FABRICATION OF LITHIUM-ION BATTERY WITH VERTICALLY ALIGNED 
CARBON NANOTUBES ON THREE-DIMENSIONAL NI FOAM

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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May, 2014
FABRICATION OF LITHIUM-ION BATTERY WITH VERTICALLY ALIGNED CARBON NANOTUBES ON THREE-DIMENSIONAL NI FOAM

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Thesis

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ABSTRACT

Lithium ion batteries (LIBs) have become one of the most popular energy storage devices in order to meet the increasing demands of high performance electronic devices. Novel anode materials with high specific capacity, rate capability, flexibility, small size and porous structure are in need. Vertically aligned carbon nanotubes (VACNTs) with short length have been successfully synthesized on three-dimensional porous Nickel foam template by water assisted chemical vapor deposition (CVD) in order to fulfill these demands. SEM, TEM and Raman characterizations confirm that they are vertically aligned few walled CNTs with good quality. Lithium ion batteries were fabricated using these VACNTs on Ni foam as anode material. Improved specific capacity, rate capability and operational life time were obtained by the novel anode material. Future works will focus on deposition of metal oxide and metal sulfide materials on the VACNTs on Ni foam to get even higher electrochemical performance.
ACKNOWLEDGEMENTS

I would like to express my deep gratitude to my advisor Dr. Yu Zhu for his help and support in my research, especially for his professional guidance when problems occurred in my research. I would like to thank Dr. Steven S.C. Chuang, who spends time on reading my thesis.

I want to acknowledge all the group members in Dr. Zhu’s group. Thanks for Yu Ming Chen, Kun Yang, Wanyao Xiao, Tianda He, Aozhen Xie and Kewei Liu for their help and the good research environment.

Finally, I want to thank for my family members, who give me a lot of encouragement during my research.
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CHAPTER I
INTRODUCTION

Lithium ion batteries (LIBs) have become one of the most popular energy storage devices in order to meet the increasing demands of high performance electronic devices, because of their potential to achieve higher energy and power density and longer cycle life compared with other rechargeable batteries.\(^1\) Energy density of Lead Acid, Ni-Cd, Ni-MH and Li-ion batteries are shown in Figure 1. Li-ion battery has an energy density of as high as two times to the other types of batteries.

Lithium ion batteries have been used in variety of portable electronic devices (PED) such as laptops, mobile phones and hybrid electric vehicles.\(^2\)-\(^3\) Although Li-ion batteries have widely range of applications, commercially used lithium ion batteries with graphite anode can hardly fulfill the demands of next generation lithium ion batteries. In this case, novel anode materials with high specific capacity, high rate capacity, flexibility, small size and porous structure are in need. Nanostructured materials on three-dimensional porous template are potential anode materials that may meet these demands. The nanoscale
dimension, ultra high active surface area and hierarchical structure can increase the energy storage, ion diffusion rate and operational life time, compared with the commercial used anodes.4,5

Figure 1. Energy density of Lead Acid, Ni-Cd, Ni-MH and Li-ion batteries.6

Nanostructured carbon materials such as carbon nanofibers7-9, carbon nanotubes3,10-16 and graphene17-18 have been explored to use as anode materials in lithium ion batteries. Carbon nanotubes (CNTs) have shown great potential to work as anode material for lithium ion batteries since they have great mechanical and electrical properties, together with their unique structure. The electrical conductivity of CNT and average Young’s modulus of individual CNT are $10^4$ S/cm and 1.8Ta, respectively.19-20 Graphite anode gives lower rate capability compared with other carbon materials since the morphology of
Vertically aligned carbon nanotubes (VACNT) with well-defined nanostructure provide high catalytic surface area and electrons can directly transport through vertically aligned tubes, which gives an even high rate capability and lithium storage capacity compared with randomly packed CNTs.

In this study, we synthesized vertically aligned carbon nanotubes by chemical vapor deposition method and use three-dimensional porous pressed Nickel foam coated with Al₂O₃/Fe/Mo catalysts as template. The VACNTs grown on Ni foam were directly used as anode material of LIBs. VACNTs grown in all the directions around each Ni wire in the Ni foam can give more pathways in every direction for the diffusion of lithium ions. The Li ions can attached to ether the outer wall or the inner wall of CNTs and quickly transferred through the tubes, which further improves the rate capability of Li-ion batteries.

