Investigation of nickel oxide and germanium for Li-ion battery anodes

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**INVESTIGATION OF NICKEL OXIDE AND
GERMANIUM FOR LI-ION BATTERY ANODES**

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2014

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IN ADVANCED MATERIALS FOR MICRO- AND NANO-
SYSTEMS (AMM&NS)

SINGAPORE-MIT ALLIANCE
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2014

DECLARATION

I hereby declare that this thesis is my original work and
it has been written by me in its entirety.

I have duly acknowledged all the sources of information
which have been used in the thesis.

This thesis has also not been submitted for any degree
in any university previously.

Rahmat Agung Susantyoko

24 November 2014

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Abstract

We aimed to develop high performance anodes for Li-ion batteries. Three approaches were investigated to minimize the aggregation, pulverization and delamination problems. Firstly, graphitic and amorphous carbon was incorporated to directly-grown NiO nanostructures. NiO-C showed better electrochemical performances than pristine-NiO due to high electrical conductance and better mechanical flexibility of graphitic and/or amorphous carbon.

Secondly, vertically-aligned MWCNT arrays were used as base structures for sputtered-NiO, amorphous-Ge and polycrystalline-Ge. The electrochemical performances of MWCNT/NiO were significantly improved than pristine-NiO since vertically-aligned MWCNTs enhanced the ionic and electronic transports and absorbed the stresses during lithiation/delithiation. MWCNT/a-Ge showed higher specific capacity than MWCNT/c-Ge as MWCNT/a-Ge skipped electrochemically-driven solid-state amorphization during first lithiation. MWCNT/a-Ge benefited from low cost processing and low anodic scan peak.

Thirdly, annealing treatment was investigated. Annealed-Ge had significantly improved electrochemical performances than as-deposited Ge due to better SS/Ge-film adhesion due to inter-diffusion at SS/Ge interface.

Keywords: alloying, anode, conversion, germanium, lithium-ion, nickel oxide

Thesis advisors:

1. Professor Zhang Qing, SMA Fellow, NTU
2. Professor Eugene A. Fitzgerald, SMA Fellow, MIT
3. Professor Dimitri A. Antoniadis, SMA Fellow, MIT

Summary

We studied three approaches to develop high performance anodes for Li-ion batteries by minimizing the aggregation, pulverization and delamination of active materials. Firstly, graphitic and amorphous carbon was incorporated to directly-grown NiO nanostructures. Secondly, vertically-aligned MWCNT arrays were used as base structures for sputtered-NiO, amorphous-Ge and polycrystalline-Ge. Thirdly, annealing treatment was performed to amorphous-Ge film.

Pristine-NiO had a poor cycle performance because of large electrical resistance and stress-induced pulverization. We investigated the effect of graphitic and amorphous carbon incorporation to pristine-NiO become NiO-C composite. NiO-C had significantly better cycle performance and rate capability than pristine-NiO. This was attributed to high electrical conductance and better mechanical flexibility of graphitic and/or amorphous carbon, which not only provide efficient channel for electrons, but also function as networks preventing NiO nanostructures from structural deformation during lithiation/delithiation. The better mechanical stability of NiO-C after 102 cycles was evidenced. NiO-C had a lower internal resistance than pristine NiO that suggested better Li-ion transport in NiO-C than pristine-NiO.

The effect of vertically-aligned MWCNT arrays as base platforms for pristine-NiO was investigated. We found the cycle performance and rate capability of MWCNT/NiO were significantly improved than those of pristine-NiO. They could be attributed to the unique MWCNT/NiO structure in which vertically-aligned MWCNT arrays enhanced the ion and electron transport, absorbed both the compressive and tensile stresses and minimized

NiO pulverization during lithiation/delithiation. MWCNT/NiO had lower internal and charge-transfer resistance than those of NiO that suggested superior ion and electron transport of MWCNT/NiO. The stability of MWCNT/NiO after 50 cycles was evidenced. The combination of vertically-aligned MWCNT arrays with conversion-type active material is a promising anode material for Li-ion batteries.

Vertically-aligned MWCNT arrays were used as platforms to systematically investigate the performance of amorphous and polycrystalline Ge. Amorphous-Ge and polycrystalline-Ge were coated to vertically-aligned MWCNT arrays, i.e., MWCNT/a-Ge and MWCNT/c-Ge, respectively. Both MWCNT/a-Ge and MWCNT/c-Ge after 100 cycles had a stable structure and conformal SEI. The MWCNT/a-Ge sample showed better performances than MWCNT/c-Ge because MWCNT/a-Ge skipped electrochemically-driven solid-state amorphization of crystalline Ge during the first lithiation. MWCNT/a-Ge had additional advantages of low temperature synthesis, low cost processing and lower anodic scan peak. We showed the potential use of amorphous-Ge for the design of Ge-based anodes.

Amorphous-Ge film on SS was studied. Initial investigation showed that thin amorphous-Ge film (< 125.8 nm) had a good cycle performance but areal capacity was limited. In contrast, thick amorphous-Ge film (> 125.8 nm) had a good areal capacity but the cycle performance was poor due to stress-induced structure disintegration and/or delamination. The effect of annealing treatment to 759.8 nm thick amorphous Ge film was investigated. Annealed Ge had a significantly improved cycle performance than as-deposited Ge. The annealing improved the adhesion between Ge film and SS substrate due to the inter-

diffusion at SS/Ge interface. Annealing also introduced a little oxygen impurities which favor better electrochemical properties than as-deposited Ge. We demonstrated improved performances of thick Ge film anode by a simple process of annealing in air.

Keywords: alloying, anode, conversion, germanium, lithium-ion, nickel oxide

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List of acronyms and abbreviations

3D	: Three-Dimension
AC	: Alternating Current
Al	: Aluminum
APCVD	: Atmospheric-Pressure Chemical Vapor Deposition
Ar	: Argon
C ₂ H ₂	: Acetylene
Co	: Cobalt
Cu	: Copper
Cu ₂ O	: Copper(I) oxide
CuO	: Copper(II) oxide
CV	: Cyclic Voltammetry
CVD	: Chemical Vapor Deposition
DC	: Direct Current
DEC	: Diethyl Carbonate
E-beam	: Electron-beam
EC	: Ethylene Carbonate
EDS	: Energy Dispersive X-ray Spectroscopy
EIS	: Electrochemical Impedance Spectroscopy
FEC	: Fluoroethylene Carbonate
FFT	: Fast Fourier Transform
FIB	: Focused Ion Beam
Ge	: Germanium
H ₂	: Hydrogen

HR-TEM	: High-Resolution Transmission Electron Microscopy
Li	: Lithium
Li ₂ O	: Lithium Oxide
LiCoO ₂	: Lithium Cobalt Oxide
LiFePO ₄	: Lithium Iron Phosphate
LiMn ₂ O ₄	: Lithium Manganese Oxide
LiPF ₆	: Lithium Hexafluorophosphate
LPCVD	: Low-Pressure Chemical Vapor Deposition
Mn	: Manganese
MW	: Molecular Weight
MWCNT	: Multiwall Carbon Nanotube
MWCNT/a-Ge	: Amorphous-Ge coated vertically-aligned MWCNT arrays
MWCNT/c-Ge	: Polycrystalline-Ge coated vertically-aligned MWCNT arrays
MWCNT/NiO	: NiO on vertically-aligned MWCNT arrays
N ₂	: Nitrogen
NH ₃	: Ammonia
Ni	: Nickel
Ni-C	: Carbon coated Ni foam
Ni-Cd	: Nickel–Cadmium battery
Ni-MH	: Nickel–Metal Hydride battery
NiO	: Nickel Oxide
NiO-C	: Nickel Oxide – Carbon
NiO _y , where y>1	: Non-stoichiometric oxygen-rich NiO

O ₂	: Oxygen
PECVD	: Plasma-Enhanced Chemical Vapor Deposition
RF	: Radio Frequency
RGO	: Reduced Graphene Oxide
RMS	: Root Mean Square
Sb	: Antimony
SEI	: Solid Electrolyte Interphase
SEM	: Scanning Electron Microscopy
Si	: Silicon
Sn	: Tin
SS	: Stainless Steel
SS/NiO	: NiO film on SS
STEM	: Scanning Transmission Electron Microscopy
T _{dep}	: Deposition temperature
TEM	: Transmission Electron Microscopy
TGA	: Thermogravimetric Analysis
Ti	: Titanium
TiN	: Titanium Nitride
TiN/Ge	: Ge on TiN
TiS ₂	: Titanium Disulfide
T _m	: Melting temperature
XRD	: X-Ray Diffraction
X-SEM	: Cross-section SEM
X-TEM	: Cross-section TEM

Chapter 1 : Introduction

1.1. Background

1.1.1. Introduction

Batteries play an important part in our daily life. Majority of the portable electronic devices we use today are powered-up using Lithium-ion (Li-ion) batteries because Li-ion has a large specific energy storage compared to other type of batteries, as shown in Figure 1-1. In addition, Li-ion battery has an electric potential exceeding 3.9 V, the highest compared to other type of batteries. Typically, Li-ion battery has a specific energy storage of 120–150 mW h g^{-1} which is 2 to 3 times of Nickel–Cadmium (Ni-Cd) battery. [1] Li-ion battery can be used for many cycles as a rechargeable battery with high stability. Finally, the safety of Li-ion battery had been proved to be superior to metallic Li battery for portable devices. [2]

Figure 1-1 - Comparison of energy storage devices. Image adapted from [1].

1.1.2. Li-ion battery structure

Battery is an electrochemical device that is able to store and release electrical energy. Figure 1-2 shows the typical Li-ion battery configuration where non-aqueous-electrolyte soaked separator is sandwiched between negative electrode (anode) and positive electrode (cathode). The anode and cathode active materials are typically graphite anode and Lithium Manganese Oxide (LiMn_2O_4) cathode or Lithium Cobalt Oxide (LiCoO_2) cathode. The anode and cathode active materials were coated on Copper (Cu) and Aluminum (Al) current-collector, respectively.

During charging, current is applied to the cathode that leads to the movement of Li-ions from cathode to the anode inside the battery. During discharging, the electron is flowed from anode to the external load to the cathode, while the Li-ions move from anode to cathode inside the battery. The separator has a function to prevent short-circuit between anode and cathode. The non-aqueous electrolyte enables the chemical stability over large potential window to support the high potential of Li-ion battery.

Figure 1-2 - The structure and mechanism of intercalation-type Li-ion battery during (a) charging and (b) discharging. [3]

1.1.3. Motivation

The Li-ion battery in Figure 1-2 uses intercalation-type anode and cathode. Graphite anode has theoretical specific and volumetric capacities of 372 mA h g^{-1} and 830 mA h cm^{-3} , respectively. [1] LiCoO_2 cathode has theoretical usable specific and volumetric capacities of 130 mA h g^{-1} [1] and 808 mA h cm^{-3} [4], respectively. The specific and volumetric capacities of intercalation-type Li-ion could probably satisfy today's demand in portable electronic devices. However, in near future, Li-ion battery performance needs to be significantly improved due to the following factors.

a. Slow development of battery

The development of batteries is relatively slow compared to transistors. Moore's prediction [5] dictates doubling of transistor density every 2 years. This resulted in exponential improvements of 5-orders of magnitude in the past 4 decades, as shown in Figure 1-3. On the contrary, the battery development is very slow. Figure 1-4 shows the specific energy storage of battery increased by 1 order of magnitude in the past century. Thus, battery often becomes the bottleneck in the electrical applications.

Figure 1-3 - Exponential development of transistor count in past decades [6].

Figure 1-4 - Slow development of battery specific energy [1, 7].

b. Advance in portable electronics

Nowadays, portable electronics need more battery power as the portable electronics have more functions (such as more sensors, faster computing speed and larger display) and smaller form factor (thinner and lighter). Figure 1-5 shows the trends of the amount of battery capacity fitted in Samsung smart-phone. As more functions are applied to new models, large battery capacity is needed to achieve similar operating time. Figure 1-5 shows the Galaxy S4 model has 2600 mA h battery capacity, which is ~1.7 times higher than that of Galaxy S model of 1500 mA h. The Galaxy Note 3 model has a battery capacity of 3200 mA h that is higher than 2600 mA h of Galaxy S4 model due to larger screen size of Galaxy Note 3. All these suggest specific and volumetric capacities of battery are important for practical applications.

Figure 1-5 - Battery capacity of Samsung's Galaxy S [8-11] and Note [12-14].

c. The advent of electric vehicles

Electric vehicles have the advantages of less dependence to global oil price as well as zero carbon emission. Tesla Motors is able to manufacture and sell electric vehicles using Li-ion battery as shown in Figure 1-6. This market requires higher energy density and power density of batteries. Generally, the electric vehicles need a high discharge rate capability for acceleration, a high specific capacity and a volumetric capacity for smaller form factor of the battery, a high capacity for long range driving, an excellent battery safety and a long cycle life.

Figure 1-6 - Model S: electric car manufactured and sold by Tesla Motors, USA [15].

The specific capacity of Li-ion battery needs to be improved to meet the requirements. Conventionally, the electric cars demand energy of $250 \text{ W h mile}^{-1}$ ($\sim 155.3 \text{ W h km}^{-1}$). [1] To be able to cruise a range of 380 mile ($\sim 611.6 \text{ km}$), $9.5 \times 10^4 \text{ W h}$ energy is needed. Using today's Li-ion battery technology, this would require 546 to 646 kg of Li-ion battery cells which is obviously too heavy for a car. If the specific capacity is improved by a factor of 3, the additional weight from the battery could be decreased to 182 to 215 kg, which is more reasonable for the applications.

d. Bright market revenue forecast of Li-ion battery

Li-ion battery is dominating the portable electronics market due to its superior performance compared to other type of batteries. With a breakthrough, Li-ion battery is also potentially dominating the electric vehicles market. A bright forecast of Li-ion battery is expected in the next 20 years as shown in Figure 1-7. The revenue of Li-ion battery is \$11.8 billion in 2010. It is predicted to be \$31.4 billion and \$53.7 billion in 2015 and 2020, respectively. [16]

Figure 1-7 - Li-ion battery market revenue forecast [16].

1.2. Objectives

The objective of this thesis was to develop high performance anodes for Li-ion batteries by minimizing the aggregation, pulverization and delamination of active materials. Nickel Oxide (NiO) and Germanium (Ge) are used as they have a high theoretical specific capacity of 718 and 1624 mA h g⁻¹, respectively, which are larger than that of graphite of 372 mA h g⁻¹.

The project has been performed in 4 phases:

- a) fabrication of Nickel Oxide – Carbon (NiO-C) composite anode that has a novel fabrication process and a high mass loading on a three-dimension (3D) substrate;

- b) fabrication of NiO on vertically-aligned MWCNT arrays (MWCNT/NiO) anode that demonstrates the beneficial use of vertically-aligned Multiwall Carbon Nanotube (MWCNT) arrays for conversion-based anode;
- c) fabrication of Amorphous-Ge coated vertically-aligned MWCNT arrays (MWCNT/a-Ge) anode that has better performance than Polycrystalline-Ge coated vertically-aligned MWCNT arrays (MWCNT/c-Ge) anode and;
- d) fabrication of annealed-Ge anode that has high specific and volumetric capacities.

1.3. Scope of the project

This project aims to fabricate Li-ion battery anodes that have better performance than graphite. NiO and Ge are used to represent conversion and alloying-type anode active materials, respectively. NiO is selected for conversion-type material because of high theoretical specific capacity of 718 mA h g⁻¹ and easily obtained material. Ge is selected for alloying-type material because of high theoretical specific capacity of 1624 mA h g⁻¹ and high Li-ion diffusion in Ge.

Half-cell configuration is used to characterize the electrochemical properties of NiO and Ge active materials because this configuration offers simplicity in the analysis of NiO and Ge active materials.

1.4. Organization of the thesis

This thesis is organized as follows:

Chapter 1 provides an introduction to the background and motivation of this project as well as the objectives and scope of the project.

Chapter 2 briefs the literature review and the historical development of Li-ion batteries. NiO and Ge active materials are reviewed in details.

Chapter 3 describes the experimental methodologies used in this project, i.e. the key process systems, electrochemical and physical characterizations.

Chapter 4 presents novel technique to fabricate NiO-C composite on 3D substrate. The fabrication, characterization, and significance of NiO-C composite are presented.

