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Enhanced 3-Dimensional Carbon Nanotube Based Anodes for Li-ion Battery Applications

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida, USA

ENHANCED 3-DIMENSIONAL CARBON NANOTUBE BASED ANODES
FOR LI-ION BATTERY APPLICATIONS

A dissertation submitted in partial fulfillment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY

in

MATERIALS SCIENCE AND ENGINEERING

by

Chi Won Kang

2013

To: Dean Amir Mirmiran
College of Engineering and Computing

This dissertation, written by Chi Won Kang, and entitled Enhanced 3-Dimensional Carbon Nanotube Based Anodes for Li-ion Battery Applications, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Date of Defense: June 28, 2013

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Dean Amir Mirmiran
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Florida International University, 2013

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DEDICATION

I would like to dedicate this dissertation to Jesus Christ as my Savior and Lord for His measureless, strong and everlasting love.

하나님이 세상을 이처럼 사랑하사
독생자를 주셨으니 이는 그를 믿는 자
마다 멸망치 않고 영생을 얻게 하려
하심이니라

요한복음 3장 16절

**“For God so loved the world, that he gave his only begotten Son, that whosoever
believeth in him should not perish, but have everlasting life.”**

John 3:16 (King James Version)

(translated from Korean to English)

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ABSTRACT OF THE DISSERTATION
ENHANCED 3-DIMENSIONAL CARBON NANOTUBE BASED ANODES
FOR LI-ION BATTERY APPLICATIONS

by

Chi Won Kang

Florida International University, 2013

Miami, Florida

Professor Wonbong Choi, Major Professor

A prototype 3-dimensional (3D) anode, based on multiwall carbon nanotubes (MWCNTs), for Li-ion batteries (LIB), with potential use in Electric Vehicles (EVs) was investigated. The unique 3D design of the anode allowed much higher areal mass density of MWCNTs as active materials, resulting in more amount of Li^+ ion intake, compared to that of a conventional 2D counterpart. Furthermore, 3D amorphous Si/MWCNTs hybrid structure offered enhancement in electrochemical response (specific capacity 549 mAhg^{-1}). Also, an anode stack was fabricated to further increase the areal or volumetric mass density of MWCNTs. An areal mass density of the anode stack 34.9 mg/cm^2 was attained, which is 1,342% higher than the value for a single layer 2.6 mg/cm^2 . Furthermore, the binder-assisted and hot-pressed anode stack yielded the average reversible, stable gravimetric and volumetric specific capacities of 213 mAhg^{-1} and 265 mAh/cm^3 , respectively (at 0.5C). Moreover, a large-scale patterned novel flexible 3D MWCNTs-graphene-polyethylene terephthalate (PET) anode structure was prepared. It generated a reversible specific capacity of 153 mAhg^{-1} at 0.17C and cycling stability of 130 mAhg^{-1} up to 50 cycles at 1.7C.

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CHAPTER 1

INTRODUCTION

1.1 Overview

Energy storage is unquestionably one of the most significant research topics in the twenty-first century [1]. Technological and social developments of humankind have been supported by the discovery of new sources of energy and its proper application in human lives [2]. Importantly, the transportation industry has used fossil fuels as a main source of energy. However, both world impending oil shortage and global warming caused by green-house gases like CO₂ are responsible for shifting the focus of power generation towards clean and carbon-free resources [3]. One essential and challengeable shift has been the electric vehicles (EVs) in which the motive power is supplied by the use of a battery. We expect the advent of EV markets based on the rapid increase in sales of hybrid electric vehicles (HEVs¹) [4]. Among various energy storage devices (e.g., nickel–cadmium battery or nickel-metal hydride battery), a lithium-ion battery (LIB) is one of the most commonly used devices for portable electronic devices and hybrid electric vehicles in modern human life [5]. Since the commercial release of LIBs by Sony in 1991 [6], Li-ion batteries (LIBs) have continued to attract great attention from many researchers around the world due to their many advantages. LIBs exhibit higher operation voltage greater than 3 V, their capability to balance specific capacity with the capability of charge and discharge rate (i.e. C-rate capability), compared to other electrochemical energy storage devices. Additionally, LIBs provide higher energy density, broader temperature range, lower self-discharge rate, and no voltage depression (i.e. “memory effect”), relative to other energy storage devices mentioned

¹ A relative small internal combustion engine is used to charge a modest-sized electric battery, which then acts to provide the vehicular propulsion

above. Such major advantages of LIBs make it possible to yield smaller, lighter, and environmentally friendly LIB cells [7].

For instance, the markets of cell-phone, laptop PC and camcorder (3C) have been powered by LIBs which are currently produced by billions of units per year [8]. The components of an LIB cell, commercially available carbon-based anode materials, and their electrochemical performances will be dealt with in chapter 2. Although such LIBs are commercially successful, we are now reaching the limits in performance using the current electrode and electrolyte materials. Demand for next-generation high-efficiency and low-cost LIBs have created excitement in the scientific community to discover new avenues for breakthrough in electrode materials [9]. The application of nanomaterials to LIB is one avenue which is being closely analyzed by many scientists and researchers.

Nanostructured materials have attracted great interest in recent years due to their unusual mechanical, electrical and optical properties endowed by confining the dimensions of such materials, and because of the combination of bulk and surface properties to their overall behavior. Currently, nanostructured materials are becoming increasingly important for electrochemical energy storage. Therefore, it is important to appreciate the advantages and disadvantages of nanomaterials for energy conversion and storage, as well as how to control their synthesis and properties [9].

There are several potential advantages and disadvantages associated with the development of nanomaterials for LIB electrodes. Advantages include:

- (i) Better accommodation of the strain of lithium insertion and extraction, improving cycle life of electrode system

- (ii) New reactions for higher charge and discharge capacities not possible with bulk materials
- (iii) Higher electrode/electrolyte contact area leading to higher charge and discharge rates (C rates)
- (iv) Short path lengths for electronic and Li^+ ion transport.

However, disadvantages include:

- (i) An increase in undesirable electrode/electrolyte reactions due to the high surface area of nanostructures for electrode materials, leading to self-discharge, poor cycling and calendar life
- (ii) Lower packing density of particles, leading to lower volumetric energy densities unless special compaction methods are employed
- (iii) Potentially more complicated synthesis methods [9].

With these advantages and disadvantages in mind, efforts have been devoted to exploring nanomaterials for negative electrodes (anodes) for LIBs (e.g. carbon nanotubes (CNTs) [10], graphene [11], silicon (Si) nanowires [12], and transition metal oxide nanoparticles [13]). Metals that store lithium ions are among the most appealing and competitive candidates for new types of anodes in LIBs. Indeed, a number of metals and semiconductors, for example tin (Sn) and silicon (Si), react with lithium to form alloys by electrochemical processes that are partially reversible and of low voltage (relative to lithium), involve a large number of atoms per formula unit, and provide a specific capacity much larger than that offered by conventional graphite (372 mAhg^{-1}). Conversely, such alloy-based anode materials have a critical limitation, which is the pulverization due to larger expansion (300-400%) during lithiation and delithiation processes, resulting in

capacity fading in a high number of cycles [14]. To overcome such limitation of bulk scaled alloy-based materials, worldwide research groups have intensively focused on novel and suitable nanomaterials, such as silicon nanotubes [15] and silicon nanowires [16-17].

A decade ago, P. Poizot proposed the new mechanism of Li reactivity, which differs from the classical Li insertion/deinsertion or Li-alloying processes and involves the formation and decomposition of Li_2O , accompanying the reduction and oxidation of metal nanoparticles (in the range 1 ± 5 nm), respectively [18-19]. Electrodes made of nanoparticles of transition-metal oxides (MO , where M is Co, Ni, Cu or Fe) demonstrated electrochemical capacities of 700 mAhg^{-1} , with 100% capacity retention for up to 100 cycles and high recharging rates (C-rate capability). Since then, many research groups have been involved in the new anode materials. B. Varghese et al. fabricated vertically aligned NiO nanowalls on nickel foils using a plasma-assisted oxidation method and reported their high specific capacity of 635 mAhg^{-1} at 1.2 C and excellent capacity retention around up to 85 number of cycles in the range of 0.005 to 3.0 V vs. Li [20]. However, those transition metal oxide-based anodes have some drawbacks, such as poor cycling stability and low electric conductivity.

In terms of carbonaceous anodes, graphite and soft or poorly ordered carbons such as mesocarbon microbeads (MCMB), spherical graphite and microcarbon fiber have been employed to be used as anode materials. The reasons behind their commercial prominence are the relatively low cost of carbon, the excellent mechanical sustainability for lithium insertion and desorption (having minimum volume change, $\sim 12\%$) and the formation of a protective surface film (e.g. SEI layer) with many different electrolytes [21-23]. Nevertheless, fully intercalated highly crystalline graphites have relatively lower specific capacity (372 mAhg^{-1} , the stoichiometric formulae of LiC_6), and the level of the specific capacity will not be able to meet the demands of next-generation LIB with respect to high specific capacity and volumetric capacity.

To address these issues, many research groups have been interested in multi-walled carbon nanotubes (MWCNTs) due to their unique multi-walled co-centric tube geometries, excellent electrical conductivity, wide electrochemical-stability window, highly accessible surface area, and short diffusion length of Li^+ ions [4, 24]. It has been speculated that a higher Li capacity may be obtained in carbon nanotubes if all the interstitial sites (inter-shell van der Waals spaces, inter-tube channels, and inner cores) are accessible for Li intercalation [25]. Electrochemical intercalation of MWCNTs [26-31] and SWCNTs [32-33] has been investigated by several groups.

Importantly, electrochemical performances were obtained from CNT-based composites composed of PVDF ($-(\text{C}_2\text{H}_2\text{F}_2)_n-$) as binder and carbon nanopowders, as conductive additives dissolved in organic solvents. On the other hand, the most commonly used binder PVDF tends to form compounds with graphite and Li metal. For instance, the high energy per gram of PVDF (7.2 kJ/g) is generated by its compound formation of Li and brings about safety issues such as possible explosions. Also, because of that, high-temperature utilization of Li-ion batteries could not be available. Therefore, it is necessary to design a novel anode system.

In the past, our research team demonstrated outstanding performance of MWCNT-based binder-free anodes in terms of high specific capacity, excellent rate capability and extremely low or nil capacity degradation during long cycle operation [34-35]. However, carbon nano-materials are known as low-density materials that result in low volumetric capacity and low volumetric energy/power density. Therefore, higher solid loading of MWCNTs as active materials is one of the most significant issue to be realized in practice. Very recently, it was argued that nanotube-based active materials have a critical shortcoming in terms of their very low weight per unit electrode area [36]. Thus, their gravimetric energy density may not provide a realistic picture of their commercial application. This critical limitation may lead to scale-up issues for their potential application in the development of EVs.

To counter this issue, we propose a new geometry of 3D Cu current collectors, which can play a crucial role in creating higher surface area to accommodate more solid loading of MWCNTs on the uniformly arrayed patterns in the 3D structure, leading to higher specific capacity and C-rate capability. Until now, efforts have been dedicated to employ a number of 3D structured current collectors, including carbon papers [37], a self-assembled 3D bicontinuous nanoarchitecture [38], aluminum nanorods [39], and nanoporous nickel [40]. The previous research proved that a self-assembled 3D bicontinuous nanoarchitecture could be one of the ideal electrode architectures in order to realize not only the high volume fraction of nanostructured electrolytically active materials (NiOOH/Nickel and MnO₂ cathodes) but also their efficient ion and electron transport [38]. In addition, atomic layer deposition (ALD) coated TiO₂ anodes on 3D aluminum nanorod current collectors showed a tenfold increase in their theoretical area and total capacity (0.0112 mAhcm⁻²), compared to those results from the same anodes on 2D flat aluminum plate and high-rate capability (the capacity ratios at 10 C/0.5 C and 20 C/0.5 C of the 3D anode were 0.4 and 0.35, respectively.) [39].

Currently, the diverse types of hybrid anode structures have been designed and synthesized in order to expect the synergetic combination of two different types of nanomaterials for higher electrochemical performance. As one of the most preferable combinations, MWCNTs/Si hybrid structure can be chosen due to better mechanical accommodation of MWCNTs of the large volume expansion/constriction of Si during the lithiation/delithiation process and higher bonding strength between MWCNTs and Si. There are several reports on MWCNTs/Si composite structures; however, data employing either the SiH₄ CVD method [41] or sputter deposition [42] were used for this dissertation, specifically.

Furthermore, we investigated a new approach which is stacking multi-layers of 3D MWCNTs to increase an area or volumetric mass density of 3D MWCNT based anode materials. Previously,

L. Hu et al. demonstrated the feasibility of novel anode systems and multi-layers stacked with the CNT/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)/paper/ LiCoO_2 (LCO)/CNT structure in order to increase the total energy density of flexible LIBs [43]. With the anode stack, the authors achieved similar electrochemical performance to that of an individual anode cell.

In addition, flexible electronics have recently attracted great attention to the next generation portable devices, such as roll/up displays, wearable devices, active radio frequency identification (RFID) tags, integrated circuit smart cards and implantable medical devices as their major applications. Flexible Li-ion batteries (LIBs) are used as the energy storage devices for the flexible electronics [44-45]. To date, many leading research groups have combined the nanomaterial-based LIB with the flexible polymer substrates. V. L. Pushparaj et al. fabricated a flexible nanocomposite thin-film battery composed of a CNT-cellulose paper electrode, which achieved a reversible capacity of 110 mAhg^{-1} over several tens of cycles [46]. J. Chen et al. prepared CVD-grown CNT/carbon layer (CL) hybrid anodes for a paper LIB and demonstrated its high reversible capacity of 572 mAhg^{-1} after 100 cycles [47]. M. Kaempgen et al. developed single-walled carbon nanotubes (SWCNTs) spray-deposited onto polyethylene terephthalate (PET, $-(\text{C}_{10}\text{H}_8\text{O}_4)_n-$) films and obtained high specific capacitances, ranging from ~ 90 to 120 F/g by using various aqueous electrolytes [48].

1.2 Motivation and Goal

This dissertation focuses on the fabrication of various 3D MWCNT-based nanoarchitectures and the application of novel nanostructures for the anode of LIBs. As mentioned earlier, MWCNTs are suitable for high-potential anode materials because of their exceptional properties such as specific surface area, great flexibility, larger electron conductivity, and short diffusion

length of lithium ions. In spite of these advantages, MWCNT based anode structures have a critical drawback, which is lower loading density.

To address this issue, this investigation is focused on the synthesis of a novel 3D anode structure which increases an area or volumetric mass density of 3D MWCNT-based active materials. In addition, it is aimed at attaining better electrochemical performance of the 3D structures, compared to that of conventional 2D structures (i.e. MWCNTs directly grown on 2D Cu). Also, owing to the highest specific capacity ($4,200 \text{ mAhg}^{-1}$), silicon-based nanostructured materials have attracted strong attention from researchers for LIB around the world. In the present work, amorphous silicon (a-Si)/3D MWCNT hybrid anode structures are presented to attain better LIB performance. Furthermore, to appreciably increase an area or volumetric specific capacity of anodes, the fabrication of 3D MWCNT-based anode stack has been carried out as an important part of this dissertation.

Currently, the flexible display market is expected to grow fast by two big market sectors, which are e-paper technology-centered new diverse applications and the field of replacement markets of the conventional applications [49]. A flexible LIB as an important energy storage device has triggered strong excitement in the scientific community and extensive research worldwide. Regarding this issue, another goal is pursued, which is the preparation for a novel anode structure composed of 3D MWCNTs-graphene-PET flexible film yielding a good electrochemical performance.

1.3 Scope of This Dissertation

Chapter 2 provides the background of the dissertation and discusses the current technology of the synthesis of CNTs and their electrochemical properties for LIBs. The basic concept of LIBs

and CNTs are described. The progress of the novel anode nanostructures and LIB performance are also discussed based on the current technology. A recent development in carbon nanostructure-based flexible electrodes has also been dealt with in this chapter. Chapter 3 deals with the synthesis process of MWCNTs through a two-step preparation method, including radio frequency (RF) magnetron sputtering and catalytic thermal chemical vapor deposition (CVD). Chapter 4 describes the fabrication of 3D MWCNTs directly grown on Cu current collector and the LIB performance with the anode system. This chapter mainly emphasizes the increased loading of MWCNT active materials and enhanced LIB properties compared with those of their 2D counterpart with MWCNTs grown on Cu foil. Furthermore, the improved LIB performance obtained with the anode system of a-Si/3D MWCNTs on Cu is investigated in terms of higher lithiation of amorphous silicon. Chapter 5 describes the fabrication of anode stacks composed of several MWCNT layers which increase the areal and volumetric loading density of MWCNTs and the characterization of LIB. The main purpose for preparation of the anode stack is strongly related to the real picture of the anode stack for its electric vehicle (EV) application which demands larger loading density of active materials for higher total power and energy density. Chapter 6 describes the synthesis of 3D MWCNTs and graphene film by CVD method and transfer of 3D MWCNTs and graphene over transparent and flexible polyethylene terephthalate (PET) films by hot press lamination and chemical etching. The LIB performance of 3D MWCNTs-graphene-PET film is also presented in this chapter. The structural integrity and electronic properties of the flexible 3D anode structure is significantly discussed, since they are important factors that are responsible for good LIB performance. Finally, chapter 7 provides a summary of the dissertation and proposes future work to be conducted.

CHAPTER 2.

BACKGROUND AND LITERATURE REVIEW

2.1 Lithium Ion Batteries

Energy storage devices have attracted great attention for their technological applications, such as hybrid-electric-vehicles (HEVs) or full-electric-vehicles (EVs) in modern human life. The development of novel energy storage devices (ESDs) and their electrode materials is required to meet current social demand, such as impending global oil shortage and the need to preserve the ecosystem from severe green-house gas emission (e.g. CO₂). Among the strong candidates of ESDs, Li-ion battery (LIB) has been intensively studied due to its 3V magnitude of operation voltage and capability to enhance both specific energy and specific power, relative to other ESDs such as Ni-Cd or Ni-metal hydride battery.