Nickel can work as a good support material to the VACNT forest which helps maintaining the alignment of CNTs. Nickel is also a good current collector since it has intimate contact with CNTs.³ Ni foam has a 3D porous structure, which can serve as a good template to get hierarchical structure, high surface area and enhanced conductivity. But the commercially available Ni foam is not an ideal template material for CNT growth. At the end of the fabrication of Li-ion battery, the coin cells are pressed for well sealing. If the Ni foam was not pressed before CNT growth, it will be pressed during the
fabrication of Li-ion batteries, which will result in cracks and collapses in the CNT forest and will decrease the electrochemical performance of the battery. In order to prevent these defects, increase the flexibility and also decrease the relatively large pore size and volume of the commercial Ni foam, it needs to be pressed to a thinner foam before the dip-coating process.
2.1 Carbon Nanotubes

Carbon nanotubes are widely used in different areas, such as batteries, capacitors, sport equipments and so on. The unique structure and resulted properties of CNTs are discussed in this section.

Figure 2. Schematics of an individual (A) SWCNT and (B) MWCNT.\textsuperscript{23}
2.1.1 Definition

Carbon nanotubes (CNTs) have a cylindrical structure made by carbon atoms. They are entirely composed by \( sp^2 \) bonds.\textsuperscript{24} CNT can be viewed as a graphene sheet which is rolled up into a nanotube. Carbon nanotubes have significantly larger length to diameter ratio than any other materials. The length is always in micrometer scale, and the diameter is in nanometer scale.\textsuperscript{23}

CNTs can be divided into two types, single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), which are shown in Figure 2. SWCNTs contain a cylindrical graphene sheet with nano-scaled diameter, whereas the MWCNTs contain several cylindrical graphene sheets.\textsuperscript{23} Carbon nanotubes have extraordinary properties such as high thermal conductivity, electrical property and mechanical property.\textsuperscript{23} CNTs are popular in many fields such as nanotechnology, electronics and optics due to these properties. CNTs can be used in battery\textsuperscript{25}, super capacitor\textsuperscript{26} and solar cells\textsuperscript{27} because of the high electrical properties.

2.1.2 Vertically Aligned Carbon Nanotubes (VACNT)

When the carbon nanotubes have very high density, the CNTs will aggregate into bundles to form vertically aligned carbon nanotubes (VACNTs) because of the Van der Waal interactions between neighboring nanotubes. The nanotubes grow vertically from substrate and form a forest structure. The VACNTs have high density, controlled growth
direction and high thermal\textsuperscript{28} and electrical\textsuperscript{29} conduction properties. These unusual properties enable some potential applications of CNTs.

2.1.3 Chemical Vapor Deposition (CVD)

Carbon nanotubes can be synthesized by several methods, such as arc-discharge method\textsuperscript{30}, laser-furnace method\textsuperscript{31} and chemical vapor deposition (CVD) method\textsuperscript{32}. CVD is a popular method because it can control the location and orientation of the CNTs, which cannot be controlled by the first two methods.\textsuperscript{23} Chemical vapor deposition has been used to synthesize carbon fibers and carbon filaments since 1960s.\textsuperscript{33} The schematic diagram of CVD is shown in Figure 3. In CVD, a catalyst material is present at high temperature to thermally decompose gas-phase materials into reactive species.\textsuperscript{23}

Figure 3. Schematic diagram of the mechanism of CVD.
CVD is a simple method to synthesize CNTs under relatively low temperature and pressure. During the CVD process, the hydrocarbon vapor flow through a tube furnace. A catalyst is present at high temperature to decompose hydrocarbons into reactive species to produce carbon nanotubes and hydrogen. CNTs are collected by cooling down the CVD system to room temperature. The parameters such as type of hydrocarbon, catalyst, growth temperature and growth time are important for the growth of CNTs.