Chapter 5 presents the important role of vertically-aligned MWCNT arrays to the performance of NiO anode. NiO is deposited on vertically-aligned MWCNT arrays. The fabrication, characterization, and significance of MWCNT/NiO are presented.

Chapter 6 discusses the effect of crystallographic nature of Ge (amorphous or polycrystalline) to the performance of Ge-based anode. Vertically-aligned MWCNT arrays are used as a platform for both MWCNT/a-Ge and MWCNT/c-Ge. The fabrication and characterization of MWCNT/a-Ge and MWCNT/c-Ge are presented.

Chapter 7 presents the effect of annealing to the performance of amorphous Ge film anode. The fabrication, characterization, and significance of annealed Ge are presented.

Chapter 8 summarizes major findings of the thesis. The developed anodes are compared. Recommendations for future work are also presented.

Chapter 2 : Literature review

2.1. Introduction

This chapter briefly reviews the historical development of Li-ion batteries. Li-ion battery anode is then reviewed in details, starting from graphite anode to conversion-type and alloying-type anodes.

2.1.1. History of Li-ion battery

The history of the Li-ion battery started with the conception of intercalation-type cathode and the use of non-aqueous electrolyte in 1976. [17] Whittingham fabricated battery made from intercalation-type cathode of Titanium Disulfide (TiS_2), non-aqueous electrolyte and Li metal. [17] The concept was further developed by Goodenough in 1980 and 1983 that proposed intercalation compounds of Li_xMO_2 , where M is Cobalt (Co), Nickel (Ni) or Manganese (Mn). [18, 19] LiCoO_2 has been used as a common Li-ion cathode today with a practical specific capacity of 130 mA h g^{-1} . [1] LiMn_2O_4 has abundant & non toxic properties with a theoretical specific capacity of 148 mA h g^{-1} . [1] Lithium Iron Phosphate (LiFePO_4) has better rate capabilities with a theoretical specific capacity of 170 mA h g^{-1} . [1] Although the development of cathode materials is very slow, it is beyond our scope. In this thesis, the problems of anode material are addressed.

2.1.2. Development of Li-ion battery anode

Li metal has a high theoretical specific capacity of 3860 mA h g^{-1} as anode material. [20] However Li metal presents safety hazard due to formation of uneven dendritic Li that can cause short circuit and explosion hazard.

One strategy is to use Li-Al alloy. Li-Al alloy has a decreased dendrite formation, but suffered from short cycle life due to disintegration and loss of electrical contacts between the particles. [21] Another strategy is to replace Li metal with other materials that can store Li-ion and has low potential with respect to Li/Li^+ . In this approach, the safety of battery is highly improved as Li travels as ion.

Yazami was among the first to investigate reversible Li-ion intercalation in graphite anode in 1983. [22] Graphite has a theoretical capacity of 372 mA h g^{-1} . Basu patented the intercalation-type graphite anode and niobium triselenide cathode in 1983. [23] In 1987, Yoshino successfully patented carbonaceous anodes made from carbon fibers, fired carbonization products or needle coke [24]. Most importantly, Yoshino also showed the safety of using a carbonaceous anode and LiCoO_2 cathode. [2] Under the supervision of Nishi, Sony was among the first to commercialize the carbonaceous anode in 1991 using a full cell configuration of carbonaceous anode, non-aqueous electrolyte and Li compound cathode. [25, 26]

Poizot et al. [27] investigated the reactivity of Li-transition metal oxide such as Copper(II) oxide or CuO , NiO , etc in 2001. These anode materials had Li driven, in situ formation of metal nanoparticles during the first lithiation, which enabled the formation and decomposition of Lithium Oxide (Li_2O) upon subsequent cycling. They are called conversion-type anodes.

Alloying type anode forms alloys with Li. This type of anode was actively developed since 2008. [28, 29] The alloying type anodes had much larger theoretical specific capacity than graphite. Both conversion- and alloying-type anodes undergo a large volume change during lithiation/delithiation which can cause pulverization and/or delamination of anode active materials.

2.2. Conversion type anode

2.2.1. Introduction

Transition metal oxides are promising anode materials for Li ion batteries where the conversion reaction of the transition metal oxide and formation/decomposition of Li_2O is reversible. [27] Figure 2-1 shows the study on conversion-type anode. After lithiation, Copper(I) oxide or Cu_2O particles transformed to Cu_2O nanoparticles in Li_2O and Solid Electrolyte Interphase (SEI) matrices. [27]

Figure 2-1 - Starting Cu_2O (left) and lithiated Cu_2O (right) [27].

One of transition metal oxide candidates is NiO anode. NiO is a conversion-type anode material for Li-ion batteries with a theoretical capacity of 718 mA h g^{-1} . It undergoes a conversion process where reduction/oxidation of NiO and formation/decomposition of Li_2O are reversible [27].

2.2.2. NiO anode

In this project, NiO is used to represent conversion-type anode. The NiO has challenges of:

- pulverization due to large volume change during lithiation/delithiation;
- low electronic conductivity due to semiconducting property of NiO with band gap of ~ 3.8 eV [30].

An approach is to fabricate NiO nanostructure, since nano-size NiO has better resistance to the pulverization than bulk NiO. The anode performance of NiO nanostructures is much better than bulk NiO anode due to decreased diffusion lengths of Li-ion and facile strain relaxation of NiO, see Figure 2-2.

Figure 2-2 - Nano NiO is better than bulk NiO [31].

2.2.2.1. NiO nanostructures

Figure 2-3 shows variety of NiO nanostructures. [31-39] Most of the nanostructured NiO had been tested under low discharge/charge rates, see Table 2-1. Although NiO nanostructures have advantages for the anode application over bulk NiO, they do have several weaknesses:

- They must be mixed with binders and carbon conductors to form slurry which is then casted on a metal current collector. Attachment of slurry to current collector is typically weak, resulting in a short cycle life.

- b) Due to aggregation and expansion/contraction of active nano NiO structures during lithiation/delithiation, their structures might not be preserved during cycling.

Figure 2-3 - Illustrations of nanostructured NiO [31, 34-39].

Due to the above problems, the anodes based on nanostructure NiO suffer from poor cycling performance. The casting process can be improved by investigating better binders and conductors. Another approach is to substitute the casting process with thin film approach whereby NiO nanostructures is directly grown or deposited on metal current collector [40-47]. This approach has the advantages of no binder usage and typically better rate capability.

2.2.2.2. Directly deposited/grown NiO on planar current collector

Direct deposition/growth of active material on current collector is an interesting method to fabricate anode materials that undergo large volume changes during lithiation/delithiation. While this method does not use additional binder, it is able to minimize the pulverization of active material due to its unique structure [48-50]. This method could achieve a good NiO performance as shown in Table 2-1. In addition, it is in favor of easy electron transport and small Li-ion diffusion distance. Figure 2-4 illustrates directly coated/grown NiO on a planar current collector.

The limitation of directly grown/deposited NiO is that the performance of NiO worsens as the initial thickness of NiO increases. Since NiO thickness is limited, the areal capacity of the anode is also limited. One solution to this problem is to use 3D current collector to increase the mass loading of active material. Ni foam, an interconnected 3D mesoporous Ni open network, has a large surface area, a good electrical conductivity, a strong mechanical characteristic and a high flexibility.

<p>Tilted view of SEM image of the NiO nanowalls [40]</p>	<p>SEM image of nanorods [41]</p>
<p>Cross-section SEM (X-SEM) image of NiO coated Si nanowire array film [42]</p>	<p>SEM image of Ni-coated NiO arrays [43]</p>
<p>SEM image of two-layer porous NiO film (side view presented in inset) [44]</p>	<p>SEM image of NiO deposited on Si substrate [45]</p>
<p>SEM image of as-deposited NiO [46]</p>	<p>Surface morphology of NiO film [47]</p>

Figure 2-4 - Illustrations of directly deposited/grown NiO on current collector [40-47].

2.2.2.3. Directly deposited/grown NiO on 3D current collector

The 3D current collector has advantages of low ionic and electronic resistance due to large surface area that increase NiO-electrolyte contact and highly-interconnected network of current collector. Deposition on planar substrate resulted in less specific capacity compared to on 3D substrate, as shown in Figure 2-5.

Figure 2-6 and Table 2-1 shows the images and performance of directly grown/deposited NiO on 3D Ni foam, respectively. [48, 51-60] The limitation of these reports is that they used a series of complex step, which is less suitable for industrial application. They also still had a limited mass loading although 3D substrate has been used.

Figure 2-5 - Better cycle performance using 3D Ni foam as current collector [51].

Figure 2-6 - Illustrations of directly deposited/grown NiO on Ni foam [48, 51-53, 55-60].

2.2.2.4. NiO-C composites

In order to improve the performance of nanostructure NiO, the incorporation of carbon composite (graphitic, amorphous, graphene nanosheet and/or multi-wall carbon nanotube) [61-68] has been reported as an effective method to achieve a good cycle life. Figure 2-7 shows the literature of carbon usage to improve NiO performance.

The performance of NiO-C composite can be found in Table 2-1. This method has a limitation of composite's low specific capacity depending on the percentage of carbon. The amount of incorporated carbon should be optimized to achieve a balanced performance of specific capacity and cycle life.

<p>SEM image of spherical NiO-C composite [61]</p>	<p>TEM image of NiO-C nanocomposite [62]</p>
<p>TEM image of NiO-C composite [63]</p>	<p>SEM image of annealed NiO/C hybrid microspheres [64]</p>
<p>Schematic illustration of the 3D-hierarchical NiO-GNS composite [65]</p>	<p>TEM image of NiO/C nanocomposite [66]</p>
<p>Schematic of hierarchically porous NiO/carbon composite [67]</p>	<p>SEM image of NiO/MWCNT composite [68]</p>

Figure 2-7 - Illustrations of the usage of carbon (graphitic, amorphous, graphene nanosheet and/or multi-wall carbon nanotube) to improve NiO performance [61-68].

Table 2-1 - The performance of NiO-based anodes in the literature.

Approach	Name	Specific capacity (mA h g ⁻¹)	Rate (mA g ⁻¹)	No of cycle (cycles)	Ref.
NiO nanostructures	Highly ordered mesoporous NiO	680	71.7	50	[31]
	NiO-Ni composite	~650	100	50	[34]
	NiO nanoshafts	410	50	30	[35]
	Hollow microspheres of NiO	560	100	45	[36]
	NiO nanoflakes	1015	100	50	[37]
	NiO nanotubes	~160	0.025	20	[38]
	Hollow spherical NiO particles	547	100	40	[39]
Directly deposited/grown NiO on planar current collector	NiO nanowall on Ni foil	~638	895	85	[40]
	NiO nanorods on alloy-600-foil	~350	0.01 mA cm ⁻²	20	[41]
	Ordered NiO coated Si nanowire	~750	50	30	[42]
	Ni-coated NiO arrays on Ti substrate	647.8	100	50	[43]
	Two-layer porous NiO film on Ni foil	501	359	50	[44]
	Nanocrystalline NiO film	~480	10 μ A cm ⁻²	100	[45]
	Nanocrystalline NiO film	~775	80 μ A cm ⁻²	100	[46]
Directly deposited/grown NiO on 3D current collector	Bias-sputter-deposited nanocrystalline NiO thin films	720	~104	30	[47]
	Electrodeposited NiO films on Ni foam	651	79	50	[51]
	Porous NiO on Ni foam	~525	144	30	[52]
	Porous NiO/polyaniline film on Ni foam	520	718	50	[53]
	Porous NiO films on Ni foam	558	718	100	[54]
	Porous core-shell structured Ni/NiO	646	156	65	[55]
	Nanostructured NiO	746	144	10	[56]
	Porous NiO-Ni composite	~375	286	100	[57]
	Nanoporous NiO films	543	144	100	[58]
	Sandwich-like NiO film	400	1436	50	[59]
	NiO nanocone array	1058	287	100	[48]
	Mesoporous NiO nanosheet networks	1043	144	80	[60]
NiO-C composites	Spherical NiO-C composite	430	359	40	[61]
	Net-structured NiO-C composite	429	71.8	40	[62]
	Spray pyrolyzed NiO-C composite	428	100	50	[63]
	NiO/C hybrid microspheres	387	30	20	[64]
	NiO-graphene nanosheet composite	1065	200	50	[65]
	Nanostructured NiO/C composite	~460	60	40	[66]
	Biotemplated porous NiO/C composite	698	71.8	10	[67]
	NiO/MWCNT composite	~800	50	50	[68]

2.3. Alloying type anode

2.3.1. Introduction

Several metals, such as Si, Ge and Al could form alloys with Li. One could refer to the phase diagram for the existence of metal-Li alloy phase. Figure 2-8 shows the phase diagram of Ge and Li. There exist alloy phases such as Ge_2Li_7 , $\text{Ge}_4\text{Li}_{15}$ and $\text{Ge}_5\text{Li}_{22}$. However, during battery lithiation, the mechanism and the formed-phase might be different than that in phase diagram. This is because the phase diagram is based on equilibrium (thermodynamically limited) while battery lithiation/delithiation is kinetically limited.

Figure 2-8 - Ge-Li phase diagram [69].

2.3.2. Ge anode

Ge is a promising anode active material for Li-ion batteries. It has the following merits of:

- high Li-ion diffusion coefficient; It was reported that the diffusivity of Li-ion in Ge might be over 400 times higher than diffusivity of Li-ion in Si at room temperature [70, 71];

- b) high electrical conductivity; Ge has a band gap of 0.67 eV which is smaller than Si band gap of 1.11 eV [72];
- c) high specific capacity; Ge theoretical specific capacity of 1624 mA h g⁻¹ (Li₂₂Ge₅) or 1384 mA h g⁻¹ (Li₁₅Ge₄) are higher than graphite theoretical specific capacity of 372 mA h g⁻¹ [71, 73].

Ge, belonging to an alloying-type anode, has the problems of agglomeration and pulverization during lithiation/delithiation that result in cracking or delamination, leading to poor cycle performance.

Many approaches were used to tackle these problems and improve the performance of Ge anode, such as Ge nanoparticles [74, 75], Ge nanowires [29, 76-79], Ge nanotubes [80, 81], Ge-carbon composites [82-94], Ge-graphene composites [95-102], Ge thin-film [71, 103-105], other unique structures [106-113], etc.

2.3.2.1. Ge nanoparticles

Ge nanoparticles were used because of facile strain release and short Li-ion diffusion length at nano-scale. Performance of porous 3D nanoparticles assembly was better than that of hollow 0D nanoparticles assembly [74]. This indicates that long-range ordering of porous Ge is important, see Figure 2-9 [74]. Figure 2-10 shows that capping ligand had an important role in controlling the irreversible capacity of Ge nanoparticles [75]. However, Ge nanoparticles had a problem of agglomeration during lithiation/delithiation.

Figure 2-9 - Scanning Electron Microscopy (SEM) image of 3D porous Ge nanoparticle assembly with long-range ordering [74].

Figure 2-10 - Transmission Electron Microscopy (TEM) image of butyl-capped Ge nanoparticles [75].

2.3.2.2. *Ge nanowires*

Chan et al. [29] was among the first to propose Ge nanowires for Li-ion battery anode. The nanowire structure has the advantage to accommodate the volume change during lithiation/delithiation. The Ge nanowire grown directly onto current collector has the advantage of direct connection of efficient electron transport. The illustrations of directly grown Ge nanowire could be seen in Figure 2-11. Although Ge nanowire structure has a good performance, see Table 2-2, Ge nanowire structure has a weakness of low active mass loading that limited the areal capacity.

Figure 2-12 shows Ge nanowires assembled using slurry-based method. Yuan et al. [76] used dodecanethiol-passivated Ge nanowires to form robust network through C-F bonding. Chockla et al. [78] showed the importance of

Fluoroethylene Carbonate (FEC) additive to cycle life of slurries-based Ge nanowire. This approach had a limitation of complex fabrication process.

Figure 2-11 - Illustrations of Ge nanowires grown directly on substrate [29, 77, 79].

Figure 2-12 - Illustrations of Ge nanowires assembled using slurry casting method [76, 78].

2.3.2.3. Ge nanotubes

Ge nanotubes, as shown in Figure 2-13, have more surface area than Ge nanowires. However, this approach has weaknesses of: 1) the fabrication of Ge nanotubes required a complex process and 2) low Ge mass loading limited the areal capacity.

Figure 2-13 - Illustrations of Ge nanotubes [80, 81].