Figure 1 represents the correlation between specific and volumetric energy densities for the major second rechargeable batteries. As seen in Figure 1, LIB shows both volumetric and specific energy densities, which can lead to the minimization of volume and mass of components in LIB. The specific energy released in the charge and discharge reaction is the product of the operation voltage and the specific capacity of the battery system. In the case of LIB, the operation voltage is around 3V and many available anode materials exhibit high specific capacities (e.g. the theoretical specific capacity of Si is 4,200 mAhg⁻¹). The basics of the major anode materials are discussed in detail in section 2.2. Owing to those advantages of LIB, portable electronics (e.g. cellular phones, laptops, camcorders *etc.*) are mainly powered by LIB, and consumers favor smaller and lighter electronic devices that are fast charged and possess long battery life. Furthermore, such a balance between high specific energy and high charge rate has sparked a

growing interest in the scientific communities, in particular among technologists and multi-discipline scientists exploring the way to incorporate lithium ion technology into next-generation EVs. Also, increased safety and appropriate cyclability are the main research goals of the next-generation and high-efficiency LIBs.

Figure 1. Diagram comparing rechargeable battery technologies as a function of volumetric and specific energy densities. The arrows indicate the direction of development to reduce battery size and weight. Figure data are adapted from references [50-52].

The electrochemical performance of LIB is strongly dependent on its component materials. The commonly used components of LIB cells are listed in Table I.

Table I. Main components and the examples of commonly used materials [53]

Components		Commonly used materials
Electrode	Positive active materials	LiCoO₂, LiMn₂O₄, LiNiO₂, LiFePO₄
	Negative active materials	Graphite, hard(soft) carbon, Li, Si, Sn, lithium alloy
	Conductive additives	Acetylene black
	Binder	PVdF, SBR/CMC
	Current collector	Cu(-), Al(+)
Electrolyte	Separator	Polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVdF)
	Lithium salt	LiPF₆, LiBF₄, LiAsF₆, LiClO₄, LiCF₃SO₃, Li(CF₃SO₂)₂N
	Electrolyte solvent	Ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), Ethylmethyl carbonate (EMC)
	Additives	Vinylene carbonate (VC), biphenyl (BP)

Figure 2(a) illustrates an active material stack composed of a cathode active material (LiCoO₂) coated on an aluminum current collector and an anode active material (mesocarbon microbeads (MCMBs)) deposited onto a copper foil current collector, and a commercial separator is placed in between the cathode and the anode. Figure 2(b) and 2(c) are representative high magnification cross-sectional scanning electron micrographs of such cathode and anode composite electrodes, respectively [54].

Figure. 2 (a) Photograph of a conventional lithium ion battery active layer stack, including a LiCoO_2 cathode composite on aluminum, microporous poly(olefin) separator, and MCMB anode composite on copper. Cross-sectional scanning electron micrographs depict the microstructure for the (b) cathode and (c) anode, respectively [54].

In lithium ion battery cells, ions can be transported through the electrolyte upon electrochemical oxidation and reduction reaction, while electrons can simultaneously migrate through external wires connected to both electrodes. In anodes, electrochemical oxidation ($\text{A} \rightarrow \text{A}^+ + \text{e}^-$) occurs upon discharge, which is a conversion process from chemical energy to electric energy. In cathodes, electrochemical reduction ($\text{B}^+ + \text{e}^- \rightarrow \text{B}$) occurs as electrons are transported from the anode through an external circuit. An electrolyte is an ionic conductor to transport ions in between the anode and the cathode without conducting electrons. As seen by the schematic in Figure 3, the lithiated metal oxides and graphite carbons have layered structures

with interstitial spaces accommodating lithium ions [51]. Such active materials are able to store the lithium ions by simultaneous electron transport from the current collector in order to reduce the lithium ion at the active material host site. The intercalation process can be carried out by a necessary solid-electrolyte-interface (SEI) that forms on the surface of electrodes, which plays a significant role in protecting the electrode surface from occurring further solvent reduction and act as a selective layer that conducts ions but nonconductive for electrons. The electrolyte formulation and origin of SEI components have been major research fields and there are current studies for new lithium salts and solvents for the improvement of ionic conductivity at various temperature ranges [55]. To date, there are three-major types of reaction mechanisms that are currently being investigated extensively for anode materials. to The mechanisms are briefly mention in the following section.

Figure 3. Schematic illustrating the operation mechanism of a lithium ion battery, including the movement of ions between electrodes (solid lines) and the electron transport through the complete electrical circuit (dashed lines) during charge (blue) and discharge (red) states. Figure 3 is adapted from reference [51].

2.2 Major Types of Reaction Mechanism and Promising Active Materials for Anode

2.2.1 Formation Reactions in Reconstitution Reactions

The equation for a formation reaction is expressed as:

in which a new phase AB is formed in one of the electrodes from its atomic constituents. The new phase AB can be created by moving one of the elements (e.g. A) from one electrode, passing across an electrochemical cell through the electrolyte, and subsequently reacting with the other component (e.g. B) in the other electrode. Since this formation reaction is accompanied by the microstructural variation in the new phase, the reaction is classified as a reconstitution reaction. For instance, lithium-silicon (Li-Si) and lithium-tin (Li-Sn) alloys are formed by such reaction mechanism. The Li-Si alloy has, in its fully lithiated composition, $\text{Li}_{4.4}\text{Si}$, a theoretical specific capacity of $4,200 \text{ mAhg}^{-1}$, which is known as the highest value, compared with $3,600 \text{ mAhg}^{-1}$ for metallic Li and 372 mAhg^{-1} for graphite. Unfortunately, the accommodation of so much lithium brings about enormous volume changes (300-400%) during prolonged alloying and de-alloying processes between Si and Li. The mechanical strain generated during the alloying and de-alloying processes leads to cracking and crumbling of the metal electrodes; as a consequence, a distinguishable loss of capacity to store charge appears in the course of a few cycles. To mitigate such pulverization effect, novel nanomaterials, such as Si nanotubes [15] and Si nanowires (Si NWs) [16], have been synthesized. C. K. Chan et al. recently demonstrated a silicon nanowire-based anode could almost constantly maintain the specific charge and discharge capacities higher than $3,000 \text{ mAhg}^{-1}$ for up to 10 cycles, as presented in Figure 4 [16].

Figure 4. (a) Cyclic voltammogram for Si NWs from 2.0 V to 0.01 V versus Li/Li⁺ at 1 mV s⁻¹ scan rate. The first seven cycles are shown. (b) Voltage profiles for the first and second galvanostatic cycles of the Si NWs at the C/20 rate. The first charge achieved the theoretical capacity of 4,200 mAhg⁻¹ for Li_{4.4}Si. (c) The voltage profiles for the Si NWs cycled at different power rates. The C/20 profile is from the second cycle. (d) Capacity versus cycle number for the Si NWs at the C/20 rate showing the charge (squares) and discharge capacity (circles). The charge data for Si nanocrystals (triangles) from reference [56] and the theoretical capacity for lithiated graphite (dashed line) are shown as a comparison to show the improvement when using Si NWs [16].

2.2.2 Displacement Reaction in Reconstitution Reactions

Another type of reconstitution reaction involves a displacement process, which can be simply written as:

where species A displaces species B in the binary phase BX, forming AX. Subsequently, a new phase accompanied by element B will be produced. A driving force creating this reaction can occur if phase AX has greater stability (i.e. the phase AX has a greater negative value of Gibbs free energy than that of phase BX). A good example is the redox reaction of transition metal oxide with Li metal. However, some transition metal oxides e.g. MO (M:Co, Ni, Fe *etc.*) have rock-salt structures; thus, there is no available empty space for insertion of lithium ions in the internal structure. Also, none of the 3d transition metal can form an alloy with Li. The mechanism of such reaction differs from the classical reaction of Li insertion/deinsertion or Li-alloying processes and involves the formation and decomposition of Li₂O, accompanying the reduction and oxidation of metal nanoparticles (in the range of 1±5 nm), respectively [10]. With smaller particle sizes of 5 and 10 nm, more atoms lie near or on the surface of nanoparticles and occupy 15-30 % and 30-60 %, respectively. Owing to the high surface energy of the metal nanoparticles, the formation of nanosize transition metal oxides e.g. MO (M:Co, Ni, Fe *etc.*) from Li₂O can occur. P. Poizot et al. proved the theory based on the fact that the electrochemical activity of nanoscale transition metal nanoparticles was more important and dependent on the degree of their division and agglomeration [18]. In the case of Co, the redox reactions can be expressed as:

According to the redox reaction, one mole of Co reacts with one mole of lithium oxide to produce two moles of Li and one mole of cobalt oxide. As seen in Figure 5(a), the first discharge profile shows the characteristic rapid drop before reaching a plateau region (the potential and amplitude can be varied with the metal species) and then, decreasing to 0.01 V. Figure 5(b) shows that the specific capacity keeps decreasing with the number of cycles, except in the case of CoO. Such a limitation has been generally shown in the electrochemical behavior of transition metal oxides due to the lower degree of division caused by the size of precursor particles, leading to further structural dismantlement of the metal particles upon cycling.

Figure 5. Properties of MO/Li cells. (a) The voltage vs. composition profile for various MO/Li cells cycled between 0.01 V and 3 V at a rate of C/5 (1 lithium in 5 hours). The capacity fading for the same cells under similar conditions is shown in (b), where we also show data for a Co₃O₄/Li cell in order to show that the reported behavior is not specific to divalent oxides. Inset, the rate capability of a CoO electrode [18].

2.2.3 Insertion Reactions

This involves the insertion of guest species into normally unoccupied interstitial sites in the crystal structure of an existing stable host material. In the insertion reaction, the chemical composition of the host phase initially present can be substantially changed; however, this reaction theoretically does not result in a change in its basic crystal structure or the number of the phases in the microstructure. On the other hand, the insertion and extraction of interstitial species into and from previous unoccupied locations in the structure generally result in a change in volume. Such volume change induces mechanical stress and energy in the structure, which plays a significant role in the hysteresis and subsequent energy loss, observed in a number of reversible battery electrode reactions. Regarding the intercalation and deintercalation reaction with Li, a lithium-graphite compound can be chosen as a good example. Graphitic carbon fundamentally comprising sp^2 -hybridized carbon atoms, which are arranged in a planar “honeycomb-like” network, i.e., a “graphene” layer is formed (see Figure 6) [57]. Van der Waals forces provide a weak cohesion of the graphene layers, resulting in the layered graphite structure. From a strictly crystallographic point of view, the term “graphite” is only used for carbons with a perfect stacking order of graphene layers, either the predominant AB (hexagonal graphite, 2H-, or α -phase) or the less common ABC (rhombohedral graphite, 3R-, or β -phase). Due to the small energy for transformation of the AB into the ABC type of stacking (and vice versa), perfectly stacked graphite crystals are not readily available. Therefore, the term “graphite” is often used regardless of stacking order.

Figure 6. Crystal structure of hexagonal graphite showing the AB layer stacking sequence, the unit cell, and the subdivision in basal plane and prismatic surfaces [57].

The ratio of hexagonal to rhombohedral structures can be varied by certain processes. Mechanical treatments, especially milling, shearing, or ultrasonic impact result in a larger extent of the β -phase, whereas thermal annealing procedures at elevated temperatures transform the material to the thermodynamically more stable α -form. By heat treatment, it is possible to create a graphite which contains 100% α -phase, whereas this could not be achieved by mechanical measures for the β -form. So far, β -phase contents up to 30% have been reported. The rhombohedral and hexagonal contents of graphites can be identified from XRD spectra [58].

It should be noted here, that in addition to a change of the stacking sequence, mechanical milling can destroy carbon-carbon bonds and thus, increase the number of structural defects. The kind and extent of defects are also dependent on the milling procedure. On the contrary, heat-treatment can increase the degree of crystallinity in graphitic structure by reducing the number of defects. Shorter milling time can confine the amorphization to the surface. Milling can also change the chemical (surface) composition of the carbon material under certain conditions since the defects created by milling are highly reactive.

Layered graphite displays basically two kinds of structural surfaces which are prismatic (edge) and basal plane (Figure 6). Ideal (i.e. defect- and contaminant-free) basal plane surfaces are homogeneous and smooth and consist of carbon atoms. In contrast, the prismatic surfaces are heterogeneous and rough and apart from carbon may contain various, mostly (but not only) oxygen-containing, surface groups. The quantity and quality of surface groups for graphitic and non-graphitic layers can be modified by mechanical (e.g., milling), thermal (e.g., heat treatment), and chemical measures (e.g., exposure to reagents creating a certain surface chemistry), or a combination of these methods. It is known that intercalation of Li^+ ions into the graphitic carbon proceeds via the prismatic planes and not via the basal planes. The interaction of graphite with the electrolyte is also dependent on the respective surface and its properties. The major advantage of graphitic materials is volume expansion of around 12 % which is presumably due to their unique mechanism of intercalation and decalation of Li^+ ions, as shown in Table II [59]. Also, as shown in Figure 7, the battery voltage is determined by the electrochemical potential difference between the cathode and anode with respect to lithium metal [51-52, 60-61]. Additionally, the open circuit voltage of graphite ranges between 0.1 and 0.2 V vs. Li/Li^+ which is the lowest value compared with any other anode material. Owing to those features, graphite has been utilized as the anode for commercially available batteries. However, the lower specific capacity of 372 mAhg^{-1} of graphite is insufficient for next-generation electric vehicles which demand higher capacity. To

address this issue, MWCNTs have been proposed as promising anode materials to open up a new avenue for high-performance electric vehicles and electronic portable devices.

Table II. Capacities and volume changes of different elements [59]

Starting material	C	Al	Si	Sn	Bi
Lithiated phase	LiC ₆	Li ₉ Al ₄	Li ₂₁ Si ₅	Li ₁₇ Sn ₄	Li ₃ Bi
Theoretical specific capacity (Ah/kg)	372	2235	4010	959	385
Theoretical volumetric capacity (Ah/l)	833	6035	9340	7000	3773
Volume change (%)	12	238	297	257	115

2.3 Brief Introduction to Carbon Nanotubes

Carbon nanotubes can be envisioned as a rolled up graphene sheet into a seamless cylinder with fullerene caps for single wall (SWCNTs) or multiple sheets (MWCNTs). Characteristics of MWCNTs are the concentric layers that are spaced 0.34 nm apart as illustrated in the transmission electron micrograph (TEM) of Figure 8(a)-(c). In the case of SWCNTs, there are van der Waals interactions between sidewalls that lead to hexagonally close-packed bundles, as shown in Figure 8(d) [62]. The electronic properties of SWCNTs are determined by the chirality of the SWCNT, which represents the diameter and helicity of the structure. The chirality determines whether the nanotubes will be metallic or semiconducting in nature. Figure 9 demonstrates the basics for assigning SWCNT chiralities with a roll-up vector ($na_1 + ma_2$) from a point of origin on a graphene sheet. The chiral angle ($\leq 30^\circ$) is the angle between the zigzag axis

and the roll-up vector [54]. The result from this exercise is a series of chiral indices with integer values of n and m , which are used to assign the uniqueness of each SWCNT.

Figure 7. Diagram illustrating the lithium ion capacity and electrochemical reduction potentials with respect to lithium metal for conventional anode (red axis) and cathode materials (blue axis). The battery potential is the relative difference between the voltage of the selected positive electrode materials (blue ovals) and voltage of the corresponding negative electrode material (red ovals). Figure data are adapted from references [51-52, 60-61].

Figure 8. Carbon nanotubes imaged by transmission electron microscopy (TEM). TEM is a technique used in the discovery of both MWCNTs and SWCNTs. (a–c) TEM images of MWCNTs with closed caps (courtesy of S. Iijima). The parallel lines are the cross-sections of the sidewalls of concentric cylinders. Diameters of MWCNTs are typically on the order of 10–20 nm. (d) TEM image of the cross-section of a bundle of SWCNTs (courtesy of R. Smalley). Each circle represents the cross-section of a SWCNT with diameter ~ 1.4 nm [62].

Figure 9. Chirality chart illustrating the assignment of (n, m) SWCNT structures using a role-up vector from an origin point on a graphene sheet and the nanotube diameter [54].

There has been intensive effort to develop control over individual CNT properties (chirality, length, purity, electronic type ratio, *etc.*) for a variety of applications. This control can either be accomplished during synthesis or in conjunction with followed chemical and physical treatments aimed at purification and separation of desired products. The most common techniques are chemical vapor deposition (CVD), arc-discharge, and laser vaporization synthesis. In this dissertation, the brief introduction to CVD method will be presented in the Chapter 3.

2.4 Carbon Nanotubes for Li-ion Battery Anode

MWCNTs are allotropes of carbon constructed with their one dimensionally long and co-centric hollow structure with the walls formed by one-atomic thick sheet of carbon, called graphene [63]. MWCNTs have been considered one of the strong candidates for anode materials for high-performance LIB, which is associated with their unique multi-walled co-centric tube

geometry, excellent electrical properties, wide electrochemical-stability window and highly accessible surface area [64]. Carbon nanotubes contain many kinds of the interstitial sites (inter-shell van der Waals spaces, inter-tube channels, and inner cores), which are accessible for Li intercalation [64]. Therefore, it has been speculated that a higher Li capacity may be obtained in carbon nanotubes. Electrochemical intercalation of MWCNTs [26-27] and SWCNTs [32] has been investigated by several groups. Figure 10 presents a galvanostatic charge and discharge profile that is typical for all the family of carbon nanomaterials, including SWCNTs, MWCNTs and carbon nanofibers [65]. A reversible capacity (C_{rev}) of 100 - 640 mAhg⁻¹ has been reported, depending on the sample processing and annealing conditions of MWCNTs [26-27] and SWCNTs [32].

Figure 10. Galvanostatic insertion-extraction of lithium into and from carbon nanotubes. Current load of 20 mA g⁻¹ [65].

In general, well-graphitized MWCNTs synthesized by an arc-discharge method have a lower reversible specific capacity (C_{rev}), compared with the value obtained from defective MWCNTs

prepared by a CVD method. From structural studies, it has been proven that alkali metals can be intercalated into the inner-shell spaces within the individual MWCNTs through defect sites [66]. However, one of the most critical disadvantages of the CNT-based materials is the large irreversible specific capacity during a primary cycle. The main reasons for such a problem are strongly related to the large surface area of a CNT-based electrode (e.g. $\sim 300 \text{ m}^2\text{g}^{-1}$ for SWCNT films measured by the Branuer-Emmett Teller (BET) method) and the formation of solid electrolyte interface (SEI) layers on the surface of the CNT-based electrodes. It should be highlighted that the research into CNT-based anode materials has been mainly performed through their composite form combined with binder and conductive additive. Consequently, there have been some drawbacks, such as harmful effect of the polymeric binder and extra weight of the active material.