2.1.4 Growth mechanisms of CNTs

![Growth mechanisms for CNTs](image)

Figure 4. Growth mechanisms for CNTs: (a) tip-growth model, (b) base-growth model.
There are basically two kinds of growth mechanisms for CNT growth, one is tip-growth mechanism and the other is base-growth mechanism. When there’s weak catalyst–substrate interaction, metal nanoparticle has an acute contact angle with the substrate. The hydrocarbon can decompose on the top of metal nanoparticle, then carbon diffuse into the metal and CNTs grow out from the bottom of the metal which pushes the iron nanoparticle up from the substrate. The CNTs grow longer and longer until the metal is fully covered by amorphous carbon.

When there’s strong catalyst–substrate interaction, metal nanoparticle has an obtuse contact angle with the substrate. In this case, the initial decomposition of hydrocarbon and diffusion of carbon take place similar with the previous mechanism, but the strong interaction determines that the CNTs cannot push the metal nanoparticles up. As a result, CNTs are compelled to grow out from the top of the metal. Carbon first grows out to make a hemispherical dome which then grows up in the shape of a graphitic cylinder. Subsequent deposition of hydrocarbon takes place on the lower peripheral surface of the metal nanoparticle, and the dissolved carbon diffuses upward to grow the graphitic cylinder.

2.1.5 Water assisted growth of VACNT

Impurities such as amorphous carbon are produced during the synthesis of CNTs. The purification steps are needed to remove the impurities, but carbon nanotubes can be easily damaged by the purification. During the chemical vapor deposition process, the
catalyst particles are coated by the amorphous carbon. As a result, the activity and lifetime of the catalysts are reduced by the amorphous carbon.\textsuperscript{35} A simple and highly efficient water-assisted growth method is used to solve these problems.\textsuperscript{36}

In the water assisted CVD process, controlled amount of water vapor is added into the CVD system. The water vapor acts as a weak oxidizer, and it can selectively remove amorphous carbon without damaging the CNTs at the growth temperature.\textsuperscript{36} By the addition of water, the catalyst lifetime can be dramatically enhanced. In a water-assisted growth, catalysts are alive even after 30 min growth, whereas the catalysts can only work for 1 min without water.\textsuperscript{36} The stimulated activity of catalysts will increase the density of CNTs and produce vertically aligned CNT forests.

2.1.6 VACNTs for Electrical Energy Storage

The traditionally used carbon materials in lithium-ion battery are 2-dimensional carbon structure like graphite. They have several disadvantages such as small catalytic surface area, and the electrons should hop between different inner structures of carbon materials.\textsuperscript{27} These problems can be solved by vertically aligned CNTs. VACNTs have high catalytic surface area because of the 3D structure, which will increase the capacitance of the battery. In addition, electrons can directly transport through the vertically aligned tubes to the current collector, which can decrease the resistance in the electrode, increase the charge/discharge rate.\textsuperscript{27} The VACNTs synthesized on nickel foam will be used to make anode for lithium-ion battery in the future work.
3.1. Synthesis of VACNTs on 3D porous Ni foam

Two solutions were prepared for the dip-coating of catalysts, one is the aluminum complex solution for Al$_2$O$_3$ deposition and the other is the M$_x$(2-ethylhexanoate)$_x$ complexes solution for Fe and Mo nanoparticles deposition. Alumina material is a good catalyst support material because of its strong interaction with metal catalyst, which makes the catalyst highly dispersed and form highly dense catalytic sites. This strong interaction can prevent the aggregation of the iron particles, which will form unwanted graphite particles and MWCNTs. And these theoretical assumptions have been confirmed by recent research of in-situ XPS of CNTs synthesized on iron catalyst and alumina co-catalyst coated silica substrates.

Iron nanoparticles are generally used as catalyst because of the high solubility of carbon at high temperature and the high diffusion rate of carbon in iron. A small amount of Mo added to the pure iron catalyst has been confirmed to give shorter but denser CNT
The size of catalyst nanoparticles is also important because it can determine the diameter of CNTs. When the size of nanoparticles is a few nanometers, it tends to produce single-walled CNTs. When the size of nanoparticles is bigger, it tends to produce multi-walled CNTs. So catalyst solutions should be fresh and without any aggregation.