2.3.2.4. *Ge-carbon composites*

To enhance the performance of Ge, carbon (graphitic, amorphous, single-wall and/or multi-wall carbon nanotube) was incorporated as a conducting agent for the electron and a buffer absorbing mechanical stress of Ge during lithiation/delithiation. Figure 2-14 and Figure 2-15 show the illustrations of Ge-carbon composite using slurry based and directly grown/deposited based assembly methods, respectively. The limitation of these anodes is that the carbonaceous buffer of Ge-C composites might significantly reduce the theoretical specific capacity. Thus, it is important to control the percentage of carbon in the composite.

<p>SEM image of Ge NWs entangled with GNFs. Inset: pristine GNFs [82]</p>	<p>SEM image and corresponding EPMA mapping of Ge-PVA [84]</p>
<p>SEM image of Ge-SWCNT [85]</p>	<p>TEM image of C/Ge composite [86]</p>
<p>Synthesis of Ge/C [87]</p>	<p>SEM image of n-C/Ge [88]</p>
<p>TEM image of C-coated Ge-NWs [89]</p>	<p>SEM image of PC-Ge NW [92]</p>
<p>SEM image of Ge/Cu₃Ge/C composite [94]</p>	

Figure 2-14 - Illustrations of the usage of carbon (graphitic, amorphous, single-wall and/or multi-wall carbon nanotube) to enhance the performance of slurry-based Ge [82, 84-89, 92, 94].

Figure 2-15 - Illustrations of the usage of carbon (graphitic, amorphous, single-wall and/or multi-wall carbon nanotube) to enhance the performance directly grown/deposited Ge [83, 90, 91, 93].

2.3.2.5. Ge-graphene composites

Graphene sheets were used to improve the Ge anode, as shown in Figure 2-16. Reduced graphene oxide was used to support Ge nanowire [95]. Since graphene sheet incorporation has the limitations of low utilization of Ge and agglomeration problem, direct coating of graphene is proposed.

Graphene coating was used because it is strong, electrically conducting, and does not hinder the Li-ion diffusion. Table 2-2 shows the excellent performance of Ge-graphene composite. However, this method needs a complex processing. Also, the majority of Ge-graphene composite had the limitation of low utilization of Ge.

Figure 2-16 - Illustrations of Ge utilizing graphene sheets [95, 96, 99, 100].

Figure 2-17 - Illustrations of Ge utilizing graphene coating [97, 98, 101].

2.3.2.6. *Ge films*

Deposition of Ge film directly onto the current collector [71, 103-105] has the advantages of no trade-off to the specific and volumetric capacity due to binderless process and high density Ge film, respectively, as illustrated in Figure 2-18. Table 2-2 shows Ge films have high specific capacities. However, the Ge films used thin Ge that limited the areal capacity [71, 103, 105]. As an example, since the Ge thickness of reference [103] was only 140 nm, the areal capacity was limited to $\sim 0.1 \text{ mA h cm}^{-2}$ which might not be qualified for commercial purpose.

There is a challenge to use thick Ge film as Li-ion battery anode since the cycle performance of Ge film depends on the initial Ge thickness. When Ge thickness is higher than the critical thickness, the cycle performance degrades because of the pulverization and/or delamination. An approach to tackle the problem is to use rough substrate / 3D substrate because lower Ge thickness is needed in rough substrate / 3D substrate to achieve the same mass loading compared to planar substrate. The usage of rough substrate [104] was consistent with the work from our group. [49]

Figure 2-18 - Illustrations of Ge film as Li-ion battery anode [71, 103-105].

2.3.2.7. Unique Ge structures

Figure 2-19 shows unique structures fabricated and assembled using slurry based method, while Figure 2-20 illustrates the unique structures that directly connected to current collector. Table 2-2 shows the unique structures had excellent performances. However, the unique Ge structures require complex fabrication processes.

Figure 2-19 - Illustrations of unique structure of slurry-based Ge [107-110].

Figure 2-20 - Illustrations of unique structure of directly grown/deposited Ge [106, 111-113].

Table 2-2 - The performance of Ge-based anodes in the literature.

Approach	Name	Specific capacity (mA h g ⁻¹)	Rate (mA g ⁻¹)	No of cycle (cycles)	Ref.
Ge nanoparticles	Porous 3D nanoparticles assembly	1415	1600	100	[74]
	Butyl-capped Ge nanoparticles	1470	300	30	[75]
Ge nanowires	Ge nanowires	1141	80	20	[29]
	Ge nanowires using tin (Sn) catalyst	1000	640	50	[77]
	Ge nanowires (Au catalyst & Ge:Sn)	~900	1600	50	[79]
	Dodecanethiol-passivated Ge nanowires	1130	138.4	100	[76]
	Ge nanowire with FEC additive	1248	138.4	100	[78]
Ge nanotubes	Ge–Antimony (Sb) core-shell nanowire	1002	320	50	[80]
	Ge nanotubes on SS substrate	~1300	80	20	[81]
Ge-carbon(graphitic, amorphous, single-wall and/or multi-wall carbon nanotube) composites	Graphite nanofiber–Ge nanowire	~1200	160	30	[82]
	Ballmilled Ge-mesocarbon microbeads	473	100	50	[84]
	Pyrolyzed Ge-poly(vinyl alcohol)	579	100	50	[84]
	Free-standing SWCNT–Ge (20 % w/w)	~775	74	10	[85]
	Embedded Ge in C	545.1	160	30	[86]
	Clustered Ge/C composite	~1200	320	50	[87]
	Ge NPs encapsulated with carbon	~900	150	50	[88]
	Carbon sheathed Ge nanowire	758	800	100	[89]
	Porous carbon–Ge NW composite	789	160	50	[92]
	Ge/Cu ₃ Ge/C composite	~530	100	50	[94]
	Ge–CNT–Cu composite	800	150	100	[83]
	Ge–MWCNT network	810	1600	200	[90]
	Ge nanoparticles–free standing SWCNT	~750	100	5	[91]
	Ge nanoparticles-carbon hybrids	1389	1600	50	[93]
Ge-graphene composites	RGO-supported Ge nanowire	600	65.4	20	[95]
	Ge nanoparticles–graphene composite	~600	200	15	[100]
	Ge–graphene composite	675	400	400	[96]
	In situ Ge nanoparticles–graphene	832	162.4	50	[99]
	Ge–RGO hybrids	1100	162.4	50	[101]
	Graphene-coated Ge nanowires	1059	6496	200	[97]
	Graphene-encapsulated Ge nanowires	1400	1600	50	[98]
	Ge@C/RGO	~940	50	50	[102]

Table 2-2 continues to the next page 32

Ge films	Amorphous Ge on planar Ni	1700	375	60	[71]
	Amorphous Ge (n-type doping)	~1460	100 $\mu\text{A cm}^{-2}$	180	[105]
	Ion-beam treated Ge thin film	~1500	649.2	25	[103]
	Ge film on a rough Cu foil	1000	167 $\mu\text{A cm}^{-2}$	50	[104]
Unique Ge structures	Ge nanopowder (FEC co-solvent)	1152	1624	200	[107]
	Mesoporous Ge	789	150	20	[108]
	Ge-Sn nanocrystals ($\text{Ge}_{0.95}\text{Sn}_{0.05}$)	1010	162.4	50	[109]
	Ge-Sn composite	~711	440	50	[110]
	Ge inverse opal with porous walls	~1134	320	100	[106]
	Cu-Ge core-shell nanowire	1419	800	40	[111]
	3D bicontinuous Au/amorphous Ge	1066	320	100	[112]
	Nanostructured ion beam-modified Ge film	1260	222	25	[113]

2.4. Summary

In this chapter, the development of the anode of Li-ion battery is summarized. The conversion-type and alloying-type anodes were described. NiO and Ge were reviewed in details.

Conversion-type anode, such as NiO, had a higher theoretical capacity than intercalation-type graphite. NiO nanostructures had a better resistance to pulverization than bulk NiO. However, NiO nanostructures suffered from aggregation during lithiation/delithiation and poor rate capability. Nanostructured NiO directly coated/grown on substrate had a better cycle life and rate capability than slurry-based nanostructured NiO, but limited by low mass loading which consequently limited the areal capacity. The usage of 3D Ni foam than planar current collector could increase the mass loading and areal capacity of directly coated/grown nanostructured NiO. However, most reports using 3D Ni foam still had a limited mass loading and complex fabrication steps. An approach to improve the cycle life of NiO was to incorporate carbon (graphitic, amorphous, graphene nanosheet and/or multi-

wall carbon nanotube) composite. From here, we could see potential research areas of: 1) combining the approaches of 3D current collector and carbon (graphitic and amorphous) coating of a directly-grown nanostructured NiO and 2) investigating the usefulness of vertically-aligned MWCNTs to NiO performances.

Alloying-type anode, such as Ge, had the highest theoretical capacity compared to intercalation-type graphite and conversion-type NiO anodes. Among alloying-type anodes, Ge has higher electrical conductivity and Li-ion diffusion than those of Si. Ge faced a problem of pulverization of the active material during lithiation/delithiation. Ge nanoparticles had a minimal pulverization problem but suffered from agglomeration during lithiation/delithiation. Ge nanowires and Ge nanotubes suffered from low active mass loading and complex fabrication process. Depending on the carbon percentage, the Ge-carbon and Ge-graphene composites might have low specific capacities. Ge thin-film and other unique structures suffered from low active mass loading and complex fabrication process, respectively. Majority of the literature investigated crystalline-based Ge, while a few investigated amorphous Ge. Moving forward, we could see potential research areas of: 1) investigating the effect of Ge microstructures to the performance of Li-ion battery anode and 2) investigating the performance of thick Ge film and finding a way to improve it.

Chapter 3 : Experimental methods

3.1. Introduction

The key process systems, including Atmospheric-Pressure Chemical Vapor Deposition (APCVD), furnace, Plasma-Enhanced Chemical Vapor Deposition (PECVD), Direct Current (DC) and Radio Frequency (RF) sputtering, Low-Pressure Chemical Vapor Deposition (LPCVD) and battery assembly tools are introduced in this chapter. The characterization methods of battery cycle test, Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) are briefly reviewed. The physical characterization techniques, such as Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and Raman spectroscopy are also briefly reviewed.

3.2. Key process systems

3.2.1. APCVD

The APCVD uses ethanol bubbler with carrier gas of Argon (Ar) and Hydrogen (H_2), see Figure 3-1. The ethanol decomposes and reacts at high temperature in the tube chamber that produces carbon coating (graphitic, amorphous, single-wall and/or multi-wall carbon nanotube) onto substrates. The chamber operates at atmospheric pressure. The residual gases are disposed via exhaust. The APCVD was used to fabricate NiO-C composites that discussed in Chapter 4.

Figure 3-1 - Schematic of simplified APCVD system.

3.2.2. Furnace

The furnace is illustrated in Figure 3-2. The chamber is filled with air. Samples are placed at the bottom center of the chamber. The furnace was used to fabricate NiO-C composite and annealed Ge that discussed in Chapters 4 and 7, respectively.

Figure 3-2 - Schematic of simplified furnace system.

3.2.3. PECVD

Figure 3-3 shows the schematic of PECVD. The PECVD with plasma of Ammonia (NH_3) and Acetylene (C_2H_2) was used to fabricate vertically-aligned MWCNT in Chapters 5 and 6. The plasma has the roles of aligning the MWCNTs and providing energy for the decomposition of C_2H_2 .

Figure 3-3 - Schematic of simplified PECVD system.

3.2.4. Sputtering

There are two mode of sputtering: DC and RF, as shown in Figure 3-4. RF sputtering is mainly used for non-conductive target. On the other hand, conductive target can be used with either DC or RF sputtering. DC sputtering has higher deposition rate than RF sputtering. DC sputtering of Ni target was used in Chapters 5 and 6. RF sputtering of Ge target was used in Chapter 7.

Figure 3-4 - Schematic of simplified sputtering system. Image adapted from reference [114].

The sputtering mainly uses Ar to form plasma. Reactive sputtering uses a mixture of gases where one of them is reactive. Reactive DC sputtering of Ti target was used in Chapters 5, 6 and 7. Ti was deposited using DC sputtering using Ar gas. By adding Nitrogen (N_2) gas, the Titanium Nitride (TiN) was

deposited using reactive DC sputtering. The reactive RF sputtering of Ni target using Ar and Oxygen (O_2) gas to deposit NiO was used in Chapter 5.

3.2.5. LPCVD

The LPCVD has an ultra-high vacuum to maintain a low pressure inside the chamber. Figure 3-5 shows the schematic of LPCVD system. LPCVD was used to deposit polycrystalline Ge that discussed in Chapter 6.

Figure 3-5 - Schematic of simplified LPCVD system.

3.2.6. Battery assembly

In order to assemble the Li-ion batteries, specialized equipments are needed. First, the mass of the active materials is determined using microbalance as shown in Figure 3-6. Mettler Toledo XP26 DeltaRange balance with readability of 0.002 mg was used to measure the mass of the active material accurately.

Figure 3-6 - Mettler Toledo XP26 DeltaRange balance.

Second, after the mass is measured, the samples are transferred to an inert glove box. The glove box uses Ar gas with very low concentration of O₂ and moisture level less of than 5 ppm. Figure 3-7 shows that our glove box manufactured by Innovative Technology, USA.

Figure 3-7 - Ar-filled glove box.

Third, to assemble the coin-cell battery, a manual crimping machine was used, as shown in Figure 3-8. The machine is placed inside the glove box. The machine can also perform disassembly of coin-cell battery, by changing the removable parts.

Figure 3-8 - MSK-110 hydraulic crimping machine.

3.3. Electrochemical characterization

3.3.1. Neware battery cycle test

The battery cycle test is performed to measure the stability of the battery performance after predetermined cycles. The minimum cycle life in our experiments is typically 50 cycles. One cycle consists of one discharge and one charge action. The cycle testing is under constant current discharge until a lower limit voltage followed by 1 minute rest, then constant current charge until an upper limit voltage, followed by 1 minute rest, see Figure 3-9. This procedure was repeated for n times. We also input the mass of the sample. The data were measured at 5-seconds interval. The acquired data are: potential, time, current, capacity, specific capacity, etc.

Table Step	Script Step									
Step	Step Type	Time(min:sec)	Voltage(V)	Current(mA)	Cap(mAh)	Energy(mWh)	ΔV (mV)	Power(mW)	Load(m Ω)	Current(mA)
1	Rest	01:00								
2	CC_DChg		0.0100	0.115						
3	Rest	01:00								
4	CC_Chg		1.2000	0.115						
5	Cycle	Cycle Count: 100								
6	Stop									

Figure 3-9 - Programming the Neware battery tester.

Figure 3-10 shows Neware battery tester has 8 channels per unit at an affordable cost. The multi-channel ability is very important during the experiment as each measurement might take weeks to months. The Neware battery testers come with rated current (maximum current) of 1, 2, 5, 10, 20 and 50 mA. One needs to select the correct rated current to get the acceptable accuracy.

Placing the battery testing system in a customized cabinet regulates the temperature to be around 33 °C. Without this enclosure, the temperature will change significantly in the whole day, hence affecting the observed results. The measurement is sensitive to the temperature.

Figure 3-10 - Neware multi-channel battery tester.

3.3.2. Autolab workstation

The Autolab workstation is powerful equipment for electrochemical characterizations. The specifications are: 1 MHz to 10 μ Hz frequency range, 0.003% applied frequency resolution, 0.2 mV to 0.35 V Root Mean Square (RMS) of alternating current (AC) amplitude and 10 V input range. We used the Autolab to perform CV and EIS.

Figure 3-11 - The Autolab modular multi potentiostat/galvanostat. [115]

CV is a popular technique in electrochemistry. It has an easy setup that provides the overview of the electrochemical interface. CV used only DC signal and two-electrode configuration. CV is performed by applying a potential sweep. A cycle consists of potential sweep from 1.2 to 0.01 V followed by 0.01 to 1.2 V. The current is measured as a function of potential

and number of cycle. The result consists of valleys and peaks which are easily recognizable in the cathodic and anodic scan.

The DC method has a limitation of only showing the sum of individual response. To retrieve more information, a small AC signal is used alongside with the DC signal in EIS method. EIS is able to distinguish the individual response, i.e. EIS is able to distinguish individual resistance value, while DC potential-sweep is only able to obtain the sum of resistance value.