To avoid such limitation, Dr. Won Bong Choi's group at FIU has recently developed engineered carbon nanotube-based system, specifically, direct MWCNT grown on Cu substrates by catalytic thermal CVD and demonstrated excellent properties for application in LIB electrodes [34]. An MWCNT grown on Cu anode showed very high specific capacity (for the second discharge cycle, it was $1,455 \text{ mAhg}^{-1}$) and exceptional stability of the reversible capacity ($\sim 900 \text{ mAhg}^{-1}$) at 1C rate, as presented in Figure 11. In addition, the anode system has major advantages of binder-free so that the LIB button cell composed of the anode can avoid any severe safety concern. It is known that the most widely used binder, poly (vinylidene fluoride) (PVdF), can react with electrolyte. Moreover, PVdF is known to react with graphitic materials and metallic lithium to form stable compounds [67-68]. Such reactions are highly exothermic; for example, the reaction with metallic Li produces 7.2 kJ of energy per gram of PVdF [67]. Thus, the presence of a binder could lead to thermal runaway, necessitating incorporation of additional safety features in the battery.

Figure 11. Electrochemical characteristics of the proposed CNT-based electrode structure. (a)

First two charge-discharge cycles of the MWNT-on-Cu anode, at 0.1 C rate. The first discharge cycle (lithiation) has shown a very high capacity of 2,547 mAhg⁻¹, while the following delithiation cycle showed a specific capacity of 1,455 mAhg⁻¹. (b) Reversible capacity of the MWNT-on-Cu anode, at different C-rates. Very high specific capacity could be observed at all C-rates. Even at the 3 C rate, a reversible capacity of 767 mAhg⁻¹ was observed, which is almost 2 times the theoretical capacity of graphite. (c) Exceptional stability of the reversible capacity (~900 mAhg⁻¹) of the MWNT-on-Cu anode in long-run, at 1 C rate. Except for the first two cycles, virtually no capacity degradation was observed for this anode structure, in 50 cycles. (d) Coulombic efficiency of the MWNT-on-Cu anode, showing very high efficiency, except for the first cycle. After the initial five cycles, the efficiency remained more than 99 % [34].

In the case of the directly grown CNTs on the current collector, several features of the novel anode system can be summarized. First, it reduces harmful effect of the polymeric binder and weight of the active material, increases specific capacity, and shows potential to be used for high-temperature application. Second, CNTs do not have any kind of expansion/contraction and pulverization problems (like Si and SnO_2), so they can sustain their capacity for long cycles. Third, each CNT is well bonded to the current collector, thus all of them contribute to the capacity. Fourth, the high specific surface area of CNTs allows more Li ion intercalation. Fifth, higher conductivity of the active anode material is important for achieving higher capacity. In that respect, MWCNTs, known to be excellent charge carriers, are an alternative option and aid in achieving higher capacity. Moreover, by the interface-control proposed in this study, an ohmic contact and strong bonding between the CNTs and substrate are ensured, which further helps in efficient charge transport [69]. Furthermore, the anode structure, consisting of MWCNTs grown on Cu foil, can be very easily fabricated using the thermal chemical vapor deposition (CVD) process. The listed advantageous features of the CNT directly grown on metal substrate can be schematically illustrated, as presented in Figure 12.

Figure 12. A schematic (not to scale) of the proposed anode structure, showing its advantageous features [34].

2.5 Hybrid Anode Structures for High-Performance Li-ion Batteries

Recently, in order to obtain better performance, many research groups are interested in the active/inactive nanocomposite concept to be applied to advanced Li ion battery anode system. Several authors have proved that this approach is effective to synergize Li-ion battery performance through intimately mixing two materials, one reacting with lithium whereas the other acting as an inactive mechanical support to avoid pulverization of the anode structure upon Li^+ cycling [41, 60]. L. F. Cui et al. synthesized a CNT-Si composite film [41]. CNTs are infiltrated in a Si film and play an important role in improving a structural reinforcement and electric conductivity in the composite anode. Figure 13(b) illustrates the free-standing CNT-Si hybrid structure and it can be rippled up to release the large strain of Si induced during Li^+ ion charge and discharge cycling. By this method, the relative thickness up to 4 μm of Si film demonstrates a good cycling performance.

Figure 13. (a) Sputtered-on Si film tends to pulverize after Li^+ cycling. (b) CNT-Si films can “ripple up” to relax the large strain during Li^+ cycling [41].

A photograph of a Si-free-standing CNT composite anode is presented in Figure 14(a). Also, Figure 14(b) shows the cycling performance of the hybrid anode. Discharge specific capacity remains $1,711 \text{ mAhg}^{-1}$ (or 82 % with respect to the initial value) after 50 cycles. The Coulombic efficiency is initially 86 % and greater than 98 % throughout the rest of cycles.

(a)

(b)

Figure 14. (a) Photograph of a free-standing CNT-Si film. (b) Charge (red) and discharge (green) capacity and Coulombic efficiency (blue) *versus* cycle number for a half cell using free-standing CNT-Si films as the working electrode cycled between 1 - 0.01 V [41].

2.6 3D Anode Architecture for High Loading Density of Active Materials

Very recently, it is argued that nanotube-based active materials have a critical shortcoming in terms of their very low weight per unit electrode area [36]. Thus, their gravimetric energy density may not give a realistic picture to commercial application. The critical limitation may lead to scale-up issues for their potential application in the development of EV.

Figure 15. One way to compare electrical energy storage devices is to use Ragone plots, which show both power density (speed of charge and discharge) and energy density (storage capacity). These plots for the same electrochemical capacitors are on a gravimetric (per weight) basis in (A) and on a volumetric basis in (B). The plots show that excellent properties of carbon materials will not translate to medium- and large-scale devices if thin-film and/or low-density electrodes are used [36].

To address this issue, we would like to propose a new geometry of 3D Cu current collectors, which can create higher surface area to accommodate higher solid loading of MWCNTs on the uniformly arrayed patterns in the 3D structure, leading to higher specific capacity and C-rate capability. To date, intensive research has been performed to improve Li-ion battery properties through introducing a number of 3D structured current collectors, including carbon papers [37], a self-assembled 3D bicontinuous nanoarchitecture [38], aluminum nanorods [39], and nanoporous nickel [40]. In the previous research, it was proved that a self-assembled 3D bicontinuous nanoarchitecture could be one of the ideal electrode architectures in order to realize not only high volume fraction of nanostructured electrolytically active materials (NiOOH/Nickel and MnO_2

cathodes) but also their efficient ion and electron transport [38]. Figure 16 shows the schematic diagram of bicontinuous electrode fabrication process. In addition, ALD coated TiO_2 anodes on 3D aluminum nanorod current collectors showed a ten-time increase in their theoretical area and total capacity ($0.0112 \text{ mAhcm}^{-2}$), compared to those resulted from the same anodes on 2D flat aluminum plate and high rate capability (The capacity ratios at 10 C/0.5 C and 20 C/0.5 C of the 3D anode were 0.4 and 0.35, respectively.) [39].

Figure 16. Bicontinuous electrode fabrication process. The electrolytically active phase is yellow and the porous metal current collector is green. The electrolyte fills the remaining pores [38].

A prototype Li-ion battery was assembled from a bicontinuous lithiated MnO_2 cathode, together with a graphite anode, a separator and 1 M LiClO_4 as the electrolyte, and sealed in a moisture barrier bag [38]. The anode capacity was selected to be about ten times greater than that of the cathode so that the anode was not rate-limiting. A constant potential (3.6 V) was applied. The initial charge current was 35 Ag^{-1} ($\sim 177 \text{ C}$) and rapidly decreased to almost zero in 120 s (see Figure 17). The discharge curves in Figure 17 show that after 60 s, the battery is charged to 75% capacity, and after 120 s, it is 90 % charged relative to a 800 s charge. Charging past 800 s resulted in insignificant increases in capacity.

Figure 17. Li-ion battery ultrafast charge behavior. Potentiostatic charging at 3.6 V for 60 s (blue), 120 s (green) and 800 s (red), and ~ 3 C galvanostatic discharging of the prototype Li-ion pouch battery after each charging cycle [38].

2.7 Flexible Li-ion Batteries for Next-Generation Flexible Electronic Devices

Flexible electronics have attracted great attention to the next-generation portable devices, such as roll/up displays, wearable devices, active radio frequency identification (RFID) tags, integrated circuit smart cards and implantable medical devices as their major applications. Flexible Li-ion batteries (LIB) are used as the energy storage devices for the flexible electronics [44-45]. To date, many leading research groups have combined the nanomaterial-based LIB with the flexible polymer substrates. V. L. Pushparaj et al. fabricated the flexible nanocomposite thin-film battery composed of CNT-cellulose paper electrode (see Figure 18) [46].

Figure 18. Fabrication of the nanocomposite paper units for supercapacitor and battery. (a) Schematic of the supercapacitor and battery assembled by using nanocomposite film units. The nanocomposite unit comprises RTIL([bmIm][Cl]) and MWCNT embedded inside cellulose paper. A thin extra layer of cellulose covers the top of the MWCNT array. Ti/Au thin film deposited on the exposed MWCNT acts as a current collector. In the battery, a thin Li electrode film is added onto the nanocomposite. (b) Photographs of the nanocomposite units demonstrating mechanical flexibility. Flat sheet (top), partially rolled (middle), and completely rolled up inside a capillary (bottom) are shown. (c) Cross-sectional SEM image of the nanocomposite paper showing MWCNT protruding from the cellulose–RTIL thin films (Scale bar, 2 μm). The schematic displays the partial exposure of MWCNT [46].

Figure 19. Electrochemical measurements of nanocomposite paper battery. (a) First charge–discharge curves of the nanocomposite thin-film battery cycled between 3.6 and 0.1 V at a constant current of 10 mA g⁻¹. (b) Charge and discharge capacities vs. number of cycles of the nanocomposite thin-film battery. (c) The flexible nanocomposite film battery used to glow a red light-emitting diode (LED). The flexible battery consists of an individual nanocomposite thin film with the Li thin film present on one side as one of the electrodes. The LED glows even when the battery device is rolled up, and the demonstration could be repeated over several tens of cycles at an initial operating voltage of 2.1 V [46].

The charge–discharge cycles of the battery were performed between 3.6 and 0.1 V, at a constant current of 10 mA g⁻¹. A large irreversible-capacity (~430 mAh g⁻¹) was observed during the first charge–discharge cycle, as shown in Figure 19(a), and further charge–discharge cycles resulted in a reversible stable capacity of 110 mAh g⁻¹ (see Figure 19(b)). It is highlighted that the battery device was operated under full mechanical flexibility. In Figure 19(c), the laminated Li-ion-based battery device was used to light up a red light-emitting diode, showing its discharge behavior. Also, such demonstration was repeated over several tens of charging and discharging cycles [46].

J. Chen et al. prepared CVD grown CNT-carbon layer (CL) hybrid anodes for a paper LIB device and demonstrated their high reversible, stable specific capacity of 572 mAh g⁻¹ after 100 cycles [47]. M. Kaempgen et al. developed single-walled carbon nanotubes (SWCNTs) spray deposited onto PET films and obtained high specific capacitance ranging from ~90 to 120 F/g by using various aqueous electrolytes [48].

CHAPTER 3.

SYNTHESIS OF MWCNT DIRECT GROWN ON METAL SUBSTRATES AND BUTTON CELL ASSEMBLY COMPOSED OF MWCNT-BASED ANODE

3.1 Ti/Ni Thin Film Deposition on Cu Substrates by Using an RF Magnetron Sputtering System

Catalysts play a very significant role in growing MWCNTs and they are generally deposited on substrates by using a sputtering system. Magnetron sputtering is one of the most commercially available techniques for deposition of high-quality films of metal, oxide and non-oxide ceramics and alloys on a substrate under vacuum. The basic fundamental of the sputtering process is the ejection of target material and its subsequent deposition on a substrate. In the case of magnetron sputtering process, the sputtering source or gun is usually a magnetron that uses strong electric and magnetic fields to trap electrons close to the surface of the magnetron, which is known as the target. The electrons conduct through helical paths around the magnetic field lines and undergo more ionizing collisions with gaseous neutrals near the target surface. The whole sputtering process is conducted under a vacuum with an Ar gas environment. Figure 20 illustrates a simple schematic of the magnetron sputtering system. Also, the photograph of the direct current (DC) - radio frequency (RF) magnetron sputtering system (AJA International) is shown in Figure 21. The main chamber is under high vacuum condition and the sputtering gun and the substrate holder function as cathode and anode, respectively. The three guns are located at the bottom side of the cylindrical main chamber, whereas the substrate holder and heater are installed under the top side of the chamber.

Figure 20. Schematic diagram of a simple magnetron sputtering system.

Figure 21. A three-gun magnetron sputtering system (AJA International), used to synthesize catalytic thin films.

For the sputtering process, the three targets were first installed over the guns, while the substrate holders were facing down towards the target guns [70]. The commonly used catalytic materials of CNT growth were transitional metal, such as Ni, Fe, and Co. In this study, Ni was chosen as catalytic metal deposited on a substrate. Ti was used as a diffusion barrier thin layer to prevent such catalytic metals from being migrated into the substrates and forming compounds. The main chamber was evacuated to the base pressure of $\sim 1 \times 10^{-7}$ Torr by means of connected turbo molecular and roughing pumps. Substrates (e.g. Cu meshes or foils) were mounted on a disk sample holder, which was subsequently transferred into the main chamber through a load lock system. The sample holder was fixed into the anode and rotated for the homogeneous thin film deposition of the metal catalysts over the substrates. 10 sccm of Ar gas was continuously flowed into the main chamber through the mass flow controller. The plasma was generated at around 25 mTorr pressure in the main chamber with the help of manual gate valve installed between turbo molecular pump and main chamber. This process was performed to increase the Ar gas concentration close to the target metals. A sputtering power of ~ 75 Watt was applied to magnetron gun. After generating plasma, the processing pressure was decreased to ~ 5 mTorr. Through tuning and loading of matching circuit, reflection power of the sputtering gun was lowered to zero value. Finally, the gun shutter was opened for starting the deposition of the catalytic metal on the substrate. After deposition of catalytic thin film across the desired time line, sputtering power and gas flow were turned off and Ti (~ 10 nm thickness)/Ni (2.5-10 nm thickness) deposited substrates were taken out through the load lock system [34, 71-72]. Table III represents the standard process condition used for Ti and Ni thin film deposition over the Cu substrate.

Table III. Standard process conditions used for Ti and Ni thin film deposition.

Target	Ni and Ti (5N purity)
Substrate	Cu mesh and Cu foil
Substrate to target distance	30 cm
Temperature	Room temperature
Base pressure	$\sim 10^{-7}$ Torr range
Process pressure	5 mTorr
Gas used	Ar
Gas flow rate	10 sccm
RF power	75 Watt
Reflection power	0 Watt

We assume that initial nucleation in the Ti/Ni thin film growth follows an island or Volmer-Weber growth mode. Island growth proceeds when the growth species (in our case, Ni atoms) are more strongly bonded to each other than to the substrate. Many metal thin films on insulator, alkali halide, graphite, and mica substrates show island nucleation during the initial film deposition. Subsequent growth leads to the coalescence of the islands to consequently form a continuous film [73].

3.2 CNT Growth by Using a Catalytic Thermal Chemical Vapor Deposition (CVD)

3.2.1 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) methods have been successful in making carbon fiber, filament and nanotube materials for the past 20-30 years [74]. Schematic experimental setup for CVD growth is depicted in Figure 22. The growth process involves heating a catalyst material to high temperatures in a tube furnace and flowing a hydrocarbon gas (designated by C_nH_m) through the tube reactor for a period of time. Materials grown over the catalyst are collected upon cooling the system to room temperature. The key parameters in nanotube CVD growth are the hydrocarbons, catalysts and growth temperature. The active catalytic species are typically transition-metal nanoparticles or thin film, such as Ni, Co, and Fe formed on various metal and ceramic substrates. The general nanotube growth mechanism (see Figure 23) in a CVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal, and dissolution and saturation of carbon atoms in the metal nanoparticle [75].

Figure 22. Schematic experimental setup for carbon nanotube growth by means of a catalytic thermal CVD method.

Figure 23. Two general growth modes of carbon nanotube in chemical vapor deposition. *Left diagram:* base growth mode. *Right diagram:* tip growth mode [75].

According to the proposed model by R. T. K. Baker et al. we can interpret the nucleation and growth mechanism of the CVD grown 3D MWCNTs on Cu in the following ways [76]:

- (1) At around CNT growth temperature 700 °C, a Ni thin layer could begin agglomerating as separate, spherical-cap shaped Ni islands by thermal diffusion of Ni atoms. Hence, the equivalent diameters of the Ni islands increased with temperature.
- (2) When introduced into the CVD chamber in the 700-750 °C temperature range, carbon precursor gas (In our case, ethylene (C_2H_4)) was decomposed and the released carbon atoms

were diffused into the Ni islands from their surface to core due to the thermal gradient in the Ni islands.

(3) The dissolution of carbon into the Ni islands ceased after passing their solubility limit of carbon and began precipitating at the trailing ends of the Ni islands and growing MWCNTs.

Since the decomposition of the ethylene precursor gas exothermically occurred, a temperature gradient existed across the Ni catalyst islands. The solubility was temperature dependent and showed the highest degree at the front-exposed surfaces of the Ni and the lowest one at the colder zone on the rear surfaces of the Ni where were close to the Cu mesh substrate. In addition, according to the bonding strength between the Ni catalyst and TiC underlayer/Cu substrate, the tip or base growth mode can be determined, as shown in Figure 23. On the left, stronger chemisorption between catalyst and substrate facilitates base growth of MWCNTs. Tip growth mode, drawn on the right, is predominant when the chemisorption does not appear to be strong enough to anchor catalyst to substrate [75]. However, a major disadvantage for CVD grown MWCNTs has been the high defect densities in their structures. The defective nature of CVD grown MWCNTs remains to be thoroughly understood, but is most likely due to relatively low growth temperature, which does not provide sufficient thermal energy to anneal nanotubes into perfectly crystalline structures.

For CNT growth by a catalytic thermal CVD process, catalyst deposited substrates are to be inserted into a quartz tube reactor in a CVD system. The internal structure of our CVD chamber is similar to the schematic diagram, as presented in Figure 22. Figure 24 shows our CVD systems (Figure 24(a) FirstNano; Figure 24(b) A-Tech system, Korea) used for MWCNT growth. The typical CNT growth conditions are listed in Table IV.