Nickel foam was used as the metallic substrate because of its three-dimensional porous structure and good electrical conductivity that can be used in battery. The inner part of nickel foam can hardly be coated by electron-beam because of its porous structure, and this problem can be solved by dip-coating method.

3.1.1. Preparation of catalyst solutions

The aluminum(2,4-pentadionate)x(iso-propoxide)x (Al(AcAc)x(iPrO)3) complex in 2-propanol was prepared using aluminum iso-propoxide (Al(iPrO)3, ACROS). Acetylacetone (AcAcH, TCI AMERICA) was added into 2-propanol to make a 2 mol/L solution, and the Al(iPrO)3 was dissolved in this solution. The precursor solution was then stirred for 2 hours and the Al(iPrO)3: AcAcH molar ratio is 0.5. After that water was added into the precursor solution for the hydrolysis of aluminum iso-propoxide. The H2O:Al(iPrO)3 molar ratio is 0.85:1. Then the solution was diluted by 2-propanol to adjust the concentration of aluminum iso-propoxide to 60 g/L. The complex solution was stirred for another 3 hours. After stirring, 65% nitric acid (Sigma-Aldrich) was added to the solution drop by drop to form a transparent and light yellow aluminum(2,4-pentadionate)x(iso-propoxide)x complex. A few amount of
hexadecyltrimethylammonium bromide (CTAB, ACROS) was added to the solution before the dip-coating process as a surfactant to increase wet ability of the substrate. The weight of surfactant is 0.05 percent of the weight of the Al(AcAc)x(iPrO)3 complex.

For the preparation of Mx(2-ethylhexanoate)x complex using Fe and Mo, Fe(2-ethylhexanoate)3 (ALFA AESAR, 50% in mineral spirits) and Mo(2-ethylhexanoate)4 (STREM CHEMICALS) were dissolved in 2-propanol. The concentration of the entire catalysts was adjusted to 0.12 mol/L, and the Fe:Mo ratio was 94:6. The density and the diameter of CNTs will be different when changing the entire catalyst concentration.

3.1.2. Dip-coating process

The nickel foam was first pressed into 0.2 mm and cut into 3×3 cm² pieces for dip-coating. Pressed Ni foam shows improved flexibility and mechanical strength when compared with the unpressed one. Moreover, the pore size and thickness of the Ni foam were decreased which gives smaller volume for the anode electrode. The general used dip-coating procedure is designed for substrate with flat surface. Unpressed Nickel foam can hardly be coated by the general procedure since the extra liquid can hardly flow out of the porous structure and the pores will be clogged after annealing. After press, the reduced pore size and volume in this 3D structure allowed the extra liquid to flow away freely, which prevented the clogging of pores.
During the dip-coating, the Ni substrate was first immersed in ethanol and sonicated by sonicator (Ultrasonic Cleaner, GB-2500B) for 30 minutes. Then the substrate was annealed by the heat plate at 300 °C. After that, the substrate was immersed in the Al(AcAc)\(\times\)(iPrO)\(\times\) complex solution for a few seconds and slowly lifted out. This step was repeated for a few times to get a homogeneous coating. Then the substrate was dried at room temperature for 5 min and annealed at 300 °C for 5 min. The substrate was then immersed in the Mx(2-ethylhexanoate)\(\times\) complex solution for a few seconds and slowly lifted out to get a homogeneous coating of Fe and Mo catalysts. Then the Ni foam was dried at room temperature for 5 min and annealed at 350 °C for 5 min.

3.1.3. CVD growth of Carbon nanotube

The vertically aligned carbon nanotubes were synthesized by atmosphere pressure chemical vapor deposition operation. The regulators of gases were opened to adjust the pressure to 15-20 psi. The pressure in the chamber was kept over 1 atm. The coated Ni foam was put into a small quartz tube as sample holder and moved into the CVD system. The pump was opened to check the vacuum, and the value on the vacuum gauge should be under 0.1 Torr quickly. Then the furnace was opened and the temperature was set to 750 °C.
Before the growth steps, Argon was opened to purge the chamber. After about 5 minutes hydrogen was opened and argon was closed a few minutes later. Then the pump angle valve was closed, and the exhausting valve was opened when the vacuum dial meter showed the pressure returned to 1 atm. After opening the exhausting valve, the chamber was in atmosphere pressure.