EIS is a study of the variation of the impedance of an electrochemical system with the frequency of a small-amplitude AC perturbation. EIS is a non destructive method. The measured system is still at equilibrium. The EIS measures the I_{ac} and V_{ac} for each frequency. The NOVA software presents the results of Nyquist and Bode plots. The data can also be fitted to equivalent circuits. The knowledge of the system is required during fitting.

EIS needs the following condition to be able to measure correctly.

- a) Linearity: The applied AC amplitude is small that the cell response in the linear region. But, the applied AC amplitude should be big enough so that response can be measured well.
- b) Stability: The state of the system should not change significantly during EIS measurement. Measurement starts from a high frequency to lower frequency since the experiment time is dominated by the low frequency. Typically, a setup of 100 kHz to 0.05 Hz with automatic current range determination takes about 5 minutes to complete.
- c) Causality: The measured AC response of the system should be directly correlated to the applied AC stimulus. Faraday cage should be used for noisy environment.

To check the validity of EIS results, Kronig-Kramers algorithm can be used to make sure the EIS meet the linearity, causality and stability requirements. The shape of Lissajous plot can also be used to detect the non-linear behavior. Outliers in low frequency data need to be removed.

3.4. Physical characterization

3.4.1. SEM

SEM is used to characterize the surface morphology of the anode samples. As electron beams reach the sample surface, the interaction takes place to form secondary electrons, backscatter electrons, characteristic X-ray, etc. In this thesis, we used secondary electron to characterize the morphology and topography of the anode samples. The SEM was used in Chapters 4 to 7 to characterize the morphology and topography of the samples.

3.4.2. EDS

EDS is used to characterize the composition of the anode samples. In SEM chamber, due to the electron beams - sample interaction, electron in the lower energy levels of the sample might be knocked-out and removed. Then the electron in the higher energy levels fills the empty levels left by knocked electrons. This creates characteristic X-ray that is inherent properties of material. The EDS detector inside the SEM chamber collects these characteristic X-rays. The EDS measures the emitted X-ray and determines the composition of sample. The EDS was used to characterize the composition in Chapters 4 and 7.

3.4.3. TEM

TEM operates by focusing a beam of electrons through a very thin sample (in the order of tens to hundreds nm). When the electron beams

transmitted through the sample, the majority of the electrons passed through without change in energy, but some electrons are diffracted by the sample lattice. TEM is able to observe the morphology at the atomic level. In this study, the TEM was used in Chapters 4 to 7 for structure characterization.

3.4.4. XRD

XRD is used to identify the composition of crystalline materials. If the sample has ordered lattices (crystalline), the incident X-ray s are diffracted according to the Bragg's law of $2d_{hkl} \sin \theta = n\lambda$, where d_{hkl} is the distance between the lattice planes (hkl), θ is the angle of incidence, n is an integer and λ is the X-ray wavelength.

The detector collected the interference of the diffracted X-rays as a function of 2θ . The peak position and intensity can be compared with database of Powder Diffraction File. In this study, XRD was used in Chapters 4 to 7.

3.4.5. Raman

The Raman spectroscopy uses a laser light to hit the sample and measures the frequency and intensity of the scattered light. In this case, most of the photon are elastically scattered, but some are inelastically scattered (having different energy and frequency). The Raman spectroscopy relies on the inelastic scattering properties of photon. The intensity of the inelastic scattering photon is detected as a function of Raman frequency shift. In this study, Raman spectroscopy was used in Chapters 4 to 7.

3.5. Summary

We discussed the various types of key systems for fabrication processes as well as the electrochemical and physical characterization techniques. Their operating principles and applications in this project were briefly discussed.

Chapter 4 : Nickel oxide-carbon composite (NiO-C) for Li-ion battery anodes

4.1. Introduction

We have mentioned in Chapter 2 that NiO nanostructures [31-39] assembled using slurry casting method have weaknesses of poor attachment to the current collector and pulverization during lithiation/delithiation if the binder is not optimized. An approach to replace the slurry with directly grown NiO nanostructures on metal current collectors [40-47] has the advantages of typically better rate capability. It is also noted that the usage of 3D current collectors improved the anode performance in comparison with planar current collectors. [48, 51-60] In addition, the incorporation of carbon (graphitic, amorphous, graphene nanosheet and/or multi-wall carbon nanotube) composite [61-68] was reported as an effective method to achieve a good cycle life. To our knowledge, no report combined both approaches of using 3D current collector and carbon (graphitic and amorphous) composite to achieve the graphitic and amorphous carbon coating on grown NiO nanostructures on 3D interconnected metal current collectors. This is because NiO could be reduced to Ni at high temperatures when coating the carbon in H₂ environment.

In this chapter, we presented a simple technical approach to achieve graphitic and amorphous carbon coating on grown NiO nanostructures on 3D interconnected metal current collectors, which could maintain the excellent

cycle life by incorporating nanostructure, 3D interconnected metal current collectors and coating of graphitic and amorphous carbon. Furthermore, a large mass loading up to around 4.5 mg cm^{-2} could be achieved, compared with other reported anodes ($< 1.0 \text{ mg cm}^{-2}$). [54, 58, 59] Finally, compared to several reported techniques of incorporating carbon [61-67], our approach is very simple that involves only CVD of ethanol & thermal annealing in air.

4.2. Methodology

4.2.1. Sample preparation

4.2.1.1. Fabrication of NiO-C

Figure 4-1a shows the schematic of the fabrication steps of NiO-C sample. Ni foam (Latech Scientific Supply Pte. Ltd., $0.03 - 0.04 \text{ m}^2 \text{ g}^{-1}$ specific surface area, $>96 \%$ porosity, 100-110 pores per inch, $600-700 \text{ g m}^{-2}$ area density, 2 mm thickness) was cut into 1.2 cm diameter disks and cleaned using ultrasound for 30 minutes in propan-2-ol and then dried inside vacuum oven at $80 \text{ }^\circ\text{C}$ for 4 hours.

First, the carbon (graphitic, amorphous and multi-wall nanotube) was formed by heating the Ni foam disks at $650 \text{ }^\circ\text{C}$ for 20 minutes inside a tube furnace where ethanol was bubbled using a mixture of 200 sccm Ar and 50 sccm H_2 gas. The ramp up (down) time was 20 (70) minutes. During the ramp up and down processes, a mixture of 200 sccm Ar and 50 sccm H_2 gas was flowed directly without going through ethanol bubbler. We found that gas flow rate and temperature distribution inside the furnace affected the reproducibility of the samples. In the experiments, the sample locations and experimental conditions were carefully controlled.

Second, the obtained carbon coated Ni foam (Ni-C) was heated inside a Thermolyne Type 47900 furnace at 500 °C for 6 hours in air, to oxidize the Ni to nickel oxide, i.e., NiO-C. The mass of the samples was measured using Mettler Toledo XP26 DeltaRange balance with readability of 0.002 mg.

Figure 4-1 - Schematic of the fabrication steps of (a) NiO-C (b) NiO and (c) Ni-C samples.

4.2.1.2. Fabrication of NiO

Figure 4-1b shows the schematic of NiO fabrication step. NiO fabrication was done by heating the Ni foam disks inside a Thermolyne Type 47900 furnace at 500 °C for 6 hours in air. The NiO was used as the control sample.

4.2.1.3. Fabrication of Ni-C

For comparison, Ni-C samples were fabricated. The Ni-C fabrication was followed the same procedure as NiO-C electrode, except without oxidizing Ni using Thermolyne Type 47900 furnace. Figure 4-1c shows the schematic of Ni-C fabrication process.

4.2.2. Physical characterization

SEM of LEO 1550 Gemini was used to characterize the morphology of the samples. The SEM accelerating voltage was set to 5 kV. Raman Spectroscopy of WITec with excitation wavelength of 532 nm and XRD of Siemens D5005 with Cu K α of 0.154 nm were used to characterize nickel oxide and carbon structures of the samples. TEM of JEOL 2010 was used to characterize the presence of nickel oxide and carbon in NiO-C. The TEM accelerating voltage was set to 200 kV. Thermogravimetric Analysis (TGA) was performed using Shimadzu DTG-60H from 30 to 750 °C at heating rate of 5 °C/min under dry air.

4.2.3. Half-cell fabrication

The samples, Celgard-2300 separator and pure Li metal were assembled in coin cells (2032) inside an Ar glove box (Innovative Technology, USA) in which O₂ and moisture levels were less than 5 ppm. The liquid electrolyte used was 1 M Lithium Hexafluorophosphate (LiPF₆) dissolved in Ethylene Carbonate (EC) and Diethyl Carbonate (DEC) with EC: DEC composition of 1:1 by volume. Since NiO, Ni-C and NiO-C anodes were tested against Li metal in a half-cell configuration, we refer them as NiO, Ni-C and NiO-C samples, respectively.

4.2.4. Electrochemical characterization

Battery cycle life testing was carried out using Neware battery testers. CV and EIS were performed using Autolab machine.

4.3. Results and discussion

From Figure 4-2a, one can see that all samples had Ni peaks at 44.49° , 51.86° , and 76.41° which correspond to Ni(111), Ni(200), and Ni(220), respectively (PDF No. 4-850, Face-centered cubic, Fm3m).

The NiO and NiO-C samples showed the peaks at 37.25° , 43.29° , and 62.90° , corresponding to NiO(101), NiO(012) and NiO(104), respectively (PDF No. 44-1159, Rhombohedral, R-3m). A weak and broad carbon peak at about 26.4° could be observed in Ni-C and NiO-C samples. This confirms the existence of amorphous carbon in the two samples.

No Raman peak was found from Ni foam, see Figure 4-2b. The NiO-C and Ni-C samples have carbon peaks at about 1352 cm^{-1} (D band), 1590 cm^{-1} (G band) and shoulder at about 1625 cm^{-1} (D' band), suggesting the existence of graphitic carbon.

The ratio of the D to G bands of NiO-C and Ni-C sample were 1.20 and 1.94, respectively, suggesting that some carbon structural defects (the origin of the D peak) in the NiO-C sample might be annealed out during the high temperature oxidation process. [116] The shoulder peak at 1625 cm^{-1} corresponds to another disorder-induced band from carbon. In addition, second-order bands of carbon [116] at about 2700 cm^{-1} and 2950 cm^{-1} were observed for both NiO-C and Ni-C sample.

The Raman spectra of NiO-C and NiO show a broad peak at about 520 cm^{-1} , which can be attributed to Ni-O stretching mode [55, 117], and other

peaks at about 1100 cm^{-1} and 1500 cm^{-1} due to 2LO (two-longitudinal-optical) and 2M (two-magnon) phonon modes of NiO, respectively [118]. The peaks at 1100 cm^{-1} and 1500 cm^{-1} on NiO-C sample were not clearly shown due to high intensity of the D, G, and D' carbon peaks.

Figure 4-2 - (a) The XRD spectra and (b) The Raman spectra of NiO-C, NiO, and Ni-C samples as well as Ni foam substrate, respectively.

Figure 4-3 shows the SEM images of Ni foam, Ni-C, NiO, and NiO-C samples before battery assembly. Initially, Ni foam (Figure 4-3a and Figure 4-3b) had a smooth surface with obvious grain boundaries. Ni-C (Figure 4-3c) has MWCNTs (Figure 4-4c) and other carbon allotropes (Figure 4-3d). NiO, which is the control sample, shows a uniform surface of nanostructure (Figure 4-3e and Figure 4-3f). On NiO-C samples, as Ni was previously roughened

due to carbon deposition, the nickel oxide in NiO-C samples was found to grow non-uniformly, see Figure 4-3g.

Figure 4-3 - SEM images of (a, b) Ni foam, (c, d) Ni-C sample, (e, f) NiO sample, (g, h) NiO-C sample.

Figure 4-4 - Comparison of (a) NiO and (b) NiO-C at high magnification. Comparison of (c) Ni-C and (d) NiO-C at carbon nanotubes area.

The NiO-C sample consisted of mainly two regions: the carbon-rich and the NiO-rich region, shown as dark and bright area, respectively, in Figure 4-3g. The NiO-rich region was located at location 1, while the carbon-rich region was located at location 2, in Figure 4-5a. The EDS showed that in all locations, nickel oxide and carbon were present, as shown in Figure 4-5b.

Figure 4-5 - (a) SEM image of NiO-C sample. (b) The EDS shows NiO-rich and carbon-rich regions.

The nanostructure of nickel oxide in the NiO-C sample (Figure 4-3h) looks similar to that in the NiO sample (Figure 4-3f). However, the nickel oxide in NiO-C sample (Figure 4-4b) looks slightly finer than that in the NiO sample (Figure 4-4a).

From the TEM image in Figure 4-6, the thickness of carbon in NiO-rich region of NiO-C sample was found to be about few nm. We cut NiO and NiO-C samples and performed cross-section SEM (X-SEM) and found the following. The thickness of carbon in carbon-rich region of NiO-C sample was ~ 1130 nm, while the thickness of carbon in Ni-C sample was ~ 1153 nm. The thickness of nickel oxide in NiO-C sample and NiO sample were ~ 221 nm and 206.9 nm, respectively. Note that the thickness value presented serves only as a rough guide, as it might not be uniform across the samples.

During thermal oxidation of Ni-C sample at 500 °C for 6 hours, although the MWCNTs were significantly removed (Figure 4-4d), the amorphous carbon and graphitic carbon, as well as nickel oxide, were present in the NiO-C sample. Significant amount of graphitic and amorphous carbon still survives and eventually incorporates into the nickel oxide, as evidenced by XRD (Figure 4-2a), Raman (Figure 4-2b), EDS (Figure 4-5b) and TEM (Figure 4-6).

The presence of carbon and nickel oxide after annealing at 500 °C for 6 hours in air was revealed by High-Resolution Transmission Electron Microscopy (HR-TEM), presented in Figure 4-6. NiO-C sample was ultrasonically dispersed in propan-2-ol and then dropped onto a holey-carbon-coated Cu grid. The fringe spacing of 0.245 and 0.210 nm are observed in Figure 4-6, corresponding to the (101) and (012) planes of NiO, respectively.

Another fringe spacing of 0.332 nm corresponds to the graphitic carbon. Figure 4-6 shows the nickel oxide particle was surrounded and covered by amorphous and graphitic carbon.

Figure 4-6 - TEM image of NiO-C sample.

The resulting graphitic and amorphous carbon percentage of NiO-C sample was found to be 7.39 % in overall. In comparison, by definition, the carbon percentage of Ni-C and NiO samples were 100 % and 0 %, respectively. The graphitic and amorphous carbon percentage of NiO-C sample was determined by heating NiO-C sample at 400 °C for 10 hours under a mixture of 100 sccm Ar and 100 sccm H₂, to reduce nickel oxide to Ni. During this process, the nickel oxide in NiO-C was reduced become Ni, while the carbon was stable. Based on the thermodynamics, the reduction of NiO by H₂ gas is spontaneous ($\Delta G < 0$) at 400 °C.

Also, the C was not able to reduce NiO ($\Delta G > 0$) at 400 °C.

The TGA of excess carbon grown on another sample confirmed the stability of the graphitic and amorphous carbon coating at 400 °C in air, see Figure 4-7. Since during reduction, there was no O₂ introduced, the stability of graphitic and amorphous carbon should be more pronounced than in air. H₂ adsorption on carbon was also negligible as high temperature (400 °C) was used. H₂ adsorption is less than 1 wt% at room temperature, and increases only if the temperature is lowered, due to the physical adsorption nature of H₂ on carbon [119]. Thus, it is safe to assume that C did not change mass during reduction.

Figure 4-7 - TGA of carbon coating at 5 °C min⁻¹ heating rate and 20 ml min⁻¹ flow rate of dry air.

Figure 4-8 shows the XRD and Raman spectra of NiO-C sample after reduction treatment at 400 °C for 10 hours under Ar (100sccm) and H₂ (100sccm). The Ni and carbon peaks were found in Figure 4-8a. The graphitic and amorphous carbon peaks were also found in Figure 4-8b. NiO peaks were

not found in both XRD and Raman spectra of Figure 4-8a and Figure 4-8b, respectively.

Figure 4-8 - (a) The XRD and (b) Raman spectra of NiO-C sample that has been reduced at 400 °C for 10 hours under a mixture of 100 sccm Ar and 100 sccm H₂.