Table IV. The summary of key conditions for CNT growth through a catalytic thermal CVD method

Step	Temperature	Gas	Flow rate (SCCM)
Ramping	Room temperature to 300°C	Argon	600
H ₂ etching	300°C	Hydrogen	300
Ramping	300°C to 750°C	Argon	600
Growth	750°C	Hydrogen : Ethylene (C ₂ H ₄)	300 : 600
Cooling	750°C to Room temperature	Argon	600

(a)

(b)

Figure 24. Thermal chemical vapor deposition systems manufactured by (a) FirstNano Inc., and (b) A-Tech system Inc.

To explore the morphology variation of the 3D MWCNTs directly grown on Cu, we controlled the growth conditions, such as growth temperature and time, and deposition time for catalytic Ni thin layer. As seen in Table V, the most probable size (which is noted in each image)

of the Ni catalyst islands (clusters) increased with not only the temperature due to higher mobility of the atoms but also the thickness of Ni thin layer due to larger volume for the formation of Ni islands. The sizes of the Ni clusters were measured by ImageJ program, and a size distribution of the clusters existed (see Figure 25). Upon heating, the sputter-deposited 2-dimensional Ni thin film underwent the compressed stress due to the mismatch of the linear thermal expansion coefficients (α) between Ni ($13 \times 10^{-6}/^{\circ}\text{C}$) and Cu ($17 \times 10^{-6}/^{\circ}\text{C}$). The compressed strained Ni thin layers tended to transform into separate semi-spherical islands to release internal strain energy. On the other hand, the Ti layer did not form clusters due to its lower ($8.5 \times 10^{-6}/^{\circ}\text{C}$) linear thermal expansion coefficient (lower strain energy) and higher melting point (lower mobility of the atoms at a given temperature) [77]. It is well understood that the segregation and precipitation of solutes favorably occur at defect sites such as dislocations and grain boundaries, where the stress fields are more intense. Therefore, polycrystalline Ni islands provide many sites for carbon nanotube growth. For lower temperature (e.g., 700°C), the solubility of carbon into the Ni islands and diffusion coefficient of carbon atoms are lower; thus, carbon nanotube nucleation starts from smaller grains of the Ni islands. However, for higher temperature (e.g., 750°C), the average size of the catalytic Ni islands increases due to larger coalescence induced by faster thermal diffusion of Ni atoms. The larger surface of the Ni islands allows a larger intake of carbon atoms, and diffusive flux of carbon through Ni islands becomes accelerated. Consequently, carbon nanotubes with larger diameters can be formed at higher growth temperature [78-79].

According to basic theory, when the average size of catalytic clusters is much larger than the diffusion length of carbon atoms, carbon atoms cannot migrate to the rear side of the clusters for CNT growth. Conversely, in the case of a thin region, most of the clusters are smaller than the diffusion length so that they can effectively assist CNT growth. Therefore, in our case, the thicknesses of Ni thin layer in the region of 2.5-10 nm belong to the transitional regions between those two extremes. Also, the diameters of as-grown MWCNTs from the Ni thin layer with

thickness (> 4 nm) showed no significant difference. However, at the elevated temperature from 700 °C to 750 °C, the diameters of as-grown MWCNTs considerably increased at each thickness of the Ni thin layer (2.5, 5, 7.5, and 10 nm). Therefore, we speculate that the temperature effect

Table V. The variation of diameter of catalyst Ni islands with the CNT growth conditions. Ethylene gas as carbon precursor was flowed into the chamber for one minute. Numerical values noted in the top-left of each image represent the most probable size of the Ni islands.

Growth condition Thickness of Ni (nm)	700 °C for 1 minute	
	750 °C for 1 minute	
2.5	32	74
5	58	94
7.5	78	123
10	95	129

Figure 25. The variation of the diameters of catalyst Ni islands and the areal weights of MWCNTs with CNT growth conditions

on the diameters of MWCNTs was more predominant, compared to the effect of the thickness of Ni thin layer. C. Ducati et al. proposed an equation to express the growth rate (R) of MWCNTs at temperature (T) with various parameters, as follows [78]:

$$R \propto \frac{D_0 S_0 \exp\left(-\frac{Q+q}{kT}\right)}{x}$$

where x is the diffusion distance or the grain size, D_0 and S_0 are the diffusivity and solubility prefactors, and Q and q are the activation energies for diffusivity and solubility, respectively.

We confirmed that the morphologies of MWCNTs shown in the SEM images of Table VI could be varied from each growth condition. As the temperature increases, the decomposition and diffusion rates of carbons increased and the growth rate of MWCNTs proportionally increased. As a result, the areal density of MWCNTs grown on by 750 °C for 50 minutes and 7.5 nm thickness of Ni thin layer was 1,800% higher than that of MWCNTs grown by 700 °C for 50 minutes and 2.5 to 10 nm thickness of Ni thin layer (see Figure 25). Also, the diffusion rate of Ni atoms on the Ti barrier layer deposited on Cu substrate promoted facilitating the agglomeration of Ni nanoparticles. The size of the agglomerated Ni islands usually determined the diameter of MWCNTs in CVD growth. In the case of 700 °C, the diameters of MWCNTs were less than 100 nm, whereas those of MWCNTs grown at 750 °C were in the range of 200-300 nm. The remarkable variation in the diameters could be found between the Ni thin layers with 2.5 and 5 nm thicknesses. In the case of 2.5 nm thickness, the average diameter of as-grown MWCNTs was smaller than 50 nm even though they showed a broad diameter distribution, while, in the case of the thicknesses higher than 5 nm, the average diameters of as-grown MWCNTs were in the range of 200 and 300 nm. According to those results, we assumed that the temperature range from 700 to 750 °C was critical enough to affect the diameters of the as-grown MWCNTs.

Table VI. The variation of morphology of 3D MWCNTs on Cu obtained from the different growth conditions.

<div> <div>Growth condition</div> <div>Thickness of Ni (nm)</div> </div>	700 °C for 30 minutes	700 °C for 50 minutes	750 °C for 30 minutes	750 °C for 50 minutes
2.5
5
7.5
10

Moreover, we chose the three different MWCNT images and referred to each one as S-CNT (T) (The smaller diameter CNTs grown at Ni 10 nm thickness and 725 °C temperature), S-CNT (C) (The smaller diameter CNTs grown at Ni 2.5 nm thickness and 750 °C temperature), and L-CNT (The larger diameter CNTs grown at Ni 10 nm thickness and 750 °C temperature), respectively. In addition, from the HRTEM images illustrated in Figure 26, we could find that the average diameters of S-CNT (C), S-CNT (T), and L-CNT were 21 nm, 32 nm, and 279 nm, respectively. We would like to mention that the blur image indicated by the red arrow represents

the depth structure of MWCNT network with the higher density (see the upper image of Figure 26(b)). Since their internal structures were composed of the lower-ordered graphene layer stacking, they were considered as turbostratic structure. However, the internal structure of S-CNT (C) was similar to herringbone structure. Recently, Y.Y. Wang et al. demonstrated the effect of the thickness of Fe catalytic thin layer (from 0.3 to 20 nm) deposited on SiO₂/Si(100) substrate for the morphological variation in the internal structure of MWCNTs (see Figure 27) [80]. Compared to their results, our cases did not show the distinguishable structural variation as a function of the thickness of catalytic Ni thin layer.

Figure 26. HRTEM images of the morphology of 3D MWCNTs synthesized at the different growth conditions designated by (a) S-CNT (C), (b) S-CNT (H), and (c) L-CNT

Figure 27. (a) Plot of the CNT film growth rate vs. Fe thickness where three regions (I, II, and III) with different internal structures are observed. (b) A schematic of the internal structure transition from hollow to bamboolike [80]

3.3 Button Cell Assembly Under Ar Gas Flow Glove Box

The coin type of cell assembly is crucial for the performance of Li-ion batteries. As seen in Figure 28(b), the components of coin cell assembly are electrode materials, Li metal, stainless steel (SS) caps, separator, spring and spacer. The very low oxygen and humidity are less than 1 ppm level, which are automatically controlled in the glove box by the combined functions of evacuation and Ar gas flowing. Figure 28 shows photograph images of the glove box installed in Nanomaterials and Nanodevice Lab at Hanyang University in Korea and button cell assembly components. Electrode materials are placed on the stainless steel bottom cap and separator is placed on the electrode. Li metal is put on the separator, followed by putting the spring and spacer on the Li metal. Finally, SS top cap is covered and coin cell assembly is completed by pressing a crimper (CR 2032, Honsen Corp.).

Figure 28. Photograph images of (a) a glove box for LIB button cell assembly and (b) components of the button cell

3.4 Battery Performance Test

The charge-discharge tests of the cells were performed in TOSCAT 3100U and MACCOR multi-channel battery testing units, at a constant temperature of 30 °C and room temperature, in galvanostatic (constant current density) mode. The cells were cycled in the voltage range 3.0 - 0.01 V, recording a current value in each 10 mV step, at a slow rate (0.1 C) during the initial formation process and at various C-rates in the following cycles.

3.5. Analytical Techniques

Morphology and structural properties of the prepared anode structures were carefully investigated using field emission scanning electron microscopes (FESEM) (JEOL, JSM-7000F),

an energy dispersive spectroscope (EDS) (Thermo Electron Corporation, NORAN System SIX), a Raman spectrometer (laser source : Ar⁺ laser with $\lambda = 514$ nm, 33 mW power) and micro Raman system (UniG2D, Korea; see Figure 29) (laser source : low noise 532 nm Diode-pumped solid-state (DPSS) laser (3.7 mW); software : iDus CCD detector) and a field emission transmission electron microscope (FETEM) (FEI, TECHNAI F20).

Figure 29. A photograph of micro Raman system

CHAPTER 4.

3-DIMENSIONAL CARBON NANOTUBE FOR LI-ION BATTERY ANODE

4.1 Introduction

Carbon nanotubes (CNTs) have been widely researched into the application of LIB anode materials due to high surface area, short diffusion length of Li^+ ions, and high electrical conductivity [54]. From our team, previous researches showed excellent performance of MWCNT-based binder-free anodes in terms of the high specific capacity, excellent rate capability, and almost no capacity degradation during a prolong cycling [34-35]. However, nanostructured carbon materials are known as low-density materials, which tend to show low volumetric capacity and low volumetric energy and power density. Hence, increase in loading density of MWCNTs as active materials should be most significantly dealt with in the practical application. Very recently, Y. Gogotsi et al. argued that carbon-based nanomaterials have a critical limitation with respect to the low area mass density [36]. As a result, even the high gravimetric energy density may bring about scale-up issues and may not be useful for the potential application to the development of electric vehicles (EVs).

To address this issue, we propose a novel architecture of 3D Cu current collector, which can function as increasing surface area to accommodate larger area or volumetric mass density of MWCNTs over the uniformly arrayed patterns in the 3D structure; thus, resulting in higher specific capacity and C-rate capability. To our best knowledge, much work has been done to enhance electrochemical performance of Li-ion batteries and supercapacitors by using 3D structured current collectors, such as carbon papers [37], a self-assembled 3D bicontinuous nanoarchitecture [38], aluminum nanorods [39], and nanoporous nickel [40]. Z. Yan et al. demonstrated that a self-assembled 3D bicontinuous nanoarchitecture could realize not only the

high volume fraction of nanostructured electrolytically active materials (NiOOH/Nickel and MnO₂ cathodes) but also the efficient ion and electron transport [38]. Additionally, atomic layer deposition (ALD) coated TiO₂ anodes on 3D aluminum nanorod current collectors showed a tenfold increase in the theoretical area capacity (0.0112 mAhcm⁻²), compared to that from the same anodes on 2D flat aluminum plate and high-rate capability (the capacity ratios at 10C/0.5C and 20C/0.5C of the 3D anode were 0.4 and 0.35, respectively.) [39].

Currently, the various types of hybrid anode structures have been proposed and synthesized to expect the synergetic combination of two different types of nanomaterials for higher electrochemical performance. Among the strong candidates of anode materials in the preferable combinations, an MWCNTs/Si hybrid structure can be significantly considered due to excellent mechanical resilience of MWCNTs against large volume expansion/constriction of Si during the lithiation/delithiation process and good bonding strength between MWCNTs and Si. There have been several reports on MWCNTs/Si composite structures; however, data employing either the SiH₄ CVD method [41] or sputter deposition [42] were particularly used for this dissertation.

In this chapter, we present a novel concept 3D anode system, comprised of MWCNTs directly grown on 3D Cu mesh using a catalytic thermal CVD method [81]. Electrochemical performances of the 3D anode structure are compared with those of MWCNTs directly grown on 2D Cu foil. Furthermore, enhanced electrochemical properties of a-Si/MWCNTs hybrid structure, synthesized on 3D Cu mesh using CVD and sputtering deposition methods, are presented. Finally, we discuss the morphology and structure of as-grown MWCNTs and a-Si/MWCNTs hybrid anode structures and their role in the electrochemical performance.

4.2 Results and Discussion

4.2.1 Experimental Details

A Cu mesh (TWP Inc.) with average dimensions of 50 μm thickness and 65 μm hole size was prepared. In parallel, a 50 μm thick pure Cu foil (Nimrod Hall Copper, 99.9 % purity) was also employed. Both types of samples were used as substrates for depositing Ti (underlayer)/Ni (catalyst) thin film through an RF and DC magnetron sputtering system. These Ti/Ni thin film deposited samples were cut to 14 mm diameter disc shape for 2032 button cell assembly, before inserting into a thermal CVD system for direct MWCNT growth. During CVD, samples were heated very rapidly, under an inert Ar gas environment, to the growth temperature of 750 $^{\circ}\text{C}$, and MWCNT growth began with flow of a mixture of ethylene (C_2H_4) and hydrogen (H_2) gas (1:2 volume ratio) in the chamber. After 50 minutes of growth, the samples were cooled to room temperature within the furnace under an Ar gas envelope. Amorphous Si (a-Si) was deposited further on the as-grown MWCNT samples using the sputtering system with the incorporation of Ti adhesion layer in order to enhance bonding strength between a-Si and MWCNTs. Weights of samples were measured before and after CVD growth to exactly identify weights of the active materials (i.e. MWCNTs and a-Si thin layer).

Morphology and structural properties of the prepared anode structures were carefully investigated using field emission scanning electron microscopes (FESEM) (JEOL, JSM-7000F), an energy dispersive spectroscopy (EDS) (Thermo Electron Corporation, NORAN System SIX), a Raman spectrometer (Ar^+ laser with $\lambda = 514 \text{ nm}$, 33 mW power) and a field emission transmission electron microscope (FETEM) (FEI, TECHNAI F20). Electrochemical performance for these anodic materials was conducted in a typical coin cell (half cell). The cells were assembled in a CR2032 press. The complete cell assembly was carried out in an argon glovebox under extremely low levels of oxygen and humidity (both individually $< 0.1 \text{ ppm}$). A pure Li

(purity, 99.9 %) metal foil (150 μm thickness) was used as both the reference electrode and counter electrode, while the MWCNTs on 3D Cu mesh, the MWCNTs on 2D Cu foil and the a-Si/MWCNTs composite on 3D Cu mesh were used as the working electrodes. All the coin cells employed a solution 1.0 M LiPF_6 in EC-DEC (ethylene carbonate : diethyl carbonate, 1:1 in volume ratio) as the electrolyte and a typical polypropylene-polyethylene material (Celgard 3401) as the separator. The charge-discharge tests of the cells were performed in TOSCAT 3100U multi-channel battery testing unit, at a constant temperature of 30 $^{\circ}\text{C}$, in galvanostatic (constant current density) mode. The cells were cycled in the voltage range 3.0 - 0.01 V, recording a current value in each 10 mV step, at a slow rate (0.1 C) during the initial formation process and at various C-rates in the following cycles.

4.2.2 Theoretical Calculation of the Surface Area of 3D Cu Mesh

The purpose to introduce 3D Cu mesh as current collector was to increase in surface area for the growth of MWCNTs, thus leading to greater amount of Li^+ intake into them, as compared to 2D Cu foil. The calculation procedure of the theoretical surface area of 3D Cu mesh consists of following steps.

Step 1.

Making a real Cu mesh simplifies the geometry arrayed by numerous rectangular cuboid holes separated by regular and repetitive rectangular barriers, as shown in Figure 30.

Figure 30. (a) A real SEM image of a 3D Cu mesh and the schematic diagrams (not to scale) to compare (b) the similar geometry of a 3D Cu mesh with (c) the simplified geometry of a 3D Cu mesh.

Next, determine an equivalent rectangular cuboid out of a right circular cylinder.

$$\pi r^2 = L^2 \dots\dots(1)$$

Bare Cu wires (A single wire has a diameter of 50.8 μm .) are interlaced to form a 3D Cu mesh (TWP, Inc.)

Substituting $r = 25.4 \mu\text{m}$ into the equation (1), we can obtain $L = 45.02 \mu\text{m}$.

Step 2.

Imagine a Cu mesh with 4 holes. As-purchased Cu mesh has a single hole area with 76 μm length (TWP, Inc.).

Figure 31. Schematic plane view of a 3D Cu mesh with 4 holes

Decide the point O as an original point and place the point at the top left corner of the Cu mesh with 2 cm by 2 cm area. From the arrangement, the number of arrayed unit cells with length L in the whole Cu mesh can be calculated as follows:

$$\frac{20000}{(L + 45.02)} \times \frac{20000}{(L + 45.02)} \dots\dots (2)$$

Step 3.

Figure 32. Schematic diagram of 3-dimensional view of a unit cell of a 3D Cu mesh

Formula for the calculation of the surface area of the unit cell has three main parts that are summed together as follows:

1. The surface area of the top planes

$$\frac{[\{(L + 45.02)^2 - L^2\} \times 2] \times \left(\frac{20000}{L + 45.02}\right)^2}{2} \dots\dots (3)$$

2. The surface area of the lateral inside planes

$$\{(L \times T) \times 4\} \times \left(\frac{20000}{L + 45.02}\right)^2 \dots\dots (4)$$

3. The surface area of the lateral outside cells should not be considered for the calculation since they are enclosed by their neighbor cells.

The formula to calculate the total surface area of the 3D Cu mesh is then obtained by summing overall the surface area mentioned above, as follows:

$$\frac{[\{(L + 45.02)^2 - L^2\} \times 2] \times \left(\frac{20000}{L + 45.02}\right)^2}{2} + \{(L \times T) \times 4\} \times \left(\frac{20000}{L + 45.02}\right)^2 \dots\dots (5)$$

Figure 33 shows the variation of the surface area and its ratio of the 3D Cu mesh to the 2D Cu foil as a function of the thickness (T) and the size of holes (L) of the 3D Cu mesh.