The substrate was annealed for 3 minutes with controlled amount of water bubbling. Then the ethylene was opened for several minutes to grow CNTs. After the growth, ethylene and water bubbling were closed immediately and the sample was moved out to the preparation position. The hydrogen and argon were opened until the sample was cooled down, after which hydrogen was closed. Then the exhausting valve was closed and the pump was opened at the same time. After several minutes, the pump was closed and the sample was taken out.

500 sccm (Standard Cubic Centimeters per Minute) Argon was used before and after the growth of CNTs to get rid of air in the system. 400 sccm Hydrogen was used as a carrier gas and reducing agent during the whole process. During the preparation of substrate, fresh metal nanoparticles were deposited on the Ni foam. But the nanoparticles were quickly oxidized by the oxygen in air before CVD process. In CVD procedure, hydrogen can reduce the metal oxide to pure metal nanoparticles, which will act as a catalyst to produce CNTs. Pure ethylene was used as carbon source. Controlled small amount of water vapor was supplied by passing hydrogen gas through the water bubbler.
Water vapor was used as a weak oxidizer to remove the amorphous carbon to increase both lifetime and activity of the catalyst layer.36

3.2. Carbon Nanotube Characterizations

The scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX) was used in this experiment to test the structure and the height of CNT forest. The transmission electron microscope (TEM) was used to test the diameter of CNTs.

Raman spectra were also taken to analyze the quality of CNTs. D-band at 1330 cm\(^{-1}\) and G-band at 1580 cm\(^{-1}\) are two main bands in the Raman spectra of CNT.45 G-band corresponds to the intrinsic property of CNTs which are related to the vibrations of sp\(^2\) carbon atoms.46 D-band corresponds to any defects in CNTs, which are related to porous carbons, impurities and other defects.46 The ratio between G-band and D-band corresponds to the quality of CNTs, a higher G:D ratio means a better quality of CNTs.

3.3. Fabrication Of Lithium Ion Battery And Electrochemical Characterizations

Lithium-ion batteries were fabricated with VACNTs on Ni foam as anode material and Li foil as cathode material. After dip-coating process, pressed Ni foam was punched into small disks with a diameter of 1/4 inch (0.317 cm\(^2\)), which is suitable for coin cells. Pressed Ni foam coated by VACNTs was directly used as anode materials without any other component.
Lithium metal foil was punched into disks with a diameter of 1/2 inch (1.267 cm²) as cathode. The Li-ion batteries were assembled and sealed using coin cells inside the glove box under Argon atmosphere. Both H₂O and O₂ contents were under 0.5 ppm. Celgard 3501 was used as separator and 1mol/L Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) was used as liquid electrolyte.

The composition of Li-ion battery and their sequence are shown in Figure 5. The Ni foam was weighted before and after CNT growth to obtain the net weight of CNTs in one piece of anode material. Several electrochemical tests were done using these Li-ion batteries. Charge-discharge experiments including c rate and long cycle tests were tested.
by MTI battery testing system. The C rate was calculated based on the theoretical capacity of graphite, which is 372 mAh/g. Cyclic voltammetry experiments (CV) were tested by electrochemical workstation.
CHAPTER IV
RESULTS AND DISCUSSION