To calculate the percentage of C and the mass of nickel oxide in the NiO-C sample, Equations (4.1) to (4.4) were used:

The mass of O = the mass after oxidation - the mass after reduction Equation (4.1)

The mass of C = the mass after reduction - the mass of nickel foam Equation (4.2)

The mass of nickel oxide in NiO-C sample was determined as follow:

The mass of NiO

$$= \left(\frac{\text{MW of Ni} + \text{MW of O}}{\text{MW of O}} \right) \times \text{the mass of O}$$

$$= \frac{74.69}{16} \times \text{the mass of O} = 4.67 \times \text{the mass of O} \quad \text{Equation (4.3)}$$

The percentage of graphitic and amorphous carbon in the NiO-C sample was determined as follow:

$$\text{Percentage of Carbon} = \frac{\text{the mass of C}}{\text{the mass of C} + \text{the mass of NiO}} \times 100\% \quad \text{Equation (4.4)}$$

The calculated mass of nickel oxide and the graphitic and amorphous carbon percentage of NiO-C sample are shown in Table 4-1.

The mass of O in the NiO sample is determined as follow:

$$\text{The mass of O} = \text{the mass after oxidation} - \text{the mass of nickel foam} \quad \text{Equation (4.5)}$$

Table 4-1 - Percentage of graphitic and amorphous carbon in NiO-C sample.

Mass of Ni foam (mg)	Mass after carbon deposition (mg)	Mass after oxidation (mg)	Mass after reduction (mg)	Mass of O (mg)	Mass of C (mg)	Mass of NiO (mg)	Percentage of graphitic & amorphous carbon (%)
69.217	72.649	70.729	69.627	1.102	0.411	5.14	7.39

The active mass loading of NiO-C and NiO samples were 4.54 mg cm^{-2} and 4.76 mg cm^{-2} , respectively. The active mass loading (nickel oxide mass loading) of NiO-C sample was calculated using Equations (4.1) and (4.3) and then normalized with the NiO-C area. The nickel oxide mass loading of NiO sample was calculated using Equations (4.3) and (4.5) and then normalized with the NiO area. The active mass loading of NiO-C sample was slightly lower than NiO sample, indicating thin graphitic and amorphous carbon coating was slightly resistive to O_2 access to Ni for Ni oxidation. The reason could be that on carbon coated Ni foam, the O_2 needs to diffuse through the

carbon layer to reach the Ni foam/carbon interface. The graphitic and amorphous carbon coating acts as a barrier layer. In contrast, there was no barrier layer on pure Ni foam.

The nickel oxide mass loading used was quite large ($\sim 4.5 \text{ mg cm}^{-2}$) to increase the areal capacity (mA h cm^{-2}) of the electrode. Figure 4-9 shows that by increasing the mass loading of nickel oxide on the NiO sample, the cycle life degrades. The larger the mass loading (the thicker the nickel oxide layer), the higher the electrical resistance and the worse the NiO pulverization during lithiation/delithiation. To solve this problem, graphitic and amorphous carbon incorporation was used in the NiO-C sample to maintain the cycle life at relatively large active mass loading.

Figure 4-9 - The effects of mass loading to the cyclic performance of NiO samples.

Battery testing performance of NiO-C and NiO samples is shown in Figure 4-10a and Figure 4-10b. The discharge-charge cycling performance was performed at 0.5 C rate ($1 \text{ C} = 718 \text{ mA g}^{-1}$) for 102 cycles in a potential window of 0.02-3.0 V vs. Li. Figure 4-10a shows that the specific capacity of NiO-C sample was found to be $389.16 \text{ mA h g}^{-1}$ after 102 cycles, much higher than $197.59 \text{ mA h g}^{-1}$ for the NiO sample. Figure 4-10a show that after 102

cycles, NiO-C sample could keep about 100 % of the 2nd cycle capacity, but the capacity loss of NiO sample after 102 cycles was 49.7 % of the 2nd cycle capacity, which indicate that NiO-C sample cycling performance was found to be significantly better than the NiO sample due to graphitic and amorphous carbon incorporation which serves as a buffering matrix of nickel oxide and as a conductor of electron.

Figure 4-10 - (a) The specific capacity vs. cycle number and (b) the capacity per unit area vs. cycle number of NiO-C and NiO samples.

Figure 4-10b shows that NiO-C sample had a stable and good capacity per unit area of 1.76 mA h cm⁻² after 102 cycles, compared with 0.94 mA h cm⁻² for NiO sample. Figure 4-11a and Figure 4-11b show that during the first discharge, NiO-C and NiO samples exhibit a wide cell potential plateau at 0.49~0.50 V, respectively, followed by a sloping curve. This plateau is

originated from initial reduction of nickel oxide to Ni and formation of amorphous Li_2O and SEI happened during the first discharge [51, 54, 120]. In the subsequent charge and discharge processes, the plateau was positioned at about 2.2 V and 1.2 V, respectively, for NiO-C sample. The initial discharge and charge capacity of NiO-C sample were $710.90 \text{ mA h g}^{-1}$ and $374.94 \text{ mA h g}^{-1}$, respectively. In contrast, the initial discharge and charge capacity of NiO sample were $695.79 \text{ mA h g}^{-1}$ and $392.88 \text{ mA h g}^{-1}$, respectively.

Figure 4-11 - The cell potential vs. specific capacity for different cycles of (a) NiO-C and (b) NiO samples.

The initial irreversible capacity loss for NiO-C and NiO samples were 47.26 % and 43.53 %, respectively (corresponds to first cycle's Coulombic efficiency of 52.74 % and 56.47 % for NiO-C and NiO samples , respectively, in Figure 4-10a and Figure 4-10b), probably due to the possible irreversible

changes, say electrolyte decomposition or/and SEI layer formation [27, 52, 121], etc. The initial irreversible capacity loss of NiO-C sample was larger than NiO sample, probably because of additional electrolyte decomposition on graphitic carbon structure [122]. The reversible discharge and charge capacity of NiO-C sample at the 102nd cycle was 389.16 mA h g⁻¹ and 384.92 mA h g⁻¹, respectively, corresponding to the Coulombic efficiency of 98.91 %. In comparison, the reversible discharge and charge capacity of NiO sample at the 102nd cycle was only 197.59 mA h g⁻¹ and 193.36 mA h g⁻¹, respectively, corresponding to a Coulombic efficiency of 97.86 %. Although the initial irreversible capacity loss of NiO-C sample was slightly larger than that of NiO sample, during 102 cycles, the Coulombic efficiency and cycle performance of NiO-C were found to be apparently better than the control sample of NiO sample. Moreover, the initial irreversible capacity loss of NiO-C sample could be minimized to 37.59 % by using lower rate of 0.11 C.

Figure 4-12 shows the specific capacities of NiO-C and NiO sample for 10 cycles at different charge and discharge rates of 0.2 C, 0.5 C, 1 C, 2 C, 4 C (1 C= 718 mA g⁻¹), respectively. NiO-C sample showed slightly lower polarization at the rates of 2 and 4 C, indicating that NiO-C sample structure was well preserved at the high discharge rates. To confirm this, the rate was tuned to 0.2 C for 20 cycles after the 4 C charge and discharge processes. NiO-C sample exhibited a significant recovery of its specific capacities. In a sharp contrast, the specific capacities of NiO sample at the 0.2 C (after the 4 C) decreased significantly with the cycle number, further suggesting that NiO-C sample was of a better rate capability than NiO sample. The specific capacity of NiO-C sample in the final few cycles at 0.2 C was slightly higher

than the initial cycles at the same rate may be contributed from the reversible growth of polymer/gel-like film from the electrolyte degradation [123-125].

Figure 4-12 - The rate capabilities for NiO-C and NiO samples.

The CV of NiO, Ni-C, and NiO-C was performed at the 0.1 mV s^{-1} scan rate from 0.02 to 3.0 V, respectively. From the first and second cycle voltammetry (Figure 4-13a and Figure 4-13b, respectively), one can find that NiO-C and NiO sample showed a similar response.

In the first cycle (Figure 4-13a), the two samples showed a peak at around 0.27 V which can be attributed to initial reduction of nickel oxide to Ni and formation of amorphous Li_2O and SEI [51, 54, 120]. During the first anodic scan, a peak at around 2.2 V could be an indication of NiO formation and Li_2O decomposition [120, 126]. Differently, Ni-C sample had a peak at around 0.51 V during the first cathodic scan, which could result from the formation of SEI layer [122] and a peak at around 0.32 V during the first anodic scan, probably due to the de-intercalation of the Li-ions from the graphitic carbon [127].

On the second cycle of the cathodic and anodic scan, see Figure 4-13b, NiO-C and NiO samples had the peaks at 1.18 V and 2.25 V, respectively. The shift of peaks of 1st and 2nd cycle of NiO-C and NiO samples was due to the

drastic Li driven, structural or textural modifications [52, 128]. A peak at 0.30 V was observed in the second cycle of the Ni-C anodic scan, suggesting the de-intercalation of Li-ions from the graphitic carbon [127]. This peak was not found in both NiO-C and NiO sample, indicating that the active material of NiO-C sample was mainly dominated by nickel oxide, not by graphitic or/and amorphous carbon. This is also the reason why NiO sample is used as a control sample instead of Ni-C sample.

Figure 4-13 - The CV of NiO, Ni-C, and NiO-C samples at (a) 1st cycle and (b) 2nd cycle.

Figure 4-14 - The equivalent circuit for NiO-C and NiO samples.

Figure 4-14 shows the equivalent circuit used to fit the Nyquist plots of NiO-C and NiO sample (Figure 4-15a and Figure 4-15b). The curves were fitted using Nova 1.9 software and the values were presented in Table 4-2. The charge transfer resistances of NiO-C and NiO sample after 102 cycles were 13.19 Ω and 11.08 Ω , respectively, which comparable within the uncertainty in the fitting. This suggests that the Ni foam was of high conductance and it had a good electrical contact with nickel oxide, the active material, during the charge/discharge cycles.

Table 4-2 - Equivalent circuit fitting parameters of NiO-C and NiO samples.

Element	Parameter	NiO-C		NiO	
		Value	Estimated Error (%)	Value	Estimated Error (%)
Re	R	5.0075	1.772	6.5068	4.193
Rf	R	3.2463	15.381	3.8895	25.623
Cf	Y0	6.22E-05	60.423	7.53E-05	91.731
	N	0.77902	7.33	0.66345	13.26
Rct	R	13.19	16.759	11.082	14.641
Cdl	Y0	0.000205	31.807	0.001066	25.932
	N	0.8388	6.601	0.59565	8.248
Zw	Y0	0.018605	1.323	0.012792	0.884
Zt	Y0	0.4461	772.423	0.26556	141.254
	B	0.14956	773.383	0.18812	142.213
	χ^2	0.009837		0.003025	

The fitting to EIS was based on two semicircles and diffusion component. The semicircle at higher frequencies is related to the formation of SEI film and/or contact resistance, while the semicircle at medium frequency is related to Li absorption/desorption or the charge-transfer impedance on electrode/electrolyte interface [129, 130]. The equivalent circuit was using the components as follow [130]. Re is the resistance of electrolyte, while Rf and Cf are the resistance and capacitance of the SEI film, respectively. The Rct

and C_{dl} are the charge-transfer resistance and double-layer capacitance, respectively. The diffusion component consists of Z_w and Z_t corresponding to Warburg impedance and Tangent hyperbolic, respectively.

Figure 4-15 - (a, b) EIS of NiO-C and NiO sample, after 102 cycles, at 2 V.

The comparison of the performance of our NiO-C sample with the reported results by several other groups is listed in Table 4-3. The porous NiO [54], nanoporous NiO [58], and sandwich-like NiO [59] had only small mass loading of $\leq 1 \text{ mg cm}^{-2}$. They achieved a cycle life of ≥ 50 cycles at rate of $\geq 359 \text{ mA g}^{-1}$. NiO films [24] had a higher mass loading of 3 mg cm^{-2} . It showed a stable performance at low rate, with a cycle life of 50 cycles. Compared to NiO films [51], our NiO-C composite sample has better cycle life of 102 cycles.

Through this comparison, the key points of our NiO-C samples can be drawn: (1) our NiO-C sample has the highest mass loading of 4.54 mg cm^{-2} ; (2) our NiO-C sample has the highest mass loading with a stable cycle life more than 100 cycles at rate of 359 mA g^{-1} and (3) our NiO-C sample has a practical capacity per unit area of $2.11 \text{ mA h cm}^{-2}$ and $1.76 \text{ mA h cm}^{-2}$ at rate of 143.6 mA g^{-1} and 359 mA g^{-1} , respectively.

Table 4-3 - The comparison of NiO sample on Ni foam works.

Works	Mass loading of active material (mg cm^{-2})	Capacity per unit area (mA h cm^{-2})	Rate (mA g^{-1})	Cycle number (cycles)	Ref.
Porous NiO on Ni foam	1	0.56	718	100	[54]
Nanoporous NiO on Ni foam	0.39	0.21	359	100	[58]
Sandwich-like NiO on Ni foam	0.92	0.37	1436	50	[59]
NiO films on Ni foam	3	1.95	78.98	50	[51]
NiO-C composite on Ni foam	4.54	2.11	143.6	10 ^{a)}	This work
	4.54	1.76	359	102	

^{a)} Stopped after 10 cycles to facilitate rate capability testing (Figure 4-12)

One might argue that the mass loading is related to the thickness of Ni foam and the level of oxidation. Ideally, same kind of Ni foams should be used by all works in Table 4-3 for a fair comparison. However, it is almost impossible in practice because references [54, 58, 59] did not provide Ni foam parameters, while reference [51] only provided several Ni foam parameters. We believe that two parameters of specific surface area and thickness of Ni foam are enough to represent the Ni foam. Other parameters such as the porosity, pore size, pore density and area density were all represented in specific surface area of Ni foam.

The specific surface area and thickness of Ni foam used in reference [51] were $3.9 \text{ cm}^2 \text{ mg}^{-1}$ and 0.16 cm , respectively. Our work used Ni foam

with specific surface area and thickness of $0.3 - 0.4 \text{ cm}^2 \text{ mg}^{-1}$ and 0.2 cm , respectively. We showed that our mass loading is higher than reference [51] by normalizing the mass loading with the specific surface area and thickness of the Ni foam, shown in Equation (4.6). Our works's normalized NiO mass loading of 56.75 to $75.67 \text{ mg}_{\text{NiO}} \text{ cm}^{-5} \text{ g}_{\text{Ni}}$ was higher than that of reference [51] of $4.81 \text{ mg}_{\text{NiO}} \text{ cm}^{-5} \text{ mg}_{\text{Ni}}$.

Normalized NiO mass loading

$$= \frac{\text{NiO mass loading } (\text{mg}_{\text{NiO}} \text{ cm}^{-2})}{\text{nickel foam specific surface area } (\text{cm}^2 \text{ mg}_{\text{Ni}}^{-1}) \times \text{nickel foam thickness } (\text{cm})}$$

Equation (4.6)

The excellent performance of NiO-C/Ni foam sample probably results from high electrical conductance and mechanical flexibility of graphitic or/and amorphous carbon coating, which not only provides an efficient channel for electrons, but also functions as a network preventing NiO nanostructures from structural deformation during charge and discharge processes.

SEM images of NiO-C and NiO samples after 102 cycles (Figure 4-16) show that the nanostructure of NiO-C looks more uniform and preserved (Figure 4-16b) than NiO (Figure 4-16d). In addition, ultrasonication in propan-2-ol for 30 minutes was used to qualitatively measure the mechanical stability of NiO-C and NiO samples after cycling. NiO-C sample was more resistant to peeling off after ultrasonication treatment, see Figure 4-17. In Figure 4-17b, more remaining films were found attached to substrate, compared to Figure 4-17d. It indicates that NiO-C sample had a better mechanical ability. The mechanical ability is important during charge/discharge because the nickel oxide expands and contracts during battery cycling.

Figure 4-16 - SEM images of (a, b) NiO-C sample after 102 cycles and (c, d) the NiO sample after 102 cycles.

Figure 4-17 - SEM images of NiO-C sample after 102 cycles, (a) before and (b) after ultrasonication for 30 minutes in propan-2-ol. SEM images of NiO sample after 102 cycles, (c) before and (d) after ultrasonication. The arrow shows the remaining film after ultrasonication.