Figure 33. The surface area and its increment of the 3D Cu mesh and the 2D Cu foil as a function of different thickness and hole sizes.

3D Cu mesh was an interlaced structure of numerous Cu wires (Figure 30(a) and Figure 30(b)). Simple geometrical model was followed to calculate the total surface area of this 3D structure, since the calculation of the actual surface area of the assembled 3D Cu mesh was very difficult. For easier calculation, the cylindrical Cu wires were simplified to rectangular wires of equivalent surface area, creating a cuboid array (Figure 30(c)). In this study, MWCNTs were synthesized on the top and lateral surface areas of the 3D Cu mesh only, hence only these areas were considered for calculation.

Figure 34(a) was a schematic view of an anode stack built up of 4 layers of MWCNTs on 3D Cu mesh. As a real example, we implemented an anode stack system using 9 individual MWCNTs on 3D Cu mesh, in which MWCNTs were coated over the entire area of the Cu

meshes as illustrated in Figure 34(b). The assembled anodes were physically bonded by adhesion force between the entangled MWCNTs. This phenomenon may be thought of as being in some way analogous to “Velcro” effect of scales on wool fibers [82]. A simple geometrical relationship was established to calculate the total surface area of 3D Cu mesh and 2D Cu foil (no hole). Variation of the surface ratio of 3D Cu mesh to 2D Cu foil as a function of the thickness (T) and the size of holes (L) of 3D Cu mesh is presented in Figure 34(c) (The detail calculation procedure is mentioned above.). Surface area increased with the thickness of the structure, though its relation with hole size was not straight forward owing to contribution from a fixed Cu wire diameter. It may be recalled here that the present study used a Cu mesh with its dimension 50 μm thickness and 65 μm hole size, which showed surface area improvement (almost 60%) as compared to 2D Cu foil. Empirically, the average weight of MWCNTs on 3D Cu mesh was 4.37 mg for a cell with 14 mm diameter and 50 μm thickness dimension, which represented solid loading increase by 400%. Thus, it was found that the theoretical calculation was inconsistent with the experimental results since it did not include the influence of control parameters on the properties of MWCNTs, such as their diameters, lengths and densities during the CVD growth. From an anode system assembled using 9 individual MWCNTs on 3D Cu mesh (The size of a cell is 15 mm diameter and 50 μm thickness.), the average maximum loading amount and packing density of MWCNTs were higher than 50 mg and 0.248 g/cm^3 , respectively. The weight of stacked anodes increased proportionally with additional anodes, which is in a good agreement with the calculation results.

Figure 34. (a) A schematic model of an anode stack assembled using 4 numbers of converted uniform stacking cuboid arrays from the geometry of a real 3D Cu mesh (The bottom right inset shows a unit cell of the cuboid arrays.), (b) SEM images exhibiting a cross-section perpendicular to the anode system stacked by 9 individual MWCNTs on 3D Cu mesh and highly entangled structures of MWCNTs, (c) The surface area and its increment of the 3D Cu mesh and the 2D Cu foil and the average real weight of MWCNTs as a function of different thickness and hole sizes (The inset illustrates a unit cell of the 3D Cu mesh with its dimension.).

4.2.3 Morphology and Structural Properties of MWCNTs and a-Si/MWCNTs on 3D Cu Mesh

Unique 3D structure of the proposed anode is expected to influence the electrochemical performance. Structural characterization, involving SEM and Raman spectroscopic analysis, has been conducted on these 3D anodes (See Figure 35). As presented in Figure 35(a), MWCNTs were homogeneously and densely grown over the whole top and lateral Cu mesh area. In addition, the high magnification SEM image showed the randomly entangled MWCNTs with their length around 30 μm and diameter in the range of 200 - 300 nm (See Figure 35(b)). Compared to the 2D Cu foil, the surface areas of the Cu wires surrounding the hole spaces could be available sites for the MWCNT growth, which is structural advantage of the 3D Cu mesh to increase the weight of the MWCNTs as active materials. In Figure 35(c), the sketch of the cross section view of MWCNTs grown on a single Cu wire exhibited the densely grown larger diameter MWCNTs on the top surface area and relatively smaller diameter MWCNTs on the lateral side area. Along with the structural characteristic, the interfacial control between active material and current collector significantly influences the electrochemical performance of the anode system. It is highlighted that the strong bonding between MWCNTs and Cu making it possible to directly grow MWCNTs on Cu mainly stemmed from TiC underlayer [34, 66]. The TiC underlayer was formed by the reaction of Ti thin film sputter deposited onto 3D Cu mesh with carbon precursor gas at high temperature about 750 $^{\circ}\text{C}$ during CVD processing. High ratio of I_D/I_G (around 1) in Raman spectra (Figure 35(e)) of the MWCNT structure also revealed high defect density in the structure. It is reported that the MWCNTs containing more defects showed the better electrochemical performance since the higher presence of defects provided with more available sites for Li^+ ion intakes into the MWCNTs structure and shortened the diffusion length of Li^+ ion [83-84]. MWCNTs possessing more defects, generated by mechanical breakage and chemical etching, resulted in an increase in specific capacity compared to untreated MWCNTs. In the case of

Figure 35. Morphology and structure of the proposed anode systems. (a) A plane view of SEM image showing the MWCNTs covered on the 3D Cu mesh, (b) The threadlike grass structures of MWCNTs on the 3D Cu mesh with their diameter in the range of 200 - 300 nm, (c) Schematic diagram (not to scale) of the geometry of the MWCNTs grown on the 3D Cu mesh and the a-Si deposited MWCNTs structure on the 3D Cu mesh, (d) EDS elemental analysis of the a-Si/MWCNTs hybrid structure in the linearly selected area across the SEM image, (e) Raman spectroscopic response indicating high defect density of MWCNTs according to I_D/I_G ratio around 1 and the amorphous Si peak at around 500 cm^{-1} in the a-Si/MWCNTs.

a-Si/MWCNTs hybrid structure, the broad intensity peak around 500 cm^{-1} (in Raman spectra) showed amorphous Si [85]. It was subsequently confirmed from the EDS analysis in the linearly selected area across the SEM image as shown in Figure 35(d) that Si was deposited on some portion of the surface of the MWCNTs. The line profile denoting Si K distinguishably appeared, demonstrating the presence of a-Si deposited layer.

4.2.4 Electrochemical Performances of the MWCNT-Based Anode Systems

4.2.4.1 Charge/Discharge Capacities

Electrochemical performance tests were conducted on these anode structures and the results were presented in Figure 36. First charge-discharge curves for all the anode systems were presented in Figure 36(a). The button cells were charged/discharged in a galvanostatic mode between 0.01 and 3 V, at C-rate of 0.1 C (specific current 38 mAhg^{-1}) determined by theoretical specific capacity of graphite (372 mAhg^{-1}). In the case of MWCNTs on 3D Cu mesh electrodes, several samples with different solid loading of MWCNTs were measured under the same condition and showed average discharge capacity 474 mAhg^{-1} , $\text{LiC}_{4.7}$. In Figure 36(a), all the discharge curves exhibited a plateau in the voltage range 0.75 - 0.9 V. Such plateau was found in most graphite or CNT-based anodes and stemmed from the decomposition of electrolyte and the formation of solid electrolyte interphase (SEI) on the carbonaceous anode materials [14, 86]. Recently, D. Aurbach reviewed extensive studies on the composition of the SEI layer formed on lithiated carbon and lithiated transition metal oxide electrodes in a wide variety of organic electrolyte solutions [55]. These studies employed spectroscopic measurements (Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Analysis (EDAX)). In our study, a fluorine-rich region in the SEI layer was

Figure 36. Electrochemical performance of the anode structures of as-grown MWCNTs on 3D Cu mesh, MWCNTs on 2D Cu foil and a-Si/MWCNTs core-shell composite on 3D Cu mesh. Part (a); first charge-discharge cycle at 0.1 C-rate, (b) comparison of the cycling stability of the different

anode structures, (c) Coulombic efficiency at 1 C-rate; (d) the variation of reversible capacities at different C-rates; (e) Scanning Transmission Electron Microscopy (STEM) and High-Angle Annular Dark Field (HAADF) cross-sectional view of a single MWCNT and the intensity profile computed along the red line displayed in the cross-sectional view.

discovered by using a Scanning Transmission Electron Microscopy (STEM) and High-Angle Annular Dark Field (HAADF) cross-sectional view of a single MWCNT, and the intensity profile computed along the red line is displayed in the image (see Figure 36(e)). We assumed that the fluorine rich region was created by the following reaction scheme:

Note that equations (6) – (8) do not offer the exact stoichiometry, but instead offer the basic reactions. However, a phosphorus-rich region was not identified from the STEM-HAADF technique.

Based on the similar first discharge curves of the MWCNT and the a-Si/MWCNT electrodes, it was implied that the MWCNTs mainly controlled the electrochemical properties in both anode structures since the major weight (above 99% weight ratio) of the structure came from the MWCNTs. However, the effects of a-Si incorporation on the electrochemical performance were investigated by the first charge curves of the anodes. The average specific charge capacities of the MWCNT and the a-Si/MWCNT electrodes were 299 mAhg⁻¹ and 345 mAhg⁻¹ (almost 16%

improvement), respectively, which were obtained from three different batches of each of the LIB cells comprising the three different anode systems. In addition, the Coulombic efficiency of the a-Si/MWCNTs was 67%, which was approximately 4% higher than that of the MWCNTs. The relatively higher irreversible capacity at the first charge-discharge cycle is considered a critical limitation of carbonaceous anode materials, and the capacity loss may be mainly associated with solid electrolyte interphase (SEI) formation or a permanent alloy formation [86]. Another possible reason involved the insertion of lithium ions into defect sites (e.g., microcavities) residing in the MWCNTs and their entangled structures [87]. Lithium ions inserted into the defect regions at the first discharge process might be trapped, and it might not be completely extracted during the charge process. Lithium oxide formation at higher voltage could also be another reason for the initial capacity loss [26]. However, Figure 36(a) showed that most Li insertion processes proceeded below 1.5V (versus Li/Li⁺) so that the possibility of charge consumption due to lithium oxide formation may be excluded, in the present case. Higher values from the a-Si/MWCNTs indicated the a-Si thin layer could play a role in maintaining the stability of SEI formation [35]. On the contrary, the first discharge curves of all the specimens of the MWCNTs on 2D Cu foil represented the average specific discharge capacity 323 mAhg⁻¹, LiC_{6.9}. The average capacity value was more than three times lower than that of our previous result [34]. It was speculated that the significant difference was due to the different morphology of MWCNTs (average diameter 80 nm, which was thinner than that of the current MWCNTs). At higher growth temperatures, the size of the catalytic Ni islands became larger on account of their more facile diffusion [88]. With respect to major electrochemically active sites being on and near the surface of MWCNTs [34], the thicker MWCNTs have less active surface area per mass available for participating in electrochemical reactions as compared to the thinner MWCNTs, thereby resulting in the lower specific capacity. During the initial cycle, the MWCNTs on 3D Cu mesh offered a 47% higher average specific capacity compared to that of the MWCNTs on 2D Cu foil. It may be noted here

that this specific capacity enhancement is close to 60% of the surface area enhancement. Compared to the MWCNTs on 3D Cu anodes, the a-Si deposited MWCNT anodes offered the higher average specific discharge capacity 517 mAhg^{-1} , $\text{LiC}_{4.3}$. This enhancement could be related to the presence of a-Si thin layer with its high specific capacity on the MWCNTs. It was observed that the weight of the deposited a-Si was lower than 1% of that of the MWCNTs; therefore, the a-Si thin layer did not have any major contribution except slight increase in the overall specific capacity of the anode, unlike the previous results from Si nanotubes [15] and Si nanowires [16].

4.2.4.2 Cycling Stability

Cycling stability tests are essential to prove electrochemical performance of the anodes at long cycling operations in the real application. Figure 36(b) illustrates a comparison of the cycling stabilities obtained from the three different kinds of anode systems up to 50 cycles at 1 C-rate (current density 372 mAg^{-1}). Although the cycling performances were conducted by single measurements of each of the three different anode systems, they could well describe the characterization of all three batch samples in each group of anodes. The primary rationale behind the hypothesis may be mentioned as follows: an LIB anode cell, exhibiting a good electrochemical performance attained from a primary charge-discharge cycle, generally shows good LIB performances in terms of a cycling stability and a C-rate capability over the prolonged cycles. In the case of the MWCNTs on 3D Cu mesh electrode, the reversible capacity slightly increased from 226 mAhg^{-1} at the first cycle to 258 mAhg^{-1} at the 39th cycle and then gradually faded to 254 mAhg^{-1} until the 50th cycle. Such a trend of increase in capacity over the whole cycles is inconsistent with previous results from the constant capacity of MWCNTs [34-35]. It was speculated that the continuous charge-discharge process led to the creation of more surface area on the densely entangled MWCNT network structure. We also investigated whether such an

activation process was due to more defects in the structures of MWCNTs induced by the charge-discharge process.

According to the SEM images presented in Figure 37(a) and (b), it was not evident that severe defects or structural damages appeared in the 150 cycled anode system and just one discharged anode system. HRTEM images revealed that for both anode systems, the structural integrity of graphene layers still remained with the shallow amorphous second phase region on the edge of the MWCNTs, as shown in Figure 37(c) and (d). In addition, it was pointed out that there was no appreciable volume variation during lithiation and delithiation. No clear evidence of diameter change was observed between the as-grown MWCNTs and the MWCNTs subjected to 150 charge-discharge cycles (Figure 35(b) and 37(a)). This observation is in agreement with small volume changes of graphitic carbon upon lithium insertion and extraction (typically LiC_6 , around 12%) [89]. In the same manner, it was confirmed that the specific capacity of the a-Si/MWCNTs on 3D Cu was gradually increased.

Along with the electrochemical activation process of MWCNTs, the result could reveal the effect of capacity improvement with additionally incorporated a-Si to take more Li^+ ion intakes (almost 10 % enhancement of the reversible capacity). Furthermore, the Si-C bonding at the interface between a-Si and MWCNTs was strong enough to avoid peeling off of the a-Si layer during the cycling test. It was highlighted that MWCNTs and a-Si/MWCNTs grown on 3D Cu mesh showed good cycling stability without severe capacity degradation. However, for the MWCNTs on 2D Cu foil, the average reversible capacity 163 mAhg^{-1} was kept constant until the number of 50 cycles. It should be noted that the larger reversible capacity of the 3D MWCNTs was presumably due to their large surface area to accommodate more Li^+ ion intercalation.

Nevertheless, we found that some kinks appeared at the cycle No. 1, 21, 38 and 39. The reasons for the kinks at each point can be explained as follows: in the case of No. 1, since the

anode is composed of 3D MWCNTs, the initial lithium insertions are taking place on the top surface of MWCNTs, but later cycles undergo deeper lithium insertions; hence, the capacity is increasing during the later cycles. In the case of No. 21, the actual reason for the kink is because the person, who took measurements, stopped after 20 cycles, and then, he continued the measurements from the 21st cycle. Once he stopped the measurements, the cell came to the chemical equilibrium stage; therefore, when he restarted the measurements, the cell did not start as before, but rather, it started at a low voltage. In the case of No. 38, the lithium insertion might have been hindered by SEI layers so that the capacity slightly decreased. Due to the decreased capacity, lithium ions might have again found free-sites to be inserted, resulting in the increase in capacity. The phenomenon solely stemmed from stabilization/finding deeper sites due to the 3D structure of our anode systems. In the case of No. 39, owing to new sites for lithium insertion into the 3D structure, capacity was slightly high, and then the capacity decreased due to chemical instability.

In terms of the reversibility of charge-discharge process, the Coulombic efficiency of the MWCNTs on 3D Cu mesh was more than 98% after the initial 4 cycles at 1.0 C-rate and then increased to 99% after 22 cycles according to the result shown in Figure 36(c). Such reversibility was ascribed to the sufficient supply of Li^+ ions from Li metal foil used as the reference electrode and counter electrode in the button cell.

(a)

(b)

(c)

(d)

Figure 37. Plane view SEM images of (a) the MWCNTs on 3D Cu mesh anodes after 150 cycling at 1 C-rate and (b) the MWCNTs after only 1 discharge cycling at the same C-rate. HRTEM images of (c) the 150 cycled one and (d) the 1 discharge cycled one.

4.2.4.3 Rate Capability

Rate capability tests are also crucial to prove electrochemical performance of the anodes at higher charge-discharge rate operations. Figure 36(d) showed the rate capability of the proposed anodes. The discharge capacity of the MWCNTs on 3D Cu mesh was almost constant around 300 mAhg^{-1} until reaching 1 C-rate (372 mAhg^{-1}), and then, decreased to 283 mAhg^{-1} at 3 C-rate ($1,116 \text{ mAhg}^{-1}$) and further to 250 mAhg^{-1} at 5 C-rate ($1,860 \text{ mAhg}^{-1}$). It may be highlighted that discharge capacity slightly increased with C-rate from 0.1 C to 1 C and the phenomenon could be attributed to the electrochemical activation process of MWCNTs during cycling as mentioned above. At higher C-rates (e.g., 3 C and 5 C), Li^+ ions were inserted and extracted into and from the only surface regions of the forest-like MWCNT structure due to the limitation of diffusion length of Li^+ ions. Another interesting observation was slight increase in specific capacity from 283 mAhg^{-1} at the 1st cycle to 320 mAhg^{-1} at the 22nd cycle at the same 0.1 C (38 mAhg^{-1}) rate. It was again confirmed that higher number of cycles during C-rate tests could be a reason to effectively carry out electrochemical activation process in the MWCNT structures. On the contrary, the MWCNTs on 2D Cu foil electrode showed a typical staircase type decreasing capacity behavior till the tested limit of 5 C-rate. The direct comparison revealed the higher C-rate capability of the MWCNTs on 3D Cu mesh electrode, as compared to the MWCNTs on 2D Cu foil. In particular, at 5 C, the average specific discharge capacity of the MWCNTs on 3D Cu mesh was 249 mAhg^{-1} (14 % increase), whereas that of the MWCNTs on 2D Cu foil was 218 mAhg^{-1} . The result could be strongly associated with the higher surface area for Li^+ ion intercalation due to approximately four times higher solid loading of MWCNTs on 3D Cu mesh. Furthermore, the higher C-rate capability is significantly attributed to the strong bonding and the lower electric resistance between Cu and MWCNTs, through TiC interfacial layer [69, 72]. Moreover, at 5 C, the average capacity of the a-Si/MWCNTs on 3D Cu mesh electrode was 334 mAhg^{-1} (34 % enhancement), while that of the MWCNTs on 3D Cu mesh was 249 mAhg^{-1} . In addition, the average capacity

ratios at 5 C/0.1 C of the MWCNTs on 3D Cu mesh and the MWCNTs on 2D Cu foil were 0.86 and 0.8, respectively, whereas the ratio of the a-Si/MWCNTs on 3D Cu mesh was around 0.93. According to the better performances, it was proved that a-Si thin layer coating on MWCNTs could play an important role in the enhancement of C-rate capability.