4.1 Characterizations of Ni foam and CNTs

After dip-coating process, coated Ni foam was tested by SEM and EDX to see the homogeneity of the coated surface and element containing of the catalyst layer. Figure 7(a), 7(b) show the SEM and EDX spectra of coated Ni foam whereas Figure 6 shows the EDX spectra of pure Ni foam for comparison. The coated surface was smooth without any cracks or collapses which is necessary for growing high quality CNT forest. EDX confirms the existence of Fe, Mo, O and Al elements, which is consistent with the dip coating solutions used. EDX mappings in Figure 8 show that all the elements on the coated Ni surface are dispersed very well.
Figure 6. EDX spectra of pure Ni foam.
Figure 7. (a). SEM image of coated Ni foam. (b). EDX spectra of coated Ni foam.
Figure 8. (a)-(e). EDX mappings for Al, Fe, Mo, Ni and O elements and (f) SEM image for the same area.
Coated Ni foam was cut into small pieces and load into CVD system for CNT growth. After growth, Ni foam with CNTs grown on was tested by SEM again to see the morphology and length of CNTs. SEM images for CNTs are shown in Figure 9(a)-9(c). Vertically aligned CNTs were obtained by CVD method, and the length of VACNTs is controlled to around 3μm. Each Ni wire in the 3D Ni foam was homogeneously coated by VACNT forest with a high density. The morphology of CNT forest confirms that catalyst layer was coated very homogeneous and the catalyst nanoparticles were dispersed very well, resulting in a homogeneous CNT forest.

CNT growth parameters used here in CVD system can produce very short VACNTs, which gives a shorter way for ion transfer in CNTs. And using short CNTs can protect the Celgard used in coin cell as well, since longer nanotubes may pierce the celgard film and resulting in unwanted irreversible side reactions or even short circuit. This has been confirmed by the discharge and charge curves using long CNTs which gives lots of shaking curves at high voltage charging part.

The relationship between growth parameters and CNT length gradient was initially investigated using silicon wafer substrate and further revised by 3D Ni foam in which the short CNTs were selected to be used in Li-ion battery for those reasons mentioned previously. The parameters and resulted CNT length are shown in Table S1 in Appendix. CNTs grown on Ni foam were shorter than those grown on Si wafer because of the 3D porous structure.
Figure 9. SEM images for VACNTs grown on pressed Ni foam with different magnification. The VACNTs have a length of around 2\(\mu m\).
TEM images were also taken to investigate the diameter of CNTs grown on Ni foam and the TEM images are shown in Figure 10. The average diameter of CNTs is around 15 nm, which is larger than CNTs grown on templates coated by electron beam. Organic solution based dip coating will obviously result in larger catalyst nanoparticle size since the aggregation of nanoparticles in solution cannot be totally avoided.

![TEM image for VACNT grown on Ni foam.](image)

Figure 10. TEM image for VACNT grown on Ni foam.

Raman spectra were taken to investigate the quality of CNTs. From the Raman spectra shown in Figure 11, the three spectra taken at different points in the same sample all show a higher G-band than D-band. The G: D ratio can be as high as 4 which means VACNTs are of good quality and there must be some SWNTs in the CNT forest.
Figure 11. Raman spectra for VACNTs grown on Ni foam. Three curves were taken in the same sample but different points.

4.2 Electrochemical Characterizations

Cyclic voltammetry tests for the first to the third cycles were took place at a scan rate of 1mV/s and the results are shown in Figure 12. The shoulder at 0.5V in 1st discharge disappeared in the 2nd and 3rd cycles, and the CV curves of 2nd and 3rd cycles are almost the same, which indicates that degradation happened after the 1st cycle and then the battery became stable.
Figure 12. CV curves of the first three cycle.

Figure 13. Discharge-charge profile for the first 10 cycle under 100mA/g.
Figure 13 shows the discharge-charge profile in the first 10 cycles under a current density of 100 mA/g. The mass based capacity of first discharge is 1706.9 mAh/g, followed by a large degradation. The capacity then gradually becomes stable and the remaining capacity is 424.2 mAh/g after 10 cycles.

Table 1. Relative charge and discharge capacities for the first 10 cycles under a current density of 0.1A/g.