4.4. Summary

We have fabricated NiO-C sample, using a simple two-step process of CVD using ethanol and annealing in air, in which a large amount of NiO active material directly forms on carbon coated Ni foam current collector. The high mass loading of active NiO of around 4.5 mg cm^{-2} enables NiO-C sample to have the capacity of $2.11 \text{ mA h cm}^{-2}$ and $1.76 \text{ mA h cm}^{-2}$ at 0.2 C and 0.5 C rate, respectively. At 0.5 C rate, the capacity is stable at $382.13\sim389.16 \text{ mA h g}^{-1}$ from the second up to 102nd cycle. The cycling and rate performances of high NiO mass loaded NiO-C sample are found to be much better than those of a counterpart NiO sample where no graphitic and amorphous carbon is introduced. The role of the incorporated graphitic and amorphous carbon could be twofold, i.e., a fluent channel for electrons and a flexible network preventing NiO nanostructures from structural deformation during charge and discharge processes.

Chapter 5 : Sputtered nickel oxide on vertically-aligned MWCNT arrays (MWCNT/NiO) for Li-ion battery anodes

5.1. Introduction

The focus of Chapter 4 was to increase the mass loading while keeping the excellent cycle performance. In this chapter, the focus is to investigate the role of vertically-aligned MWCNT to improve performance of conversion-type anode active material of NiO. The vertically-aligned MWCNT arrays with a relatively high aspect ratio and sparse spacing had been found to be a promising current collector for alloying-based anode active material. [50] The high aspect ratio enabled the vertically-aligned MWCNT arrays to hold more active material than rough current collector [48, 49], while the spacing between MWCNTs provided rooms for expansion of coated active material.

Chapter 2 mentioned many ways to directly deposit NiO onto the current collector. NiO can be fabricated by plasma-assisted oxidation [40], electrochemical deposition followed by oxidation [51], thermal evaporation followed by oxidation [45], pulsed laser deposition [46], reactive RF sputtering [47], thermal oxidation of Ni foam [56], etc.

Chiu et al. [47] deposited nanocrystalline NiO thin film using bias-sputter-deposition and achieved a specific capacity of $\sim 720 \text{ mA h g}^{-1}$ up to 30 cycles. A discharge cut-off voltage of 0.5 V vs. Li/Li⁺ was used to minimize pulverization. Xu et al. [68] prepared NiO-MWCNT composites using direct

thermal decomposition method. Their material showed a specific capacity of $\sim 800 \text{ mA h g}^{-1}$ after 50 discharge/charge cycles.

To our knowledge, due to pulverization of the film during lithiation/delithiation, no report has ever presented a stable cycle performance of sputtered NiO in the potential window of 0.02 – 3 V vs. Li/Li⁺. In addition, no one has demonstrated vertically-aligned MWCNTs as a key to minimize NiO pulverization. In this chapter, we investigate the electrochemical properties of MWCNT/NiO samples where NiO was deposited by DC reactive sputtering method.

5.2. Methodology

5.2.1. Sample preparation

5.2.1.1. Fabrication of vertically-aligned MWCNTs

Vertically-aligned MWCNT arrays were grown on 16.2 mm-diameter SS disks purchased from Lee & Lim International. Initially SS disks were cleaned in an ultrasonic bath for 30 minutes in propan-2-ol and then dried inside vacuum oven at 80 °C for 4 hours. A thin Ti/TiN barrier layer was deposited using DC sputtering system of Elite Sputter. Then, 20 nm Ni film was deposited using Electron-beam (E-beam) evaporation system of Edwards E-Beam Evaporation. After Ni deposition, the samples were placed inside a chamber of a PECVD of Nanoinstruments Ltd system, with the base pressure of typically 3 Pa. The NH₃ gas was flowed to maintain a pressure of 8.7×10^2 Pa. To dewet the Ni thin film into Ni nanoparticle arrays, the temperature was rapidly increased to 800 °C. Subsequently, to grow the vertically-aligned MWCNT arrays, 120 Watt plasma was switched on and the C₂H₂ gas was flowed. The deposition time was 10 minutes.

5.2.1.2. Fabrication of MWCNT/NiO

To fabricate MWCNT/NiO, NiO was sputtered on vertically-aligned MWCNT arrays in a DC sputtering chamber of Elite Sputter. NiO was sputtered from a pure Ni target at 300 Watts. The Ar and O₂ were flowed at 75 and 25 sccm, respectively. The base pressure and deposition pressure were typically 4×10^{-4} and 1.2 Pa, respectively. The sputtering was carried out without substrate heating.

5.2.1.3. Fabrication of SS/NiO

For a comparison, NiO film on SS (SS/NiO) was also prepared under the same sputtering condition. The SS/NiO serves as a control sample. The NiO mass loading of both MWCNT/NiO and SS/NiO samples were 0.90 mg cm^{-2} , as measured by Mettler Toledo XP26 DeltaRange balance with readability of 0.002 mg.

5.2.2. Physical characterization

The sputtered NiO was characterized using XRD of Siemens D5005 with Cu K α of 0.1540 nm and θ of 3°. Raman Spectroscopy was performed using WITec with excitation wavelengths of 532 nm. The initial morphology of the samples was investigated using SEM of FEI Nova Nanolab DualBeam 600i with accelerating voltage of 5.00 kV. Using the same machine, the Focused Ion Beam (FIB) was used for the preparation of samples prior the X-SEM. TEM was performed using JEOL 2010 with accelerating voltage of 200 kV. The morphology of the samples after 50 cycles was characterized using LEO 1550 Gemini SEM with accelerating voltage of 5.00 kV.

5.2.3. *Electrochemical characterization*

The samples, Celgard-2300 separators, liquid electrolytes and pure Li metals were assembled in 2032-type coin cells inside an Ar glove box. The O₂ and moisture level inside the glove box were less than 5 ppm. The liquid electrolyte used was 1 M LiPF₆ dissolved in 1:1 by volume of EC and DEC. Since MWCNT/NiO and SS/NiO anodes were tested in a half-cell configuration against the Li metal, we refer them to be MWCNT/NiO and SS/NiO samples, respectively. Battery cycle life testing and CV were performed using Neware battery tester and Autolab machine, respectively.

EIS was performed using Autolab machine at 0.01 V amplitude from 1×10^5 Hz to 0.22 Hz frequency. The discharge and charge referred to lithiation and delithiation, respectively. The 3rd cycle's discharge/charge at the rate of 0.05 C were paused when EIS measurements were performed. The potentials were chosen at a regular interval for EIS measurements at 3, 2.7, 2.4, 2.1, 1.8, 1.5, 1.2, 0.9, 0.6, 0.3 and 0.02 V during discharge and 0.3, 0.6, 0.9, 1.2, 1.5, 1.8, 2.1, 2.4, 2.7 and 3 V during charge. All EIS data were verified using Kronig-Kramers algorithm.

5.3. Results and discussion

Successful coating of NiO was confirmed using XRD and Raman spectra. Figure 5-1a shows the XRD pattern of MWCNT/NiO sample. There were noticeable shifts of the NiO peak to a lower value of 2θ . The NiO peaks at 37.0°, 43.0°, 62.3°, 62.5°, 75.1°, 78.6°, and 78.8° could be assigned to NiO (101), (012), (110), (104), (113), (202), and (006), respectively. The lattice spacing was slightly enlarged probably due to the formation of non-stoichiometric oxygen-rich NiO (NiO_y, where $y > 1$) due to the creation of Ni

vacancies or oxygen interstitial during sputtering [131-134]. The small shoulders could be attributed to the SS substrate with powder-diffraction-file number of 33-397. SS signals were detected because small area of the MWCNT/NiO sample was not covered by MWCNT/NiO for easier handling during fabrication steps. Figure 5-1b shows the MWCNT/NiO sample had Raman peak at about 515 cm^{-1} due to Ni-O stretching mode [55, 117]. The MWCNTs were not detected by XRD and Raman due the thick NiO coating.

Figure 5-1 - (a) The XRD and (b) Raman spectra of MWCNT/NiO sample.

Figure 5-2a shows the HR-TEM image of NiO in MWCNT/NiO sample. The fringe spacing of 0.242 nm was observed in Figure 5-2a, corresponding to the (101) plane of NiO. The TiN and pure Ni signal were not detected by XRD analysis probably because they were 1) blocked by thick NiO and 2) very thin so that their signals were too weak to be detected. Although most MWCNTs

were covered with thick NiO as shown in Figure 5-2b, we managed to observe the Ni catalyst using TEM in Figure 5-2c.

Figure 5-2 - (a) The HR-TEM image of nickel oxide in MWCNT/NiO sample. The TEM images of MWCNT/NiO sample showing (b) thick-NiO-coated MWCNT and (c) thin-NiO-coated MWCNT.

The SEM images of SS substrate, MWCNT array, SS/NiO sample and MWCNT/NiO sample are displayed in Figure 5-3. The SS had a relatively smooth microstructure as shown in Figure 5-3a and Figure 5-3b. After growing the vertically-aligned MWCNT arrays, the microstructure became relatively rough as seen in Figure 5-3c and Figure 5-3d. The MWCNT arrays were seen protruding out with an angle normal to the surface in Figure 5-3d. The rough microstructure of the substrate is a desirable feature to minimize pulverization of NiO during lithiation/delithiation. [49] A significant difference of the morphologies of SS/NiO and MWCNT/NiO samples can be seen in Figure 5-3e to Figure 5-3h. Figure 5-3e and Figure 5-3f show the deposited nickel oxide film on SS/NiO sample had a relatively smooth film. In

contrast, Figure 5-3g and Figure 5-3h show the deposited NiO film on MWCNT/NiO sample had a relatively disperse NiO particles with spacing between them.

Figure 5-3 - The SEM images of (a, b) SS substrate; (c, d) vertically-aligned MWCNT array; (e, f) SS/NiO sample; (g, h) MWCNT/NiO sample.

Using FIB machine, a protective layer was deposited locally prior to FIB milling. The purpose of introducing the protective layer was to prevent the damage on the area-of-interest during FIB milling. The FIB milling operation was performed adjacent to the area-of-interest to reveal the cross-section of the structure. The NiO particles were attached to the vertically-aligned MWCNT arrays on the SS current collector as shown from the X-SEM image of Figure 5-4a and Figure 5-4b. The average height of the vertically-aligned MWCNT arrays with NiO coating of the MWCNT/NiO sample was 5.97 μm . Although we did not perform the cleaning after FIB process, the re-deposition of the milled material was negligible since depth and width of the hole were comparable. Most of the milled material was sucked by the vacuum system.

Figure 5-4 - (a, b) The cross-section of MWCNT/NiO sample.

Battery testing performance of MWCNT/NiO sample, SS/NiO sample, and MWCNT substrate at the rate of 143.6 mA g^{-1} is shown in Figure 5-5a. All capacities were normalized with NiO mass. For MWCNT/NiO sample, the first cycle's specific discharge capacity, specific charge capacity and Coulombic efficiency were $1146.3 \text{ mA h g}^{-1}$, $863.2 \text{ mA h g}^{-1}$ and 75.3%, respectively. The corresponding values for the second cycle were $865.4 \text{ mA h g}^{-1}$, $841.9 \text{ mA h g}^{-1}$ and 97.3%. The specific discharge capacity was stable from the 2nd to 50th cycle at about $864.8 \text{ mA h g}^{-1}$. In contrast, SS/NiO sample

showed apparent degradation with a specific discharge capacity of $285.9 \text{ mA h g}^{-1}$ at the 50th cycle. The specific capacity contributed from the vertically-aligned MWCNTs was only 21.1 mA h g^{-1} . It was negligible to the overall specific capacity of MWCNT/NiO sample.

Figure 5-5 - (a) The specific capacity vs. cycle number and (b) the rate capabilities of MWCNT/NiO, SS/NiO and MWCNT samples.

The experimental specific discharge capacity of MWCNT/NiO sample was found to be $864.8 \text{ mA h g}^{-1}$, higher than the NiO theoretical specific capacity of 718 mA h g^{-1} . This could be tentatively attributed to

- the contribution from polymeric gel-like film resulting from kinetically activated electrolyte degradation [123-125] and

- b) the NiO_y , where $y > 1$ has a higher theoretical specific capacity than NiO. The electrochemical reaction for NiO_y , where $y > 1$, was modified from stoichiometric NiO [32]:

The theoretical specific capacity of $\text{NiO}_{y, \text{ where } y > 1}$

$$\begin{aligned} &= \frac{\text{no. of electron transfer} \times \text{Faraday constant} \left(\text{A} \cdot \frac{\text{s}}{\text{mol}} \right) \times 1000 \left(\frac{\text{mA}}{\text{A}} \right)}{\text{NiO}_{y, \text{ where } y > 1} \text{ mass} \left(\frac{\text{g}}{\text{mol}} \right) \times 3600 \left(\frac{\text{s}}{\text{h}} \right)} \\ &= \frac{2y \times 96485.3365 \times 1000}{(58.693 + 15.999y) \times 3600} \quad \text{Equation (5.2)} \end{aligned}$$

The theoretical specific capacity of NiO

$$= \frac{2 \times 96485.3365 \times 1000}{(58.693 + 15.999) \times 3600} \quad \text{Equation (5.3)}$$

The theoretical specific capacity of $\text{NiO}_{y, \text{ where } y > 1}$

$$\begin{aligned} &\frac{\text{The theoretical specific capacity of } \text{NiO}_{y, \text{ where } y > 1}}{\text{The theoretical specific capacity of NiO}} \\ &= \frac{74.692y}{(58.693 + 15.999y)} > 1 \quad \text{Equation (5.4)} \end{aligned}$$

The theoretical specific capacity of $\text{NiO}_{y, \text{ where } y > 1}$ is always higher than that of NiO as shown in Equation (5.4). In this study, the mass measurement error was negligible, considering the high resolution of the mass balance and no significant side reaction during sputter deposition of NiO at room temperature.

Figure 5-5b shows the specific capacities of MWCNT/NiO sample, SS/NiO sample, and MWCNT substrate. Different charge and discharge rates were programmed each for 10 cycles at the rate of 0.1, 0.2, 0.5, and 1 C (1 C =

718 mA g⁻¹). MWCNT/NiO sample showed a relatively stable specific capacity of 958.2, 936.6, 889.7, and 820.1 mA h g⁻¹ at the rate of 0.1, 0.2, 0.5, and 1 C, respectively. In contrast, the SS/NiO sample showed a degraded specific capacity of 398.6, 293.7, 215.1 and 159.2 mA h g⁻¹ at the rate of 0.1, 0.2, 0.5, and 1 C, respectively. The MWCNT specific capacity was only 22.5, 19.8, 16.1 and 13.4 mA h g⁻¹ at 0.1, 0.2, 0.5, and 1 C rate, respectively.

After the rate was tuned back to 0.1 C, MWCNT/NiO sample showed a significant recovery compared with SS/NiO sample. These results indicate that MWCNT/NiO sample did have much better performance than SS/NiO sample. The vertically-aligned MWCNT arrays must play important roles in enhancing the electronic paths, absorbing the compressive and tensile stresses, and minimizing NiO pulverization during lithiation/delithiation.

The first cycle's discharge voltage profile of MWCNT/NiO sample shown in Figure 5-6a was different from the subsequent discharge voltage profile probably due to the drastic Li driven, structural or textural modifications. [52, 128] Figure 5-6b shows the CV of MWCNT/NiO sample at a scan rate of 0.1 mV s⁻¹ and a potential window of 0.02 – 3.0 V. In the first cycle, a peak at around 0.45 V and a shoulder at around 0.5 V could result from initial reduction of NiO to Ni nanoparticles and a formation of amorphous Li₂O and SEI [51, 54, 120]. During the first anodic scan, the peaks at around 1.50 and 2.25 V could be attributed to SEI decomposition, NiO formation and Li₂O decomposition [120, 126]. On the subsequent cycles, the cathodic scan peak stabilized at around 0.96 V with a shoulder at around 1.1 V and the anodic scan peak stabilized at 2.25 V with a weak peak at 1.50 V.

Figure 5-6 - (a) The cell potential vs. specific capacity of MWCNT/NiO sample at 1st, 2nd, 25th and 50th cycle. (b) The CV of MWCNT/NiO sample at 1st, 2nd, and 3rd cycle.

Compared to NiO-MWCNT composites using direct thermal decomposition method [68], our structure has two advantages:

- Our MWCNT/NiO sample contained vertically-aligned MWCNT arrays which directly grown on current collector. The direct connection offered an advantage of easy electron transport from NiO to the current collector.
- Our MWCNT/NiO sample featured a relatively regular spacing between vertically-aligned MWCNTs. It enabled easy ion transport due to easy access of electrolyte to the active material. The spacing also acted as a room to accommodate the expansion/contraction of NiO during lithiation/delithiation.