4.3 Conclusion

A novel 3D MWCNTs on Cu current collectors as an anode of LIB was developed. The 3D anodes showed higher specific capacity, cycling stability and C-rate efficiency, as compared to those of the MWCNTs on 2D Cu foil anodes. The better performances of the 3D anodes were attributed to higher average solid loading of MWCNTs, which was four times higher than that of the 2D anodes. The addition of the a-Si onto the 3D MWCNTs/Cu showed the further enhancement of electrochemical properties.

CHAPTER 5.

3D ANODE STACK ASSEMBLED BY MULTIWALL CARBON NANOTUBES (MWCNTS) FOR LI-ION BATTERY ANODE

5.1 Introduction

It was very recently argued whether most carbon nanomaterial-based LIB anodes would or would not be practically available for their next generation EV application [36]. One of the reasons behind that could be relevant to their lower volumetric specific energy and power densities regardless of their higher gravimetric energy and power densities. To counter the issue, we would like to propose a similar novel approach, which is stacking of a number of individual free-standing 3D MWCNT mesh structures suitable for remarkable increase in solid loading of MWCNTs as active materials. The stacking method is simply placing one free-standing 3D MWCNT mesh structure formed by chemically etching away 3D Cu mesh on top of another, one by one, resulting in an increase of active 3D MWCNT materials' weight and volume in the anode stacks. The 3D free-standing MWCNT mesh structures contained approximately 35% of void area that inhibit crack propagation, which can otherwise induce severe mechanical fracture in the structures. Thus, structural integrity of the 3D free-standing MWCNT mesh structures could remain while one handles them during their etching process from Cu mesh or stacking of the 3D free-standing MWCNT mesh structures by pressing them. The thread-like MWCNTs are randomly connected, enhancing the self-adhesion of a whole anode for the higher electric conductivity and robust structural integrity in the overall anode stacks. Furthermore, to enhance the bonding strength of individual MWCNT layers and their volumetric mass loading density, we use a polyvinylidene fluoride (PVDF)-based binder solution.

In this chapter, we would like to present the unique preparation methods of the anode stack by using free-standing MWCNTs and their structural properties through some essential analytical techniques, including scanning electron microscopy (SEM), electron dispersion spectroscopy (EDS) and Raman spectroscopy. In addition, Li-ion coin cells have been assembled by using the multi-stacked MWCNT anodes and their electrochemical performances have been discussed with respect to loading amount. Furthermore, we propose a novel anode stack prepared by using the binder solution and pressing at high pressure and temperature to enhance the LIB performance and deal with the correlation between the structural and electrochemical properties of the new proposed anode stack.

5.2 Results and Discussion

5.2.1 Experimental Details

MWCNT stacks composed of multiple layers of 3D free-standing MWCNT mesh structures have been prepared with a combination of chemical vapor deposition (CVD) techniques through a two-step approach and formation of 3D free-standing MWCNT meshes after etching process of Cu mesh (50 μm thickness and 65 μm hole size, TWP Inc.) substrates, as shown in Figure 38(a). Samples of 3D MWCNTs on Cu mesh were first synthesized by deposition of Ti as barrier layer to carbon diffusion into Cu; Ni as catalytic thin layer for MWCNT growth onto a Cu mesh using an RF and DC magnetron sputtering system, and subsequently followed by the CVD growth of MWCNTs. In order to prepare CVD grown 3D MWCNTs on Cu mesh, the Ti/Ni sputter deposited Cu meshes were placed in a tubular furnace and rapidly heated to 750 $^{\circ}\text{C}$ in argon flow. And then, at 750 $^{\circ}\text{C}$, a mixture of H_2 and C_2H_4 (1 : 2 volume ratio of H_2 to C_2H_4) was flowed into the furnace for 50 minutes. Finally, the furnace was cooled down to room temperature in an Ar

environment. Weights of each sample before and after CVD growth were measured for net weight of MWCNTs as active materials being applied to LIB performance tests. After 4~5 hours of Cu etching process, Cu mesh was completely dissolved into the concentrated ferric chloride (FeCl₃) solution (Transene Company, Inc.), and the solution left 3D free-standing MWCNT mesh structures. One of the reactions for etching of copper with ferric chloride is as follows [90]:

The 3D free-standing MWCNTs were thoroughly washed with de-ionized water and dried in vacuum oven at 120 °C for at least 5 hours. 5 to 8 individual 3D free-standing MWCNT meshes were placed one by one and pressed using a precision disc cutter (MTI Corp.), resulting in a whole structure of 3D MWCNT-based anode stack with its dimension of 14 mm diameter disk shape. A Cu mesh current collector was placed at the bottom side of the MWCNT stack for its efficient electron charge transfer. Furthermore, to prepare a highly dense anode stack, we introduced a binder solution composed of Polyvinylidene fluoride (PVDF, Sigma-Aldrich) and carbon nanoparticles (Sigma-Aldrich) (7 : 3 weight ratio) dissolved into N Methyl 2-pyrrolidone (NMP, Sigma-Aldrich) solvent. The binder solution was dropped and spread onto each free-standing MWCNT layer one by one, consequently forming five layered anode stacks. The as-prepared anode stack samples were dried under the step-up temperature profile in vacuum oven at 50 °C for 1 hour, 60 °C for 40 minutes, and 80 °C for 3 hours. The relative lower drying temperatures were selected to avoid any oxidation of the Cu current collector placed at the bottom side of the samples. The subsequent compression of the samples created anode stacks with the areal mass density of 9 mg/cm² and the volumetric mass density of 1.25 g/cm³.

The surface morphology of as-grown MWCNTs was observed or measured using a field emission scanning electron microscope (FESEM) (JEOL, JSM-7000F), an energy dispersive

spectroscopy (EDS) (Thermo Electron Corporation, NORAN System SIX), a Raman spectrometer (Ar^+ laser with $\lambda = 514 \text{ nm}$, 33 mW power) and a field emission transmission electron microscope (FETEM) (FEI, TECHNAI F20). For the electrochemical performance tests, a coin type (CR 2032) of half-cell assembly was carried out in an argon filled glovebox under

Figure 38. Process flow for anode stack system from an individual 3D MWCNTs on Cu mesh current collector to 3D free-standing MWCNT anode stack system. (a) As-received commercially available 3D Cu mesh, (b) CVD grown 3D MWCNTs on the surface of the Cu mesh, (c) Chemical etching process of the Cu mesh via FeCl_3 etching solution, (d) 3D free-standing

MWCNT mesh structure after the etching process, (e) Fabrication of anode stack consisted of multiple layers of 3D free-standing MWCNT meshes by finally pressing them together.

extremely low level of humidity (< 1 ppm). The MWCNT stack was used as working electrode, whereas Li metal foil as both counter and reference electrodes. 1 M solution of LiPF_6 salt in 1:1 (v/v) mixture solvent of ethylene carbonate (EC) and dimethylene carbonate (DMC) was used as electrolyte. Typical polypropylene (PP) material (Separator 2400) was used as separator. The cell was finally assembled by using CR 2032 coin-cell crimping tool (Honsen Corp.). The charge and discharge tests of the assembled cells were performed in a multi-channel battery testing unit (MACCOR) at a room temperature in galvanostatic mode (constant current density). The cells were cycled in the voltage range 3.0 to 0.01V, recording a current value in each 10 mV step, at a slower C-rate (e.g., 0.05C) during the initial formation process and at a faster rate (e.g., 0.5C) in the following cycles.

5.2.2 Morphology and Structural Properties of MWCNT-Based Anode Stack

Figure 39 shows surface morphology, TEM, EDS and Raman spectra of free-standing 3D MWCNT mesh. For the free-standing 3D MWCNTs as shown in Figure 39(a), it was very difficult to measure the overall length of MWCNTs due to their entangled structure, and the as-prepared MWCNTs had an outer diameter about 300 nm (see Figure 39(a) inset). As seen in the HRTEM image of Figure 39(b), the internal structure of MWCNTs comprised disorder graphitic (turbostratic) stacking. Figure 39(c) represents the spot selected for EDS element analysis in order to verify whether the Cu was completely etched away, and the spot was intentionally chosen at the bottom side of the free-standing MWCNT structure. As seen in Figure 39(d), the EDS spectrum related to carbon appeared quite strong (higher than 93wt%), despite little of the Cu

(lower than 3wt%) remained. The 2.2wt% Fe was due to the residue of Fe element or compound after the Cu etching process by an aqueous FeCl_3 etching solution. However, we would like to argue that Fe can be negligible in LIB performance based on the previous report by Poizot et al. [18]. They found that Fe as one of the transitional metals did not act as Fe-Li intercalating compound. Instead, they proposed a new mechanism of Li reactivity with the transitional metals which involves the formation and decomposition of Li_2O , accompanying the reduction and oxidation of metal nanoparticles (in the range of 1 ± 5 nm). In addition, 1.1wt% Ti comes from a barrier layer deposited on Cu mesh by using a sputtering system to prevent Ni from being diffused into Cu mesh substrate during the MWCNT growth process at high temperature, and Ti reacts with carbon at high temperature, forming TiC thin layer [34]. But, we speculate that Ti does not serve as an active material for LIB anode. Also, the average atomic percentages of C and Cu elements in four different spots are 99.4% and 0.4%, respectively. Therefore, most 3D free-standing MWCNTs comprised carbon and their electrochemical performance was strongly dependent on the disordered graphitic structure. Similar to the other lower temperature CVD grown nanocarbon structures, as-prepared MWCNTs contained many defects which could be found from the higher peak ratio of D-band and G-band peaks I_D/I_G (around 1), as illustrated in Figure 39(e). Figure 39(f) exhibited the SEM image of a MWCNT stack composed of the 8 number of the 3D free-standing MWCNT mesh layers and a single layer of 3D MWCNT on Cu mesh as a bottom side (The areal density is 34.9 mg/cm^2 , and the overall thickness is $780 \text{ }\mu\text{m}$.). In addition, the photographs of the MWCNT anode stacks for the Li-ion coin-cell fabrication are shown in Figure 39(g) which indicates the bottom side of the MWCNT stacked sample was bound with 3D Cu mesh current collector in order to enhance the electrical contact between the stacked MWCNTs and the stainless-steel bottom cap of the button cell. Furthermore, to reinforce the bonding strength among MWCNT network in the anode stack, we prepared a binder solution composed of PVDF binder, carbon nanoparticles as conducting agent, and N Methyl 2-

Figure 39. Structural properties of anode stack composed of 3D MWCNTs presented by diverse analysis techniques. Part (a). SEM plane view of 3D free-standing MWCNT structure. Inset shows higher magnification SEM image of the thread-like MWCNT structure; (b) high resolution TEM (HRTEM) image of a single MWCNT; (c) SEM image indicating the point, denoted by the red cross, where Cu mesh originally existed before Cu etching process; (d) EDS spectra of 3D free-standing MWCNTs obtained from the spot indicated by the red cross shown in the SEM image of (c); (e) Raman spectra of 3D MWCNTs; (f) SEM image of the cross-sectioned

MWCNT-based anode stack showing high areal mass density of MWCNTs around 34.9 mg/cm²; (g) photographs of the final product of anode stack for its button cell assembly; (h) cross-sectional SEM image of the binder-assisted and hot-pressed anode stack.

pyrrolidone (NMP) solvent, as mentioned in the experimental section, and applied the binder solution to the anode stack. By compressing the binder assisted anode stack at high temperature and pressure, the 3D MWCNT network structure was strongly bonded, as shown in Figure 39(h). (The areal density is 9.0 mg/cm², and the overall thickness is 72 μm). PVDF binder was possibly formed as the physical cross-linked structure in the uniform film which holds 3D MWCNT based anode stack network, leading to the maintenance of the electrical conduction throughout the anode stack during cycling [91].

5.2.3 Electrochemical Properties of MWCNT-Based Anode Stack

Charge and discharge profiles are very important to understand the electrochemical characteristics of LIB with an anode. As mentioned earlier, a coin-type of cell composed of MWCNT stacked anode and Li metal as counter and reference electrodes is subjected to the charge and discharge cycles at 0.05C (19 mA g⁻¹). As seen in Figure 40(a), the values of the gravimetric specific discharge capacity after lithiation of the anode stack labeled 1 stack (2.6 mg/cm²), 5 stack (H) (9.0 mg/cm²), and 7 stack (18.7 mg/cm²) are 813 mAh g⁻¹, 905 mAh g⁻¹, and 679 mAh g⁻¹, respectively. In addition, the values of the volumetric specific discharge capacity after lithiation of the anode stack labeled 1 stack, 5 stack (H), and 7 stack are 231 mAh/cm³, 1,127 mAh/cm³, and 316 mAh/cm³, respectively. We would like to highlight that the value of the gravimetric specific discharge capacity of 5 stack (H) is 111 % and 133 % higher than that of 1

stack and 7 stack, respectively. In addition, the volumetric specific discharge capacity of 5 stack (H) is 488 % and 357 % higher than that of 1 stack and 7 stack, respectively. Such excellent results could stem from two main reasons. The first reason involves the better electrical contact among MWCNTs through a polyvinylidene fluoride (PVDF) binder and hot pressing. Furthermore, carbon nanoparticles were served as electric conducting agent. The similar principle has been established, and such a binder solution has been commonly used for casting of slurry active materials for LIB [92]. In this study, we would like to emphasize the first application of the principle to the anode stack composed of the 3D free-standing MWCNTs. The second reason involved the morphological variation, such as open-end structures, fractures, and shortened lengths of the MWCNTs after their hot-pressing, and the modified structure could make it more efficient to insert and extract lithium ions into and from the internal structure of MWCNTs, as reported in the previous publication [83, 93]. In Figure 41, the SEM images of the novel hot-pressed anode stack qualitatively showed the strong evidences to prove the two reasons. In addition, it should be noted that current anode stack samples were fabricated by relatively lower temperature (750 °C) for MWCNT growth on Cu mesh using a catalytic thermal CVD method. Since the growth temperature was not high enough to create well-ordered graphitized structure in MWCNTs, MWCNTs contained defective structures composed of carbons present at the layer edges or in smaller polyaromatic domains. The high I_D/I_G intensity ratio (around 1.0) as a metric for the degree of graphitization was calculated based on Figure 39(e). The electrochemical behavior is quite different when a mixed structure of disordered and graphitic carbon has not been further heat treated for high degree of graphitization. Such structure contains wide range of possible sites with different energies in which the lithium can reside. The result is that the open circuit potential vs. Li^+/Li gradually varies, as shown in Figure 40(a), rather than showing the steps characteristic of more ordered structures [94]. Furthermore, it is found that there is considerable irreversible capacity (C_{irr}) loss defined by the difference of specific capacities

Figure 40. Electrochemical performance of the anode stacks with different areal loading density of 3D MWCNTs as active materials for LIB application. A primary charge and discharge profile of the anode stacks in terms of (a), gravimetric and (b), volumetric specific capacities at 0.05C. Cycling stabilities of the two different anode stacks with respect to (c), gravimetric and (d), volumetric specific capacities at 0.5C.

(a)

(b)

(c)

(d)

Figure 41. Cross-sectional FESEM images of (a), mechanically compressed anode stack with the lower pressure and (b), thermal compressed anode stack with the higher pressure; (c-d), plane-view FESEM micrographs taken from different regions of the thermal compressed anode stack with higher pressure. The insets show the magnified regions of the FESEM images to identify the morphology of MWCNT network structure.

obtained during the initial charge and discharge process. The primary reason for the disappointing result is related to the electrolyte decomposition occurred at around 0.8V, resulting in a distinguishable plateau region, as shown in the initial discharge curve of Figure 40(a) and (b) [95]. This phenomenon is typically observed in the CNT-based anodes [54]. Another reason for the irreversible capacity loss is probably due to trapped Li^+ ions inside of the anode structure. During charge process followed by discharge, the Li^+ ions were not completely extracted from the structure and remained.

The cyclability is the essential LIB performance to determine the cycle life of anode and evaluated by number of cycles. Figure 40(c) showed the variation of reversible gravimetric specific capacity (C_{rev}) of the each sample with the different areal mass density as a function of cycle number. The samples of 1 stack and 5 stack (H) presented almost constant capacities. In the case of the anode labeled 1 stack, at 0.5C (186 mAhg^{-1}), the gravimetric capacity response with number of cycles showed the increasing wave like trend till the 50th cycle which indicated the creation of free sites for lithium ion migration into the dense entangled CNT network structure due to the electrochemical alteration upon cycling. The sample of 1 stack retained 105% (264 mAhg^{-1}) of its initial C_{rev} 252 mAhg^{-1} , whereas the sample of 7 stack retained 69% (141 mAhg^{-1}) of its initial C_{rev} 205 mAhg^{-1} after the 46th cycles at 0.5 C. For the anode labeled 7 stack, the values of the C_{rev} kept decreasing as cycling test proceeded. In contrast, the binder-assisted and hot-pressed sample denoted by 5 stack (H) remarkably retained 89% (211 mAhg^{-1}) of its initial C_{rev} 238 mAhg^{-1} after the 46th cycle at 0.5C. The gravimetric and volumetric specific reversible capacities of the sample of 5 stack (H) were 211 mAhg^{-1} and 263 mAh/cm^3 , respectively, which were comparable to those obtained from the current commercially available Li_xC_6 anodes [96]. According to the results from the samples of 5 stack (H) and 7 stack, we could find the correlation of the strong bonding among MWCNT networks and the cycling stability of MWCNT-based anode stack. The possible reason for the lower values of gravimetric specific C_{rev}

of 7 stack designated sample is associated with the overpotential (IR drop) with the thickness of the anode stack. The thick anode physically connected by the multi-layered free-standing MWCNT meshes intrinsically contained the non-homogeneous voltage distribution in the inner structure of the anode, which resulted in a rate-limit process by Li^+ ion diffusion in the electrode. That meant different degrees of connectivity of MWCNTs were exhibited so that the distribution of electrical resistances was not uniform throughout the thickness of the anode stack. Furthermore, after the prolonged charge-discharge cycling processes, bonding among the MWCNT network could be loosened. As a result, ohmic resistance in the anode increases, which deteriorates the cycle life of anode. To overcome such a drawback, the sample denoted by 5 stack (H) was composed of well-bonded multi-layers of the free-standing MWCNT meshes by using a two-step process of PVDF based binder application and thermal-compression. The novel hot-pressed anode stack showed the high volumetric density 1.25 g/cm^3 , which was comparable to that of current commercially available LIBs [96]. Therefore, the approach of chemical binding and physically strong adhesion effectively reduced the interfacial resistance between neighbor MWCNTs, which was the limitation of anode stack pressed with the lower pressure, and provided charge transfers with multiple conducting pathways [44]. For all the sample cases, the Coulombic efficiency from the charge and discharge capacities was almost 100% for each cycle number except the first cycle.