<table>
<thead>
<tr>
<th>Cycle ID</th>
<th>Relative charge capacity (mAh/g)</th>
<th>Relative discharge capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>—</td>
<td>1706.9136</td>
</tr>
<tr>
<td>2</td>
<td>432.7021</td>
<td>803.5354</td>
</tr>
<tr>
<td>3</td>
<td>387.2316</td>
<td>623.2413</td>
</tr>
<tr>
<td>4</td>
<td>366.9288</td>
<td>599.9918</td>
</tr>
<tr>
<td>5</td>
<td>356.0893</td>
<td>500.6302</td>
</tr>
<tr>
<td>6</td>
<td>333.7044</td>
<td>481.7996</td>
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<td>7</td>
<td>332.596</td>
<td>464.2222</td>
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<td>9</td>
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<td>411.4571</td>
</tr>
<tr>
<td>10</td>
<td>308.536</td>
<td>424.2448</td>
</tr>
</tbody>
</table>
The discharge and charge capacities for the first 10 cycles are shown in Table 1. The discharge capacity became very stable after 10 cycles. After the first 10 cycles, current density was increased to 0.5 c, 1c, 2c and then turned back to 0.1A/g for c rate test. From the results shown in Figure 14, a capacity as high as x mAh/g was retained even at 2c rate, indicates a good rate capability. When current density turned back to 100mA/g, a capacity of x mAh/g was recovered which can be contribute to the gradual activation of active materials.

![Figure 14. c rate test at 0.1A/g, 0.5c, 1c, 2c and 0.1A/g.](image)

In order to see the long cycle performance of the battery, the Li-ion cells were run for 500 cycles under a current density of 1c. Figure 15 shows the long cycle performance under 1c rate. The columbic efficiency became quite stable after the first few cycles, which is almost 100%.
Impedance was tested to investigate the mechanism in this battery system. Figure 16 shows the impedance curves of as prepared battery, and battery after 1\textsuperscript{st}, 5\textsuperscript{th}, 10\textsuperscript{th} and 30\textsuperscript{th} cycles. The semicircle part becomes larger after the first cycle of discharge-charge test compared with the as-prepared battery, and then it becomes quite stable in the following cycles.

Equivalent circuit shown in Figure 17 was made based on the Nyquist plot after first cycle of charge and discharge. The first intercept with x axis corresponds to the internal resistance of the cell (Rs), which combines the resistance of the electrodes, electrolyte and separator together. Since there is a semicircle part in the Nyquist plot of as-prepared battery, the semicircle part for battery after discharge and charge is a combination of two
semicircles. The high frequency part corresponds to $R_{sei}$ which is the resistance associated from the migration of Li-ions through the SEI film and $CPE_{sei}$ which is the SEI film capacitance. The medium frequency part corresponds to $R_{ct}$ which is charge-transfer resistance and $CPE_{dl}$ which is the double-layer capacitance. The low frequency part with a constant slope corresponds to $Z_w$ which is the Warburg impedance from the diffusion of Li-ions on the electrode-electrolyte interface. The equivalent circuit fitting curve and the original Nyquist plot are shown in Figure 18, the equivalent circuit fits very well.

![Impedance curves for as-prepared, 1st cycle, 5th cycle, 10th cycle and 30th cycle battery.](image)

Figure 16. Impedance curves for as-prepared, 1\textsuperscript{st} cycle, 5\textsuperscript{th} cycle, 10\textsuperscript{th} cycle and 30\textsuperscript{th} cycle battery.
Figure 17. Equivalent circuit for the VACNT/Ni foam battery system.

Figure 18. Impedance fitting curve in which the black curve is the original Nyquist plot and the green curve is the fitting result.
CHAPTER V
CONCLUSION

Vertically aligned Carbon nanotubes with short length have been successfully synthesized on three-dimensional porous Nickel foam template by water vapor assisted chemical vapor deposition. SEM, TEM and Raman characterizations confirm that they are vertically aligned a few walled CNTs with good quality. Lithium ion batteries were fabricated using these VACNTs on 3D Ni foam as anode material. Parameter and CNT length gradient was obtained on silicon wafer and further revised on 3D Ni foam, in which the short CNTs were selected to be used in Li-ion batteries. Improved specific capacity, rate capability and operational life time were obtained by the novel anode material.

Future work will be focusing on the deposition of metal oxide and metal sulfide materials on the VACNTs on Ni foam to get even higher electrochemical performance.
REFERENCES


20. Treacy, M.; Ebbesen, T.; Gibson, J., Exceptionally high Young's modulus observed for individual carbon nanotubes. **1996**.


APPENDIX

Table S1. Parameters and resulting CNT height on silicon wafer using different parameters.

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Table S1. Parameters and resulting CNT height on silicon wafer using different parameters (continued).

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