These advantages enabled our structure to have a stable cycle performance at the rate of 143.6 mA g^{-1} for 50 cycles and an ability to be discharged/charged at higher rates up to 718 mA g^{-1} as shown in Figure 5-5a and Figure 5-5b, respectively. In contrast, reference [68] showed the battery characterization at a small rate of 50 mA g^{-1} .

The superior electron and ion transport of MWCNT/NiO were studied using EIS. Figure 5-7a and Figure 5-7b represent the typical Nyquist plot generated from EIS measurements. Each point in the Nyquist plot corresponds to EIS measurement at a specific frequency where high to low frequencies were presented from left to right. The x and y axis correspond to the real and imaginary value of the impedance, respectively. The small semicircle at higher frequencies is related to the formation of SEI film, while the semicircle at medium frequency is related to the charge-transfer resistance on electrode/electrolyte interface [129, 130]. The inclined line at the lower frequencies is related to the diffusion of Li ions [130]. Internal resistance and charge-transfer resistance could be extracted from the Nyquist plots. Figure 5-8a and Figure 5-8b summarized the internal resistance and charge-transfer resistance of SS/NiO and MWCNT/NiO, respectively.

Barsukov and Qian [135] suggested that low frequency impedance measurement could determine the internal resistance more accurately than 1 kHz high frequency impedance measurement. In our set-up, the lowest frequency we achieved for valid EIS data was 0.22 Hz, which corresponds to the relaxation time of 4.55 s. This relaxation time was long enough to accurately determine the internal resistance.

Figure 5-7 - The Nyquist plot of SS/NiO and MWCNT/NiO samples during 3rd cycle's discharge at (a) 1.5 V and (b) 0.9 V.

Figure 5-8a shows the resistance at 0.22 Hz was a function of the potential during discharge and charge process. This was comparable to the variation of resistance with the state-of-charge in reference [135]. The resistances of MWCNT/NiO sample varied in the range of 62.2 Ω (at 0.6 V discharge) to 228 Ω (at 2.1 V discharge). In contrast, the resistances of SS/NiO samples varied greatly from 130.8 Ω (at 0.3 V discharge) to 1653.8 Ω (at 3 V charge). The resistances of MWCNT/NiO were smaller than the resistances of SS/NiO in all potentials. The highest and lowest differences in the resistances were 1517.3 Ω (at 3 V charge) and 30.3 Ω (at 0.3 V charge), respectively. The difference was less significant at lower potentials probably due to domination of charge-transfer resistance at lower potentials. Since the

resistance at low frequencies is related to the diffusion component of the Li-ion, this shows that MWCNT/NiO has better ion transport than SS/NiO in all potential.

Figure 5-8 - (a) The resistance at 0.22 Hz and (b) the charge-transfer resistance during 3rd cycle's discharge and charge of SS/NiO and MWCNT/NiO samples.

Figure 5-8b shows the charge-transfer resistance of SS/NiO and MWCNT/NiO samples. MWCNT/NiO sample had lower charge-transfer resistances than SS/NiO sample in all potentials. The charge-transfer resistance was dominated at the lowest potential of 0.02 V. Since the charge-transfer resistance is related with the electron transport, this shows that the MWCNT/NiO has better electron transport than SS/NiO. The superior rate

capability of MWCNT/NiO was probably caused by better ion and electron transport as indicated by low internal resistance and low charge-transfer resistance, respectively.

Figure 5-9 - The SEM images of MWCNT/NiO before cycling and after 50 cycles.

The structure of the MWCNT/NiO and SS/NiO after 50 cycles was investigated using SEM. Figure 5-9 shows the morphology of MWCNT/NiO before and after 50 cycles. After being cycled, MWCNT/NiO surface showed different morphology: from disperse NiO particles to relatively smooth surface. This could be explained by the structural change during the first lithiation when NiO structure was converted to Ni nanoparticles-inside- Li_2O and gel-like matrixes [52, 128]. Unlike alloying-type materials that simply expand during lithiation [50], the conversion-type material involves reduction of the metal oxides to metal nanoparticles and formation of Li_2O and SEI matrixes during lithiation [51, 54, 120]. After 50 cycles, MWCNT/NiO also showed relatively uniform inter-cracks between the active materials but still remained stable structures across a large area, as shown in Figure 5-10a and Figure 5-10b, which is similar with the finding in reference [50]. In contrast, SS/NiO showed large irregular cracks as shown in Figure 5-10c and Figure 5-10d.

Figure 5-10 - The SEM images of (a, b) MWCNT/NiO and (c, d) SS/NiO after 50 cycles at different magnification.

Figure 5-11 shows the optical photograph of MWCNT/NiO and SS/NiO after 50 cycles evidenced that the active material film of SS/NiO sample was easily peeled-off due to pulverization of the active material and weak adhesion of the active material to SS. In contrary, these problems did not occur in the MWCNT/NiO samples.

Figure 5-11 - The pictures of MWCNT/NiO and SS/NiO after 50 cycles.

The MWCNT/NiO structure remained stable mainly due to

- the vertically-aligned MWCNT arrays acted as buffers that provided strain relaxation and volume change accommodation and
- the strong adhesion of active materials to vertically-aligned MWCNT arrays.

5.4. Summary

We have successfully fabricated high performance MWCNT/NiO anode for Li-ion batteries. The MWCNT/NiO structure was prepared by sputtering Ni target in Ar and O₂ ambient onto vertically-aligned MWCNT arrays on SS. A specific capacity of 864.8 mA h g⁻¹ was achieved after 50 cycles at a rate of 143.6 mA g⁻¹. The high performance can be attributed to the unique MWCNT/NiO structure in which vertically-aligned MWCNTs enhance the ion and electron transport, absorb both the compressive and tensile stresses and minimize NiO pulverization during lithiation/delithiation. EIS study of MWCNT/NiO showed low internal and charge-transfer resistance that suggest superior ion and electron transport, respectively. SEM of MWCNT/NiO after 50 cycles evidenced stable structures across a large area. The combination of vertically-aligned MWCNT arrays with conversion-type anode active material is a promising anode material for Li-ion batteries.

Chapter 6 : Amorphous-Ge coated vertically-aligned MWCNT arrays (MWCNT/a-Ge) for Li-ion battery anodes

6.1. Introduction

Chapter 4 and Chapter 5 describe conversion-type anode active materials of NiO. In this chapter and Chapter 7, alloying-type anode active material of Ge are used. In Chapter 2, we mentioned that many approaches were used to improve the cycle performance of Ge by using Ge nanoparticles [74, 75], Ge nanowires [29, 76-79], Ge nanotubes [80, 81], Ge-carbon composites [82-94], Ge-graphene composites [95-102], Ge thin-film [71, 103-105], other unique structures [106-113], etc. However, most studies in the literature used complicated processes/treatments. Also, most of them involved crystalline Ge than amorphous Ge. To our knowledge, there was no systematic study that compared the performance of amorphous and polycrystalline Ge on the same platform.

Vertically-aligned MWCNT arrays were used as a platform to prevent agglomeration and minimize pulverization. Vertically-aligned MWCNT arrays have been proved to be a promising current collector especially for anode active materials that undergo large volume change during lithiation/delithiation [50, 136]. The vertically-aligned MWCNT arrays have several advantages such as:

- a) fast electron conduction paths to the coated active material,

- b) fast Li-ion transports due to short Li-ion diffusion distance of the active material and high coverage of electrolyte to the active material and
- c) excellent buffers that minimize the pulverization of active material during lithiation/delithiation.

In this chapter, amorphous and polycrystalline Ge are coated to vertically-aligned MWCNT arrays to form MWCNT/a-Ge anode and MWCNT/c-Ge anode, respectively. The performance of the anodes was studied in details.

6.2. Methodology

6.2.1. Sample preparation

6.2.1.1. Fabrication of vertically-aligned MWCNTs

The vertically-aligned MWCNT arrays were grown on 16.2 mm-diameter SS disks. Initially, SS disks were cleaned in an ultrasonic bath for 30 minutes in propan-2-ol and then dried inside vacuum oven at 353.15 K for 4 hours. Ti/TiN barrier layer was deposited using DC sputtering system of Elite Sputter. Afterward, 20 nm Ni catalyst was deposited using E-beam evaporation system of Edwards E-Beam Evaporation. After Ni deposition, the samples were placed inside the chamber of a PECVD of Nanoinstruments Ltd system, with the base pressure of typically 3 Pa. The NH_3 gas was flowed to maintain a pressure of 8.7×10^2 Pa while the temperature was rapidly increased to 1073.15 K to dewet the Ni thin film become Ni nanoparticles. Subsequently, 120 Watt plasma was switched-on and the C_2H_2 gas was flowed to grow the vertically-aligned MWCNT arrays. The deposition time was 10 minutes. The mass loading was measured by Mettler Toledo XP26

DeltaRange balance that has readability of 0.002 mg. The average mass of CNTs was 0.12 mg cm^{-2} .

6.2.1.2. Fabrication of MWCNT/c-Ge

Polycrystalline Ge was deposited on vertically-aligned MWCNT platform using LPCVD system of Semco LPCVD with base pressure of 1.33 Pa. The temperature was increased to 803.15 K with ramping up time of 30 minutes. The deposition was performed by flowing 88 sccm of 1 % GeH_4 in H_2 at deposition pressure of 83.1 Pa. Mass loading of MWCNT/c-Ge was 0.33 mg cm^{-2} . The weight percent of crystalline Ge in MWCNT/c-Ge was 74 %.

6.2.1.3. Fabrication of MWCNT/a-Ge

Amorphous Ge was deposited on vertically-aligned MWCNT platform using RF sputtering of Denton sputter system using 99.999% pure Ge target. The base pressure was 8.7×10^{-4} Pa. Then, Ar was flowed at 50 sccm and pressure was maintained at 4.2 Pa. The deposition was performed with 100 watts plasma power and carried out at room temperature. Mass loading of MWCNT/a-Ge was 0.37 mg cm^{-2} . The weight percent of amorphous Ge in MWCNT/a-Ge was 76 %.

6.2.2. Physical characterization

The MWCNT/c-Ge and MWCNT/a-Ge were characterized using XRD of Siemens D5005 XRD with $\text{Cu K}\alpha$ of 0.1540 nm and Raman Spectroscopy of WITec with 532 nm excitation wavelength. The morphology of the samples was investigated using SEM of LEO-SEM with accelerating voltage of 5.00 kV. TEM was performed using JEOL 2010 with accelerating voltage of 200 kV.

6.2.3. *Electrochemical characterization*

The MWCNT/c-Ge and MWCNT/a-Ge, Celgard-2300 separators, liquid electrolytes and pure Li metals were assembled in 2032-type coin cells inside an Ar glove box that had O₂ and moisture level of less than 5 ppm. The liquid electrolyte used was 1 M LiPF₆ dissolved in 1:1 by volume of EC and DEC. Since MWCNT/c-Ge and MWCNT/a-Ge anodes were tested vs. Li metal in a half-cell configuration, we refer them as MWCNT/c-Ge and MWCNT/a-Ge samples, respectively. Battery cycle life testing was performed using Neware battery tester at the rate of 0.1 C (1 C = 1624 mA g⁻¹) for both MWCNT/c-Ge and MWCNT/a-Ge. The potential window was 1.2 – 0.01 V vs. Li/Li⁺. All capacities were normalized with Ge mass. CV was performed using Autolab machine at the scan rate of 0.1 mV s⁻¹.

6.3. Results and discussion

Deposition of amorphous and polycrystalline Ge on vertically-aligned MWCNT arrays were performed using RF sputtering at room temperature and LPCVD at 803.15 K, respectively. Ge is reported to have a melting temperature (T_m) of 1211.4 K. In MWCNT/a-Ge sample, Ge was deposited by RF sputtering at a relatively low deposition temperature (T_{dep}) of 298.15 K, with T_{dep}/T_m=0.25. At low T_{dep}/T_m ratio, Ge adatoms have low mobility and self-diffusion that promote the formation of amorphous Ge. [137] In MWCNT/c-Ge sample, the LPCVD at relatively high T_{dep} of 803.15 K, with T_{dep}/T_m=0.66, provided enough energy for Ge adatoms' nucleation and self-diffusion to form polycrystalline Ge. [137]

Figure 6-1 - (a) The XRD and (b) Raman spectra of MWCNT/a-Ge and MWCNT/c-Ge samples.

The XRD pattern in Figure 6-1a shows MWCNT/c-Ge sample has peaks at 27.23° , 45.28° , and 53.67° that correspond to Ge (111), Ge (220), and Ge (311) with PDF No. 4-545. In contrast, the MWCNT/a-Ge only shows the SS substrate peaks. These indicate amorphous nature of Ge in MWCNT/a-Ge and higher degree of crystallinity of Ge in MWCNT/c-Ge. The Raman data at Figure 6-1b shows the sharp peak at about 296.54 cm^{-1} appeared for MWCNT/c-Ge sample that corresponds to the crystalline peak of bulk Ge of 300.4 cm^{-1} . [138] In comparison, a broad peak at $\sim 289 \text{ cm}^{-1}$ with shoulder at $\sim 265 \text{ cm}^{-1}$ were observed for MWCNT/a-Ge that correspond to amorphous form of Ge. [138] The MWCNT peak was not detected in XRD, but detected in the Raman as the Raman scattering is very sensitive to carbon peaks. The

peak at about 1350 and 1585 cm^{-1} corresponds to the D and G band of MWCNTs. [116, 139]

The TEM further evidenced the amorphous Ge coating in MWCNT/a-Ge and polycrystalline Ge coating in MWCNT/c-Ge. Figure 6-2a shows the MWCNT/a-Ge has amorphous Ge. The Fast Fourier Transform (FFT) in Figure 6-2b only show the spots from the carbon nanotubes, that corresponds to 0.34 nm lattice spacing. Figure 6-2c shows the crystalline nature of the MWCNT/c-Ge. Figure 6-2d shows FFT of MWCNT/c-Ge shows the spots from Ge with lattice spacing of 0.20 nm corresponds to Ge (220) with polycrystalline structure.

Figure 6-2 - (a) The HR-TEM image of MWCNT/a-Ge (b) The FFT of HR-TEM image of MWCNT/a-Ge (c) The HR-TEM image of MWCNT/c-Ge (d) The FFT of HR-TEM image of MWCNT/c-Ge.

The MWCNT arrays with the average length of $2.5\text{ }\mu\text{m}$, and average diameter of 179 nm and spacing of 289 nm is shown in Figure 6-3a and Figure 6-3b. We deposited similar Ge mass loading for both MWCNT/a-Ge and

MWCNT/c-Ge. After deposition of amorphous Ge, the MWCNT/a-Ge is shown in Figure 6-3c and Figure 6-3d. The average diameter of the top part of MWCNT/a-Ge was 623 nm. Polycrystalline Ge was deposited as shown in Figure 6-3e and Figure 6-3f. The average diameter MWCNT/c-Ge was 269 nm. Both MWCNT/a-Ge and MWCNT/c-Ge have spacing and directly connected to the MWCNT current collector.

Figure 6-3 - (a) Top-view and (b) tilted-view SEM image of vertically-aligned MWCNT arrays. (c) Top-view and (d) tilted-view SEM image of MWCNT/a-Ge. (e) Top-view and (f) tilted-view SEM image of MWCNT/c-Ge.

As shown in Figure 6-4, MWCNT/a-Ge has amorphous Ge mainly coated on the top of MWCNT arrays. Unlike MWCNT/a-Ge which shows relatively smooth coating, MWCNT/c-Ge shows polycrystalline Ge particles attached to the MWCNT, see Figure 6-4. Although Ni catalyst was not

detected in XRD, it is evident in the TEM image of thin-coated MWCNT/a-Ge as shown in Figure 6-5.

Figure 6-4 - Illustrations of the structure of vertically-aligned MWCNT arrays, MWCNT/a-Ge and MWCNT/c-Ge.

Figure 6-5 - Ni catalyst is shown in the TEM image.