5.3 Conclusion

We proposed a model to enhance the areal mass density of carbon nanostructures (In our case, multiwall carbon nanotubes (MWCNTs)) for the anode system in high-efficiency LIB. The way to increase the loading amount of MWCNTs was stacking of the several free-standing 3D MWCNT mesh layers after the Cu etching process. Based on the LIB performance tests with the

fabricated anode stacks, it was found that the lower values of gravimetric specific C_{rev} were shown in the sample of higher areal mass density, which was caused by the overpotential (IR-drop and activation and concentration polarization) occurred in the anode stacks. To overcome such limitation, we made a novel binder-assisted and hot-pressed anode stack and confirmed that it showed the excellent LIB performance, which was comparable to that of the commercial available anode.

CHAPTER 6.

LARGE SCALE PATTERNABLE 3D CARBON NANOTUBE-GRAPHENE STRUCTURE FOR FLEXIBLE LI-ION BATTERY

6.1 Introduction

Flexible electronics have been considered as next generation portable devices, such as roll/up displays, wearable devices, active radio frequency identification (RFID) tags, integrated circuit smart cards and implantable medical devices. It is expected that flexible Li-ion batteries (LIB) can be used as the energy storage devices for the flexible electronics [44-45]. Currently, several worldwide research teams have prepared nanomaterial-based LIB with the flexible polymer substrates and yielded the excellent LIB performance. V. L. Pushparaj et al. synthesized the flexible nanocomposite thin-film battery comprising CNT-cellulose paper electrode and demonstrated a reversible capacity of 110 mAhg^{-1} in several tens of cycles [46]. J. Chen et al. prepared CVD grown CNT-carbon layer (CL) hybrid anodes for a paper LIB and demonstrated a high reversible capacity of 572 mAhg^{-1} after 100 cycles [47]. M. Kaempgen et al. fabricated printable thin film supercapacitor by using single-walled carbon nanotubes (SWCNTs) spray deposited onto PET films and attained high specific capacitances in the range from ~ 90 to 120 F/g by using various aqueous electrolytes [48]. However, these previous results have some drawbacks, such as lower film adhesion properties of the active materials without compromising their electrochemical performance and employment of complicated coating process. Nevertheless, higher specific and volumetric capacities of the anodes have been motivated for the development of emerging flexible electrodes without metallic current collectors or even polymer substrates (e.g. SWCNT papers) [43].

Another major research into LIB has been currently focused on high-efficiency LIB composed of nanomaterial-based electrodes for the next generation electric vehicles (EVs) as one of the most attractive application. The strong candidates of the nanomaterials can be listed as carbon nanotubes (CNTs) [10], carbon nanofibers (CNFs) [97-98], graphene [11], Si nanowires [12], transition metal oxide nanoparticles [13] and so on. In particular, the LIB cell assembled by those nanostructured anodes have demonstrated their excellent electrochemical properties with respect to safety, high energy density, C-rate capability and long cycle lifetime relative to those of the conventional graphite anodes. In our previous study, we used directly grown multiwall carbon nanotubes (MWCNTs) on metal films with major advantages over conventional mesocarbon microbeads (MCMB) or hard carbon-based electrodes since MWCNTs have their unique properties, including high surface area to accommodate more Li^+ ion intake, good electric conductivity for the faster electron charge transfer and good structural resilience for Li^+ ion insertion and extraction into and from the host structure [26, 99]. However, it is difficult to obtain high volume or mass loading density of nanostructured active materials for their real application by using their conventional coating or direct growth method on the 2D metal substrate [36]. To overcome the limitation, there have been many reports to show 3D electrode architectures to be applied to supercapacitor and LIB. H. Zhang et al. prepared 3D network electrode structure for effective electron and ion pathways and assembled a prototype lithium-ion pouch battery, comprised of a bicontinuous lithiated MnO_2 cathode and a graphite anode. They demonstrated relatively high specific capacity value (c.a. 110 mAhg^{-1}) obtained from charge and discharge cycling at 60C [38]. Very recently, direct growth of CNT-graphene seamlessly grown on 3D Ni foam was reported, demonstrating the field emitter and supercapacitor applications of the novel structure [100]. In the structure, the use of 3D Ni foam can promote the surface-area-utilization efficiency of the metal current collectors and graphene can serve as a linking agent between CNTs and metal interface to improve the bonding strength and electrical properties between the

two phases. Additionally, MWCNTs directly grown on 3D Cu mesh anode architecture has been proposed by Dr. Wonbong Choi's group at FIU and the anode demonstrated not only mass loading density of MWCNT as active materials is four times higher than that of MWCNTs grown on 2D Cu but also 160% improvement of specific capacity in the cycling performance with 254 mAhg⁻¹ at 50th cycle [81].

In this chapter, we propose the architecture of large-scale patternable 3D MWCNTs-graphene hybrids transferred over transparent flexible films, where graphene functions as an underlayer film to enhance the electrical conductivity for 3D MWCNT network structure. The 3D MWCNT structure was transferred by a roll-to-roll lamination process and formed as a patterned structure of 3D carbon nanotubes (CNTs)-graphene [99]. As-prepared 3D MWCNTs-graphene-PET structure was subjected to electrochemical performance tests with a coin-cell type of LIB. In addition, it is proved that the novel structure can be available for high efficiency flexible LIB. It is noted that the fabricated 3D MWCNTs-graphene-PET anode does not include any binders which may have harmful effect during the LIB operation. Furthermore, flexing of 3D MWCNTs-graphene on PET substrates leads to no significant film cracking or peel-off, which is inconsistent with the previous report [43]. Moreover, a commonly used roll-to-roll lamination method implies the potential for high-throughput production of the novel 3D MWCNTs-graphene-PET anode structure.

6.2 Results and Discussion

6.2.1 Experimental Details

A Cu mesh (200 Mesh Copper, TWP) with average dimensions of 50 μm thickness and wire size and 65 μm hole size was prepared. 3D multiwall carbon nanotubes (MWCNTs) grown on Cu

mesh was used as anodes for Li-ion battery. The anode materials were prepared by a two-step process, including Ti (underlayer, ~10 nm thickness)/Ni (catalyst, 2.5-10 nm thickness) thin film deposition on the Cu mesh by using a radio frequency (RF)-direct current (DC) magnetron sputtering system followed by direct growth of MWCNTs through thermal chemical vapor deposition (CVD). In the first step, Ti underlayer played an important role in preventing Ni thin layer from being diffused into the Cu mesh underneath, maintaining activity of catalytic Ni thin layer. In addition, formation of titanium carbide (TiC) thin layer at around 750 °C could improve electrical conductivity and be an effective bonding bridge between MWCNTs and Cu mesh. The presence of a TiC thin layer was evidenced in the interface between MWCNTs and Cu, which was previously confirmed by HRTEM [34, 66]. In the second step, the Ti/Ni deposited Cu mesh was rapidly heated to 750 °C in an Ar gas environment with very low humidity level. Carbon precursor ethylene (C_2H_4) gas carried by hydrogen (H_2) gas (1:2 volume ratio of C_2H_4 to H_2) was fed into the chamber for growth time 50 minutes. Once the growth time was reached, mixture gases of ethylene and hydrogen were turned off and the chamber was cooled down to the room temperature by flowing inert Ar gas.

We have introduced a simple hot lamination process to transfer MWCNTs grown on 3D Cu mesh onto graphene laminated polyethylene terephthalate (PET) flexible substrate. Graphene film was synthesized by a CVD method [101]. A commercially available Cu foil of 50 to 200 μm thickness (Nimrod Hall Copper, 99.9% purity) was first annealed at 1,000 °C for 1 hour under an Ar gas atmosphere. After annealing, Cu foil was acid-treated for 10 minutes in 1 M acetic acid at 60 °C to remove oxide layer created on the Cu foil surface during the annealing process. Subsequently, copper foils were thoroughly washed with de-ionized water and dried at the ambient conditions. Graphene on the Cu foil was synthesized at 1,000 °C and 1 atm pressure, using a 5 minute flow of CH_4 and H_2 gases in 1 : 4 ratios. At the end of this process, the foil was cooled down to room temperature. We used a hot-press lamination and a chemical etching

process for transferring graphene grown on the Cu foil to a transparent flexible PET substrate. A Cu foil with graphene was hot-press rolled with a transparent flexible PET film having thickness $\sim 50\ \mu\text{m}$. To completely remove Cu from the graphene and laminated film, a concentrated FeCl_3 solution was used. The laminated PET film with graphene and Cu foil underneath was floated over the FeCl_3 acid bath at room temperature. After 40 minutes of the etching process, Cu was completely dissolved into the solution, leaving graphene film with the PET substrate. The resultant transparent flexible film was thoroughly washed with de-ionized water and dried in ambient conditions. In addition, Figure 42 shows the processing flow for each step for the transferring of 3D MWCNTs on the graphene-PET films. The as-grown MWCNTs/Cu mesh and the graphene-PET were held in a “face-to-face” orientation. In the similar manner, the hybrid samples of 3D MWCNTs-graphene-PET were hot press rolled at around $70\ ^\circ\text{C}$. After the lamination process, MWCNTs were strongly adhered to the graphene on PET films. In order to completely remove the Cu mesh from the sandwich-like hybrid structure, we used concentrated FeCl_3 etching solution (Transene Company, Inc.). Laminated PET films with 3D MWCNTs-graphene and Cu mesh underneath were floated over FeCl_3 acid bath at room temperature. After longer than four hours, the Cu mesh was completely etched away, leaving 3D MWCNT mesh patterns transferred onto graphene on PET films. Such a patterned hybrid structure was thoroughly washed with de-ionized water and dried in the oven at $80\ ^\circ\text{C}$ for 15 minutes. As presented in the inset of Figure 42(e) and Figure 43, the as-prepared structure was flexible enough to form various geometries without any damage to the MWCNT patterns. The primary reason behind this is the important role of pressure-sensitive adhesives coating of the PET films to make it possible to strongly bond between MWCNTs-graphene and PET.

Figure 42. Process flow of transferring techniques of 3D MWCNTs/Cu mesh onto the graphene/transparent flexible PET substrate. Part (a). Graphene transferred onto PET film, (b) 3D MWCNTs on Cu mesh directly grown by CVD, (c) hot lamination of 3D MWCNTs/Cu mesh with graphene-PET, (d) etching process of Cu mesh by using FeCl₃ oxidation acid, (e) 3D MWCNTs pattern transferred onto the graphene-PET film. Inset shows a digital image of high flexibility of the 3D MWCNTs transferred onto the graphene-PET films.

Surface morphology and structural properties of the prepared 3D MWCNTs-graphene-PET structures were observed using a field emission scanning electron microscope (FESEM) (JEOL, JSM-7000F; HITACHI, S-4800), an energy dispersive spectroscope (EDS) (Thermo Electron Corporation, NORAN System SIX), a micro Raman system (UniG2D, Korea; see Figure 28) (laser source : low noise 532 nm Diode-pumped solid-state (DPSS) laser (3.7 mW); software : iDus CCD detector) and a field emission transmission electron microscope (FETEM) (FEI, TECHNAI F20). Electron conductivity of the structure was measured using a four-probe station (MS Tech, Korea) connected to a digital multi-meter (Keithley, 2400). Measurements were performed after flexing the samples at different bending angles, ranging from 0 ° to 180 °.

Figure 43. Digital images of the 3D MWCNTs-graphene-PET structure.

Prior to using the as-prepared structure as an anode for Li-ion battery, the anode was cut into a disk with 14 mm diameter and dried by heating at 50 °C under high vacuum for longer than 12 hours to ensure complete water removal. For the electrochemical performance tests, a coin type (CR 2032) of half-cell assembly was carried out in an argon filled glovebox under extremely low level of humidity (< 1 ppm). The 3D MWCNTs-graphene-PET structure was used as working electrode, whereas Li metal foil as both counter and reference electrodes. PET acted as a flexible substrate for the 3D MWCNTs-graphene, however due to its insulating behavior, a crescent shaped Cu current collector was used to cover the edges of the electrode in order to make electrons feasibly conduce between the active 3D MWCNT materials and the bottom of coin cell. 1 M solution of LiPF_6 salt in 1:1 (v/v) mixture solvent of ethylene carbonate (EC) and dimethylene carbonate (DMC) was used as electrolyte. Typical polypropylene (PP) material (Separator 2400) was used as separator. The cell was finally assembled by using a CR 2032 coin cell crimping tool (Honsen Corp.). The charge and discharge tests of the assembled cells were

performed in a multi-channel battery testing unit (MACCOR) at room temperature ($\sim 25\text{ }^{\circ}\text{C}$) in galvanostatic mode (constant current density).

6.2.2 Structural and Electrical Properties of 3D MWCNTs-Graphene-PET

Recently, it has been proposed that 3D anode structure for LIB has significantly improved mass amount of electrochemical active materials for ion and electron transport [39-40]. MWCNTs-graphene hybrid anode has been attracted a great attention as anode materials for LIB since their unique morphology and structure have advantages over other reported anodes, such as high electrochemical active area, good electric conductivity and structural adjustment for Li^{+} ion insertion and extraction. In Figure 44(a), SEM image showed regularly patterned 3D MWCNT structure was successfully transferred and uniformly distributed over the graphene on PET film. Two-dimensional EDS mapping for the carbon distribution was illustrated in Figure 45(a). Note that the red-color arrow, which represents the length and direction of linear scan of EDS for elemental analysis for the selected area (see Figure 45(b)). From the two spots of 3D MWCNTs on graphene-PET film, EDS spectra represented higher than 99 atom% of carbon and less than 0.2 atom% of copper (Figure 45(c)). Zoomed-in SEM plane view of the transferred 3D MWCNTs on PET structure was shown in Figure 44(b). The structure was composed of the lower MWCNT density region in the four square shaped areas which had been originally holes in the pristine Cu mesh and the higher MWCNT density region were originally grown on the interwoven Cu wires before the Cu etching process. As the loading density of MWCNTs increased, the more MWCNTs were filled, creating high density pillars and the transparency of the 3D MWCNTs-graphene-PET film accordingly decreased. In our knowledge, such patterned 3D MWCNTs-graphene-PET films were unique structures compared to the previous result showing MWCNTs transferred over polycarbonate (PC) film by a rolled quartz cylinder [99]. The promising

advantages of PET as a substrate are its flexibility, good adherence with active materials and ease of transferring of thin layers like graphene without structural degrading for its application to the flexible electronic devices. Some researchers previously used PET as a flexible substrate in order to fabricate supercapacitors [48, 99]. Also, it should be noted that our proposed anode structure is distinct in several perspectives compared to the previously patterned 3D structure which was prepared by using a small scale laser-jet patterning technique [99]. We employed a commercially available copper mesh, which could be easily etched away and scalable, with roll-to-roll fashion. As presented in Figure 44(c), the high magnification SEM image shows the randomly oriented 3D MWCNT structure grown by thermal CVD and the captured 3D MWCNTs are their diameters in the range of 200 nm to 300 nm which are relatively higher than those in the previous results around 100 nm [34, 71]. Damage of the PET films by electron beam irradiation limits the observation of the transferred graphene on PET. As illustrated in Figure 44(d), the 3D MWCNTs are strongly bonded to the PET film with their average length around 40 μm and such adhesion is due to the patent pressure sensitive adhesion layer coated on the commercial PET film. The schematic of the cross-sectional image and the description for each component of the 3D MWCNTs-graphene-PET anode structure are presented in Figure 44(e).

In contrast, polymer binders or adhesives have been used to enhance the bonding strength between nanomaterial-based film and polymer flexible substrates, but these can also decrease in the electric conductivity of the film [43]. Thus, our binder-free transfer process can result in low cost and high-throughput. It is investigated that the real bonding strength of graphene and CNTs is negligibly weak so that the adhesion layer can physically attach the both non-attractive materials. During a thermal lamination process, the PET film is under the condition of high pressure and temperature around 70 $^{\circ}\text{C}$ and the adhesion layer functions as a glue between MWCNTs and graphene on PET film. HRTEM image reveals that graphene layer stacking inside

a MWCNT of ~ 300 nm diameter is randomly oriented (turbostratic structure), forming internal layer structure instead of being aligned parallel to each other (co-centric tube structure), as shown

Figure 44. Structural analysis of as-synthesized 3D MWCNTs-graphene-PET structure. (a) The magnified SEM image, (b) Zoomed-in SEM image showing detailed morphology of the structure, (c) The magnified SEM image of the randomly oriented CNF structures in the patterned structure, (d) Zoomed-in SEM cross sectional image, (e) Schematic diagram (not to scale) of the cross sectional image shown in Figure 44(d).

