to 159 F/g and then displays a slight increase with increasing cell voltage. The highest capacitance from the ASC device at a current density of 5 A/g was 187 F/g.
(a) Graph showing current (mA) vs. potential (V) at different scan rates (100 mv/s, 30 mv/s, 10 mv/s, 5 mv/s).

(b) Graph showing capacitance (F/g) vs. scan rate (mv/s) with a chemical window of 1.6 V.
Figure 3-4: (a) CV curves of the asymmetric supercapacitor measured at different scan rate. (c) The specific capacitance of the ASC device at different scan rate. (b) Charge and discharge of the asymmetric supercapacitor measured at different potential windows at a current density of 5 A/g. (d) the specific capacitance of the ASC device with an increase of the cell voltage. (f) Charge and discharge of the asymmetric supercapacitor measured at different potential windows at a current density of 2 A/g.

The cycling stability of the as-fabricated ASC is carried out by repeating the CV test within 0−1.6 V at a scan rate of 100 mv/s (Figure 6). The capacitance of the device before cycles was 187 F/g, after 1000 cycles, it changed to 181 F/g. The ASC device exhibits an excellent electrochemical stability with only 1.2% deterioration of the initial specific capacitance after 1000 cycles,
a) Voltage vs. Time for 1st cycle and after 1000 cycles.

b) Impedance spectrum for 1st cycle and after 1000 cycles.
Figure 3-5: (a) Cycling performance of the device measured at a current density of 5 A/g. (b) Nyquist plots of the VO$_2$/graphene/Ni//CNT asymmetric pseudocapacitors in the frequency range of 100 kHz to 0.1 Hz measured during the cycle life tests. (c) The Ragone plots (energy density vs. power density) of symmetric supercapacitors and ASC devices based on VGN and CNT.

The electrochemical impedance spectroscopy (EIS) analysis has been performed to examine the changes of asymmetric supercapacitors during the cycling. The impedance spectra of the asymmetric supercapacitor after 1000 cycles and 3000 cycles were measured. They are compared with the initial impedance spectrum of device. (Figure 7c).

Finally, in order to compare this results and previous reported work. The Ragone plot is used (Figure 3-5c). The results from this work are compared with other vanadium oxide based asymmetric capacitor research. It is clear that the asymmetric capacitors fabricated in this work has higher energy and power densities than the reported vanadium oxide based devices. $^{23,26}$
CHAPTER IV

CONCLUSION

In this study, a novel asymmetric capacitor based on VO$_2$/graphene positive electrode and vertically aligned carbon nanotube negative electrode has been fabricated. By rational design the bi-continuous positive electrode to enhance the charge transport process and high surface area negative electrode to increase the capacitance, the resulting asymmetric capacitor can be optimized. Taking advantage of the asymmetric capacitors large chemical window (1.6 V with aqueous electrolyte), the achieved a remarkable energy density of 16.6 W h/kg at a power density of 1.99 KW/kg, which is significantly better than the symmetric supercapacitor and previous reported vanadium oxide based asymmetric supercapacitors. The device also exhibit an excellent charge/discharge cycling performance in with a capacitance retention of 98.8% after 1000 cycles and 87.7% after 3000 cycles. The results indicated that the asymmetric supercapacitor can largely enhance the power density and energy density of corresponding symmetric analogs by rational optimizing the electrode materials.
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