Figure 45. (a) 2 dimensional EDS mapping for the carbon distribution in Figure 44(a), (b) Line scanned EDS mapping according to the red colored arrow presented in Figure 44(a) showing the presence of the predominant carbon element, (c) EDS spectra of a spot of 3D MWCNTs on graphene-PET film showing higher than 99 atom% carbon and less than 0.2 atom% of copper, (d) An HRTEM image of the randomly oriented distribution of the graphene layer in a MWCNT.

in Figure 45(d). Importantly, it may be recalled here that structural integrity without defilement and retention of the electrical property of electrochemical active materials are essential for their flexible Li-ion battery performance. Considering the insulating PET film substrate, it is very difficult to expect the electron conductivity through the 3D MWCNTs-graphene-PET structure, whereas 3D MWCNT networks in this study shows high electric conductivity (low sheet resistance $\sim 95 \text{ } \Omega/\text{sq}$) which is comparable to $\sim 40\text{-}50 \text{ } \Omega/\text{sq}$ obtained from the highly SWCNT-spray coated PET substrates [48]. Therefore, 3D MWCNT networks along the structure can be used as both current collectors and electrochemical active materials. Furthermore, true flexible nature of the structure is strongly related to the complete elastic deformation after severe bending. To examine such requirements, the sheet resistance of the 3D MWCNTs-graphene-PET structure was measured as a function of bending angle. As a result, even after severe flexing around 180° , the normalized sheet resistance with respect to that obtained from the structure without bending (R_{deg}/R_0) is around 1 (see Figure 46). The structural integrity and the retention of electrical properties are presumably associated with the combined effect of the flexibility of individual MWCNTs, the strong adhesion of the MWCNTs to the PET films, and the macroscopic porous morphology of the 3D MWCNT structure, releasing the bending strain. Based on the finding, it is noteworthy mentioning here that our proposed novel 3D MWCNTs-graphene-PET structure meets key requirements for flexible Li-ion battery. In many cases, MWCNTs and graphene are characterized by two main features which are the G mode, coming from the first-order scattering of the E_{2g} phonon of sp^2 C atoms (usually observed at $\sim 1580 \text{ cm}^{-1}$) and the D mode, a breathing mode of k-point photons of A_{1g} symmetry ($\sim 1350 \text{ cm}^{-1}$) [97]. Raman results also show the typical G and D peaks presented in Figure 47(a) and (b), indicating that graphene and MWCNTs are successfully CVD grown on Cu and transferred over PET. Figure 47(b) presents the magnified Raman spectra from graphene-PET structure and pristine PET film to clearly identify D and G mode peaks. In addition, it is found that the MWCNTs contain defective structure based

Figure 46. Variation in the normalized resistance (R_{deg}/R_o) as a function of the angle of curvature.

on the ratio of the intensity of D-band to that of G-band around 1 which is presumably due to the relatively lower temperature (750 °C) CVD synthesis. Unlikely, the graphene on Cu and PET shows 2D peak appearing at around 3,000 cm^{-1} Raman shift, which is different from the typical 2D mode at 2,700 cm^{-1} .

Figure 47. Raman spectra of (a) 3D MWCNTs and graphene on two different substrates Cu foil and PET film and pristine PET film and (b) magnified Raman spectra of graphene on PET and pristine PET film.

6.2.3 Li-ion Battery Performance of 3D MWCNTs-Graphene-PET

Electrochemical performance using a half-cell, which is composed of the 3D MWCNTs-graphene-PET structure as working electrode and Li metal foil as reference and counter electrode is shown in Figure 48. Initial charge and discharge cycle, measured at a current rate of 63 mA g^{-1} ($0.17C$), is shown in Figure 48(a). Primary lithiation and delithiation capacities for the 3D MWCNTs-graphene-PET sample are 293 mAh g^{-1} ($\text{LiC}_{7.6}$) and 153 mAh g^{-1} ($\text{LiC}_{14.6}$), respectively and the corresponding Coulombic efficiency (irreversible capacity) is around 52%. The values of the discharge and charge specific capacities are lower than those obtained from 3D MWCNTs on Cu mesh anode systems [81], but they are still comparable with a reversible capacity of 110 mAh g^{-1} from CNT-cellulose paper electrode [46]. Even though PET is a good flexible substrate for 3D MWCNTs-graphene, the electronically insulating behavior of the substrate acts as a barrier for the effective electronic transport. As mentioned in the experimental section, instead of using crescent shaped electrode on the top edges of MWCNTs to enforce redox reactions, it would be recommended to insert the electrode during the graphene-PET lamination process in order to obtain improved electrochemical performance. However, due to the lack of facilities to fabricate flexible batteries which normally require sophisticated tool, in this circumstance, we tested by using coin cells to show the performance of the electrode as demonstrated in the experimental section.

In addition, the low sheet resistance ($95 \Omega/\text{sq}$) of the anode plays a crucial role to activate the electrochemical redox reactions between current collector and MWCNTs-Graphene. The primary reason for the relatively higher irreversibility is related to the electrolyte decomposition occurred around 0.8V resulting in a plateau region as shown in the initial lithiation curve of Figure 48(a) and the larger surface area of the 3D MWCNTs. This phenomenon is typically observed in the carbon nanostructure-based anodes in the previous reports [14, 86]. Graphene is known as high

potential anode materials for LIB with excellent LIB performance in the previous reports [102]. It should be highlighted that the graphene layer lying between 3D MWCNTs and PET film is too light to be considered practical electrochemical active material for Li^+ ion insertion and extraction into and from the graphene structure.

Figure 48(b) presents the cycling stability for the 3D MWCNTs-graphene-PET anode structures in long-cycle operation as one of the key electrochemical properties for LIB. Specific capacity of the anode has been recorded for 50 cycles at 1.7C (current density of 632 mA g^{-1}). The lithiation capacity slightly increases from 96 mAh g^{-1} at the 1st cycle to 130 mAh g^{-1} at the 47th cycle and then gradually decreases to 124 mAh g^{-1} until the 50th cycle. Such a variation of the capacity over the whole cycles is inconsistent with the constant capacities as a function of cycle number shown in our past results [34-35]. It is speculated that one possible reason for such increasing trend of capacity upon number of cycles is associated with the more electrochemical active area on the densely entangled 3D MWCNTs structure created by the continuous charge and discharge process. In our previous publication, it was found that no severe defect or structural damage appeared in the 150 cycled 3D MWCNT-based anode system through observing FESEM and HRTEM images [81]. In the whole charge and discharge cycles, Coulombic efficiency is higher than 98%, indicating the high reversibility of our proposed anode system (see Figure 48(c)). The high reversibility of feasible Li/Li^+ redox reactions might be due to the 3D structure of MWCNTs and co-centric graphene covered MWCNT's formation at the bottom of the MWCNT which paves ease of lithium ion insertion and extraction. The 3D structure is able to accommodate more lithium ion in the MWCNT structure since electrolyte penetrates into the structure and spread over everywhere so that lithium ion can be facilely transported back and forth. Also, 3D structure could avoid SEI inactive layer formation due to the porous structure to allow electrolyte to reach the outer walls of MWCNTs to the core.

Figure 48. Electrochemical performance of the 3D MWCNTs-graphene-PET anode. (a) Initial Galvanostatic charge and discharge profiles of 3D MWCNTs-graphene-PET film anode structure, (b) Cycling performance of the anode in higher number of cycles, (c) Coulombic efficiency of the anode at 1.7C, (d) C-rate capability of the anode at seven different current densities. Numerical values noted in (d) indicate current densities, at which charge and discharge cycles were conducted.

Another essential performance of the LIB anodes is the rate capability. The values of specific capacities are measured at different current densities as illustrated in Figure 48(d). A typical staircase type of decreasing behavior is shown from 254 mAhg⁻¹ to 59 mAhg⁻¹ with the increase of the current densities from 0.17C to 1.7C, respectively. Such trend can be presumably due to the slower rate of charge transfer reaction between Li⁺ ions and electrons through the anode structure at the higher C-rate condition. But, the specific capacity retained to earlier ~254 mAhg⁻¹ (at 0.17C) at 37th cycle even after undergoing high rate till 1.7C which indicates the persistence and enormous capability of withstanding different C rate of the flexible battery. The ability of the flexible electrode to withstand against bending angle till ~180°, uncomplicated transfer without getting modified structural and vibrational properties and the relative good performance of the electrochemical properties divulge the effectiveness of the flexible MWCNTs-graphene-PET electrode.

6.3 Conclusion

We have demonstrated a novel 3D MWCNTs-graphene-PET flexible anode structure for flexible LIB. The 3D MWCNTs and graphene are directly grown on Cu substrates by using a CVD method and the 3D MWCNTs-graphene structure is transferred onto flexible PET film using a thermal lamination method and wet-etching process for Cu. It is confirmed from Raman spectra that graphene and MWCNT show similar G and D peak intensity before and after their transfer over PET substrate which indicates no degradation of the crystallographic order of the MWCNTs after transferring process. Also, the Cu etched 3D structure contains carbon higher than 99% which is estimated from the EDS analysis. The low sheet resistance (~95Ω/sq) of 3D MWCNTs-graphene-PET even after bending the substrate and extreme connectivity indicates the flexibility of the anode. The anode structure shows high reversible specific capacity (153 mAhg⁻¹

at 0.17C) and good cycling stability up to the measured range of 50 cycles at 1.7C yielding 124 mAhg⁻¹. Moreover, the specific capacity retains to ~254 mAhg⁻¹ at 37th cycle at 0.17C even after undergoing charge-discharge cycling till 1.7C. Such good electrochemical properties are strongly related to the interconnecting electronic pathways between 3D MWCNTs and graphene due to the good bonding strength between 3D MWCNTs-graphene hybrid structure and PET substrate. Considering all those features, our proposed 3D MWCNTs-graphene-PET flexible structure is expected to be a promising anode for next generation flexible Li-ion batteries.

CHAPTER 7

SUMMARY AND FUTURE WORK

7.1 Summary

Recently, high-efficiency and environmentally friendly electric vehicles (EVs) have attracted strong attention from researchers and industries around the world. Among the candidate power sources for EVs, Li-ion battery (LIB) has been used due to its major advantages, such as high specific energy and volumetric energy density. Also, to enhance the LIB performance, a high quality of anode materials is required, and hence carbon based materials, silicon and transition metal oxides have been proposed for the application to EVs. However, those materials of bulk size have some limitations for the EV applications (e.g., lower specific capacity for graphite, pulverization problem for silicon, etc.). To overcome these drawbacks, many research societies have been interested in the use of nanomaterials (e.g., carbon nanotubes, graphene, silicon nanowires or nanotubes, nanoscale transition metal oxides, and so on) in anode systems. Nanomaterials have their own unique properties; including high surface area, short diffusion length of lithium ion in the nanostructure, and mechanical sustainability. In this study, we have focused on multi-wall carbon nanotube-based anode materials and the synthesis of the various 3D anode nanoarchitectures to address a critical limitation of carbon based nanomaterials, which is a low areal or volumetric density.

A 3D MWCNT-based Li-ion battery (LIB) anode has been synthesized by a two-step process of catalytic thin layer deposition through a sputtering system and direct growth of MWCNTs on Cu substrates via a catalytic thermal chemical vapor deposition (CVD) method. In this dissertation, we have focused on the development of the preparation methods for the various

novel anode structures; such as, 3D MWCNTs on Cu mesh, 3D MWCNT-based anode stack, and flexible 3D MWCNTs-graphene-PET architecture. Also, their structural and electrochemical properties have been further investigated for their applications to the next-generation LIB for electric vehicles (EVs).

The 3D MWCNTs on Cu mesh anode structures proved their higher specific capacity, cycling stability, and C-rate efficiency in comparison to those of the MWCNTs on 2D Cu foil anodes. The higher efficiency of the 3D anodes was strongly related to the higher average mass loading density of MWCNTs, which was fourfold higher than that of the 2D anodes. The a-Si deposited onto the 3D MWCNTs/Cu hybrid anodes demonstrated the further improvement of electrochemical properties.

In addition, we proposed a prototype model for the increment of the volumetric mass density of MWCNTs as active materials for the anode system used for high-efficiency LIB. The method to increase the volumetric mass density of MWCNTs was developed with several layers of free-standing 3D MWCNT structures through a Cu etching process and pressing them together. Based on the LIB performance obtained from the as-prepared anode stacks, the volumetric specific reversible capacities (C_{rev}) increased with the areal mass density of MWCNTs in initial cycles. However, the higher number stacked MWCNTs resulted in the loss of (C_{rev}) in later cycles, which is associated with the greater interfacial resistance among the 3D MWCNT network during cycling. To circumvent such drawbacks, we synthesized a novel binder-assisted and hot-pressed anode stack and obtained appreciably improved LIB performance from the novel anode stack.

Finally, we have fabricated a novel 3D MWCNTs-graphene-PET anode structure for application to flexible LIBs incorporated into both existing and emerging flexible electronic devices. Such 3D MWCNTs and graphene were directly grown on Cu substrates by using a CVD method and transferred onto flexible PET film using a thermal lamination method and a Cu

etching process. According to the Raman spectra, graphene and MWCNT exhibited almost no change in G and D peak intensities before and after their transfer over the PET substrate, which means no degradation of the crystallographic order during the transfer process. The low value of sheet resistance ($\sim 95 \text{ } \Omega/\text{sq}$) of 3D MWCNTs-graphene-PET structure, measured after bending test, clarified the high flexibility of the anode. In addition, the anode structure showed highly reversible specific capacity (153 mAhg^{-1}) up to 50 cycles and good cycling performance and C-rate capability. Based on those excellent results, our proposed 3D MWCNTs-graphene-PET flexible structure can be considered as a high potential anode system for next-generation flexible and light weight Li-ion batteries.

7.2 Future Scope of This Work

MWCNTs have been considered as promising active materials for Li-ion battery anodes. However, one of the drawbacks of MWCNT-based anodes is lower loading density of MWCNTs, which is also a common problem with other nanomaterials. To address this issue, we introduced a novel geometry of 3D Cu current collectors, which can provide larger surface area to accommodate higher solid loading of MWCNTs for better specific capacities, compared to that of 2D MWCNTs. Also, anode stacks assembled by several 3D MWCNT layers can be a novel approach to increase the areal or volumetric density of MWCNT-based active materials. Nevertheless, one of the drawbacks found in our proposed anode was that the value of the reversible, stable specific capacity (229 mAhg^{-1} at 50th cycle and 1C) was lower than the theoretical specific capacity 372 mAhg^{-1} of graphite-based anode. We speculate that a possible reason for the problem can be strongly related to the increase in the weight portion of the MWCNTs as active materials without their contribution to capacitance. Since the as-prepared 3D MWCNTs showed the lower degree of order in the graphene stacking structure, their internal

structure could not be favorable to facilitated lithium ion diffusion. Thus, during the cycling process under the moderate C-rate condition, it could be hard to expect that lithium ions would be inserted or extracted in or from the innermost structure of defective 3D MWCNTs with the larger diameter (average diameter 300 nm). For improving the Li-ion battery performance, future experimentation should explore the optimized morphology of the 3D MWCNTs by controlling growth conditions, such as growth temperature and time, and thickness of a catalytic Ni thin layer. In addition, analysis of EIS can be performed to generate Nyquist plots where the imaginary part of the impedance is plotted as a function of the real part over a wide range of frequencies. Also, diffusion coefficient of lithium ions (D_{Li}) of the 3D MWCNTs with different diameters can be calculated based on the AC impedance results and the Wechselstrom² intermittent titration method (WITT) [103-104].

As stated in Chapter 4, amorphous silicon deposited on 3D MWCNT hybrid anode structure generated better Li-ion battery performance than that of the pristine 3D MWCNTs. However, the specific capacity 280 mAhg⁻¹ at the end of 50 cycles measured at 1C, which is much lower than that of previous reports [15-16]. It was observed that the weight of the deposited a-Si was lower than 1% of that of the MWCNTs; therefore, the a-Si thin layer did not have any major contribution except slight increase in the overall specific capacity of the anode, unlike the previous results from Si nanotubes [15] and Si nanowires [16]. To increase the loading density of Si, the author would like to focus on incorporating silicon quantum dots into MWCNTs to create a hybrid core-shell structure with the enhanced capacity.

As mentioned in Chapter 6, the 3D MWCNTs-graphene-PET flexible anodes showed good electrochemical properties. The main reason for this is strongly related to the interconnecting electronic pathways between 3D MWCNTs and graphene due to the good bonding strength

² The German word for alternating current

between 3D MWCNTs-graphene hybrid structure and PET substrate. In spite of this, the specific capacity 124 mAhg^{-1} up to the 50 cycles at 1.7C is still not high enough to be applied to commercial flexible Li-ion batteries. To overcome the limitation, it is proposed to exclude the effect of the insulating nature of PET film on the slower rate of charge transfer reaction between Li^+ ions and electrons through the anode structure at the higher C-rate condition. It is anticipated that fabricating a pouch-type of a full Li-ion battery cell is a good cell design to realize the high potential of our proposed 3D MWCNTs-graphene-PET film anode structure, instead of using a conventional coin type of a cell.

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EDUCATION

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JOURNAL PUBLICATIONS

1. **C.W. Kang**, R. Baskaran, W.B. Choi, “Large Scale Patternable 3-Dimensional Carbon Nanotubes-Graphene Structure for Flexible Li-ion Battery”, submitted to Carbon (under review).
2. **C.W. Kang**, I. Lahiri, R. Baskaran, W.-G. Kim, Y.-K. Sun, W.B. Choi, “3-dimensional carbon nanotube for Li-ion battery anode”, J. Power Sources. 219 (2012) 364-370.
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INTERNATIONAL CONFERENCE PROCEEDINGS

1. **C.W. Kang**, R. Baskaran, W.-G. Kim, Y.-K. Sun, W.B. Choi, "3-Dimensional Carbon Nanostructures for Li-ion Battery Anode," 2012 MRS Fall Meeting, Volume 1505 (2013), - Symposium W - Carbon Nanomaterials.

2. **C.W. Kang**, I. Lahiri, R. Baskaran, M.S. Choi, W.-G. Kim, Y.-K. Sun, W.B. Choi, "3D Multiwall Carbon Nanotubes (MWCNTs) for Li-Ion Battery Anode," TMS 2012 Supplemental Proceedings: Materials Properties, Characterization, and Modeling, Volume 2, pp. 35-41.

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1. R. Baskaran, **C.W. Kang**, J.G. Park, H.T. Jeon, W.B. Choi, "Surface modified MWCNT by ALD coated RuO₂ anode for Li-ion battery", NANO KOREA 2013, July 10-12, 2013, Seoul, Republic of Korea.

2. **C.W. Kang**, R. Baskaran, W.-G. Kim, Y.-K. Sun, W.B. Choi, "3-Dimensional Carbon Nanostructures for Li-ion Battery Anode", 2012 MRS Fall Meeting, November 25-30, 2012, Boston, Massachusetts, USA.

3. R. Baskaran, **C.W. Kang**, I. Lahiri, W.B. Choi, "Ex-situ investigations on 3D MWCNT anode for Li-ion battery", NANO KOREA 2012, August 16-18, 2012, Seoul, Republic of Korea.

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