The cycle performance of MWCNT/c-Ge and MWCNT/a-Ge is shown in Figure 6-6a and Figure 6-6b, respectively. MWCNT/c-Ge showed first cycle discharge and charge of 955.6 and 710.8 mA h g⁻¹, respectively. It became stable from 2nd to 100th cycle with the specific capacity decreasing from 774.3 to 730.2 mA h g⁻¹. The stability could be attributed to MWCNT supporting structures that minimized pulverization of the active Ge [50]. After 100 cycles, the discharge and charge specific capacity of MWCNT/c-Ge were 730.2 mA h g⁻¹ and 713.4 mA h g⁻¹ at 0.1 C, respectively. MWCNT/a-Ge showed better performance. MWCNT/a-Ge showed first cycle discharge and

charge of 1725.8 and 1234 mA h g⁻¹ in Figure 6-6b. The specific capacity of MWCNT/a-Ge was 1096.1 mA h g⁻¹ at 0.1 C after 100 cycles.

The first cycle Coulombic efficiency of MWCNT/a-Ge and MWCNT/c-Ge of 73.5 and 71.3 % in average, respectively, were higher than most reports [29, 81, 86, 90, 92, 93, 98-102, 107, 108] but still lower than reference [89]. The irreversible capacity during the first cycle was probably due to the formation of SEI layer at high potential.

The MWCNT's contribution was negligible as shown in Figure 6-6a and Figure 6-6b. The specific capacity of MWCNT normalized to Ge mass was only ~33 mA h g⁻¹ after 100 cycles, less than 5 % contribution to the structure.

Figure 6-6 - The cycle performance of (a) MWCNT/c-Ge at the rate of 0.1 C and (b) MWCNT/a-Ge at the rate of 0.5 C for 100 cycles.

The areal capacity after 100 cycles of MWCNT/a-Ge and MWCNT/c-Ge were 0.41 and 0.24 mA h cm⁻², respectively. The volumetric capacity of MWCNT/a-Ge and MWCNT/c-Ge were 1623 and 952 mA h cm⁻³, respectively. The specific and volumetric capacity of both MWCNT/a-Ge and MWCNT/c-Ge were higher than the theoretical specific and volumetric capacity of graphite of 372 mA h g⁻¹ and 830 mA h cm⁻³. [1]

The morphology of the samples after cycling was investigated by opening the cells, followed by washing in propylene carbonate, acetone and propan-2-ol, consecutively and then vacuum anneal at 333.15 K. The SEM images of MWCNT/a-Ge and MWCNT/c-Ge in Figure 6-7 confirmed the stability of the structures. The MWCNTs in both samples were intact. They formed bundles probably because of the drying effect. We observed that after 100 cycles, both MWCNT/a-Ge and MWCNT/c-Ge have a stable, thick, and conformal SEI.

MWCNT/a-Ge and MWCNT/c-Ge showed inter-cracks between the active materials in Figure 6-7c and Figure 6-7d, but remained stable structures across a large area, as shown in Figure 6-7e and Figure 6-7f. These inter-cracks were originated from strain relaxation of the structures during lithiation/delithiation. [50] Figure 6-7e and Figure 6-7f show the inter-cracks of MWCNT/a-Ge were lesser in extent than those of MWCNT/c-Ge.

Figure 6-7 - Top-view SEM images of (a) MWCNT/a-Ge after 1 cycle, (b) MWCNT/c-Ge after 1 cycle, (c) MWCNT/a-Ge after 100 cycles and (d) MWCNT/c-Ge after 100 cycles. Top-view SEM images at low magnification of (e) MWCNT/a-Ge after 100 cycles and (f) MWCNT/c-Ge after 100 cycles.

The CV of the samples was performed at the scan rate of 0.1 mV s^{-1} and potential window from 0.01 to 1.2 V. A control sample of MWCNT arrays without Ge coating had small/negligible signal compared to Figure 6-8. MWCNT/a-Ge showed a strong peak at around 0.01 V in the first cathodic scan, as shown in Figure 6-8a. In contrast, MWCNT/c-Ge showed strong peaks at around 0.27 and 0.14 V and no peak at 0.01 V, as shown in Figure 6-8b. The peaks at 0.27 and 0.14 V could be attributed to lithiation of polycrystalline Ge into amorphous Li_xGe ($0 < x < 3.75$) [105, 140-142] and related to electrochemically-driven solid-state amorphization of

polycrystalline Ge. [141] The peak at 0.01 V could be attributed to crystallization of amorphous Li_xGe ($0 < x < 3.75$) to crystalline $\text{Li}_{15}\text{Ge}_4$. [140, 142]

Figure 6-8 - The CV of (a) MWCNT/a-Ge and (b) MWCNT/c-Ge at first, second and third cycle.

The first cycle's cathodic scan of both samples was different, probably because MWCNT/a-Ge did not go through electrochemically-driven solid-state amorphization. Thus, less structural change was expected during first lithiation of MWCNT/a-Ge. During the first anodic scan, MWCNT/a-Ge showed a broad peak at around 0.44 V and a shoulder at around 0.55 V. In contrast, the MWCNT/c-Ge showed a shoulder at 0.44 V and a sharp peak at 0.55 V. The difference in the first cycle's anodic scan was probably because of

different structural ordering and history of lithiation during the previous cathodic scan. [142]

Figure 6-8a shows during the second to third cathodic scan of MWCNT/a-Ge, the peak at about 0.16 and 0.34 V and shoulder at about 0.45 V increased. During the anodic scan of MWCNT/a-Ge, the peak was at around 0.42 V and shoulder at around 0.55 and 0.75 V were found. From the second to third cathodic scan, the MWCNT/c-Ge showed the peaks at around 0.14, 0.35 and 0.5 V, as shown in Figure 6-8b. The anodic scan of MWCNT/c-Ge showed shoulder at around 0.42 V, peak at around 0.55 V and shoulder at around 0.75 V. The first cathodic scan of MWCNT/c-Ge was different with its second and third cathodic scan, while the MWCNT/c-Ge first anodic scan remains the same as the second and third anodic scan, suggesting that polycrystalline Ge was amorphized during the first cathodic scan, and did not recover to polycrystalline structure during subsequent anodic scans. [141]

The CV peaks during cathodic and anodic scan in Figure 6-8a and Figure 6-8b could transform to potential plateaus during lithiation and delithiation, respectively, in Figure 6-9a and Figure 6-9b. Figure 6-9a and Figure 6-9b show the voltage profiles of MWCNT/c-Ge and MWCNT/a-Ge, respectively. Since MWCNT/a-Ge has the lower peak at 0.42 V compared with the peak at 0.55 V of MWCNT/c-Ge during the anodic scan, MWCNT/a-Ge could favor higher energy density than MWCNT/c-Ge when paired with cathode active material such as LiCoO_2 . However, this condition only last for about 50 cycles.

Figure 6-9 - The voltage profile of (a) MWCNT/c-Ge and (b) MWCNT/a-Ge.

Our finding can be summarized as follows:

- MWCNT/a-Ge had a higher specific capacity than MWCNT/c-Ge after 100 cycles;
- both MWCNT/a-Ge and MWCNT/c-Ge had a stable SEI film after 100 cycles;
- the lower peak during initial anodic scan in MWCNT/a-Ge favor higher energy density than MWCNT/c-Ge when paired with cathode materials.

Amorphous Ge has preferable characteristics when designing Ge-based anodes. Amorphous Ge was better than polycrystalline Ge mainly because MWCNT/a-Ge skipped electrochemically-driven solid-state amorphization of crystalline Ge during the first lithiation. [141] Also, the synthesis of

amorphous Ge can be generally completed at lower temperatures than polycrystalline Ge.

Our finding was consistent with the majority of reports of Ge based anodes, as shown in Figure 6-10. Most of amorphous Ge based anodes have specific capacity above 1000 mA h g^{-1} . [71, 75, 80, 81, 103, 104, 106, 111, 143] On the contrary, most of the crystalline Ge based anodes have specific capacity below 1000 mA h g^{-1} . [83, 84, 86, 88-92, 95, 96, 99, 100, 102, 108] Crystalline Ge based anodes could only have specific capacities comparable to amorphous Ge based anodes when processed with special treatments, few-layer graphene coating [97, 98, 101], alkanethiol passivation [76], formation of $\text{Ge}_{0.95}\text{Sn}_{0.05}$ [109], use of FEC based electrolyte [78, 107], deployment of unique structure such as single crystalline Ge nanowires [29, 77, 82], 3D porous Ge assembly [74], and Ge nanoparticles–carbon core–shell nanostructure [87, 93], etc. In comparison, amorphous Ge has more relaxed requirements to achieve a similar high performance.

Figure 6-10 - The specific capacity of amorphous Ge [71, 75, 80, 81, 103, 104, 106, 111, 143] and crystalline Ge [29, 74, 76-78, 82-84, 86-93, 95-102, 107-109] from literature.

Figure 6-11 show that MWCNT/a-Ge has a good rate capability. Different charge and discharge rates were programmed each for 5 cycles at the rate of 0.1, 0.5, 1, 2, and 4 C ($1\text{ C} = 1624\text{ mA g}^{-1}$) in Figure 6-11a. MWCNT/a-Ge sample showed a relatively stable specific capacity of 1315.1, 1158.4, 1120.1, 1049.1 and 906 mA h g^{-1} at the rate of 0.1, 0.5, 1, 2, and 4 C, respectively. After the rate was adjusted back to 0.1 C for 5 cycles, MWCNT/a-Ge showed a significant recovery at a specific capacity of 1246.1 mA h g^{-1} . Figure 6-11b shows MWCNT/a-Ge specific capacity at the 100th cycle of 957.2 mA h g^{-1} was achieved at the rate of 1 C.

Figure 6-11 - (a) The rate capability of MWCNT/a-Ge. (b) The cycle performance of MWCNT/a-Ge at the rate of 1 C for 100 cycles.

6.4. Summary

We have fabricated MWCNT/a-Ge and MWCNT/c-Ge anodes using RF sputtering at room temperature and LPCVD at 803.15 K, respectively. Our MWCNT/a-Ge had a specific capacity of 1096.1 mA h g⁻¹ at the rate of 162.4 mA g⁻¹ for 100 cycles. In contrast, MWCNT/c-Ge had a specific capacity of 730.2 mA h g⁻¹ at the rate of 162.4 mA g⁻¹ for 100 cycles. Vertically-aligned MWCNT arrays play a role of minimizing pulverization of Ge coatings in both samples. Our MWCNT/a-Ge has better performances than MWCNT/c-Ge as amorphous Ge coating could skip the electrochemically-driven solid-state amorphization of crystalline Ge during the first lithiation. The potential use of amorphous Ge for the design of Ge-based anodes was shown.

Chapter 7 : Annealed amorphous-Ge film for Li-ion battery anodes

7.1. Introduction

Chapter 6 describes the prospect of amorphous Ge as a good candidate of anode active material. In this chapter, we focused on getting high specific and volumetric capacities of amorphous Ge based anodes. Since Ge has a high bulk density of 5.3234 g cm^{-3} [144], Ge film has a high theoretical volumetric capacity of $8643 \text{ mA h cm}^{-3}$ ($\text{Li}_{22}\text{Ge}_5$) or $7367 \text{ mA h cm}^{-3}$ ($\text{Li}_{15}\text{Ge}_4$). Clearly, Ge volumetric capacity are superior to graphite anode of 830 mA h cm^{-3} . [1] However, Ge undergoes huge volume change ($\sim 260 \%$) [73] during lithiation/delithiation that induces structure disintegration and/or delamination from current collector. Several approaches have been used to solve this challenge.

The first approach was to alleviate the stress by reducing the size to nano scale such as Ge nanowires [78, 79], Ge nanotubes [80], porous nanostructure [108, 112, 113], etc. However, the nanostructures tend to have a lower density which reduces the theoretical volumetric capacity of the material.

The second approach was to introduce buffering matrix to coat Ge [97, 98, 102] or to be coated by Ge [111], Ge composite [94], etc. Depending on the ratio of active material to buffering matrix, the buffering matrix might significantly decrease the theoretical specific capacity of the composite.

The third approach was to deposit the Ge film directly onto the current collector. [71, 103, 105] Graetz [71] deposited 60 – 250 nm of amorphous Ge on planar Ni current collector and showed specific capacity of 1700 mA h g⁻¹ at the rate of 375 mA g⁻¹ for 60 cycles. Laforge [105] showed amorphous Ge with n-type doping and 200 nm thickness had specific capacity of ~1460 mA h g⁻¹ at the rate of 100 μ A cm⁻² for 180 cycles. Recently, Rudawski [103] applied ion-beam treatment to Ge thin film and achieved ~1500 mA h g⁻¹ at the rate of 649.2 mA g⁻¹ for 25 cycles. However, because the Ge thickness was only 140 nm, the areal capacity was limited to ~0.1 mA h cm⁻² which might not be qualified for commercial purpose.

There is a challenge to employ thick Ge film as Li-ion battery anode since the cycle performance of Ge film depends on the initial Ge thickness. When Ge thickness is higher than the critical thickness, the cycle performance degrades because of the pulverization and/or delamination. When the deposited Ge is thin, the areal capacity is limited.

In this chapter, we deposited at least 759.8 nm thick of Ge film on SS substrate to achieve an excellent performance of Ge based anode. Annealing treatment in air was used to improve the specific capacity, volumetric capacity and cycle performance of thick Ge film on SS substrate.

7.2. Methodology

7.2.1. Sample preparation

Figure 7-1 shows the schematics of the fabrication process of our samples. Four different samples were fabricated. Annealed Ge was the main sample. As-deposited Ge was the control sample. As-deposited Ge on TiN

(TiN/Ge) and annealed TiN/Ge were fabricated to investigate the effect of diffusion barrier in the SS/Ge interface.

Figure 7-1 - Schematic of fabrication process of the as-deposited Ge, annealed Ge, as-deposited TiN/Ge and annealed TiN/Ge.

7.2.1.1. Fabrication of As-deposited Ge

SS disks (304 type, 15.5 mm diameter) were cleaned by ultrasonication in isopropanol followed by vacuum oven for 4 hours at 60 C. The SS samples were put inside RF sputtering chamber (Denton Sputter). Ge target with 99.999% purity was used. The base pressure was 1×10^{-3} Pa. We flowed 50 sccm Ar gas. Deposition pressure was ~ 1.2 Pa. The deposition was performed with 100 watts plasma power. The Ge mass of as-deposited Ge sample was accurately determined by measuring the mass difference of sample before and after sputtering using Mettler Toledo XP26 DeltaRange balance that has readability of 0.002 mg.

Figure 7-2 – X-SEM image of 759.8 nm as-deposited Ge.

Figure 7-2 shows the X-SEM of Ge on polished Si substrate for thickness measurement. Using TEM, we confirmed that the thickness of Ge deposited on polished Si was similar with that on SS substrate. The deposition rate of Ge was $\sim 12.7 \text{ nm min}^{-1}$ as shown in Figure 7-3. As-deposited Ge samples were fabricated at different thickness of 72.7, 125.8, 183, 357.5 and 759.8 nm.

Figure 7-3 - Ge thickness vs. deposition time of as-deposited Ge.

7.2.1.2. Fabrication of Annealed Ge

Annealed Ge sample was fabricated by annealing the as-deposited Ge inside Thermolyne furnace at 500 °C for 1 hour. The ramp-up was 5 °C/min. The ramp-down was overnight. The Ge mass was determined using the same way as as-deposited Ge. We fabricated 759.8 and 1530 nm annealed Ge samples.

7.2.1.3. Fabrication of As-deposited TiN/Ge

As-deposited TiN/Ge was fabricated the same way with as-deposited Ge, except prior Ge deposition, Ti adhesion layer and TiN diffusion barrier layer were deposited using DC sputtering (Elite sputter) as shown in Figure 7-1. Ge mass was determined the same way with as-deposited Ge. We fabricated as-deposited TiN/Ge with Ge thickness of 125.8 and 759.8 nm.

7.2.1.4. Fabrication of Annealed TiN/Ge

Annealed TiN/Ge was fabricated in the same way as annealed Ge, except that prior Ge deposition, Ti adhesion layer and TiN diffusion barrier layer were deposited using DC sputtering (Elite sputter). Ge mass was determined in the same way as as-deposited Ge. We fabricated annealed TiN/Ge with Ge thickness of 125.8 and 759.8 nm.

7.2.2. Physical characterization

The as-deposited Ge and annealed Ge were characterized using XRD of Siemens D5005 XRD with Cu K α of 0.1540 nm and Raman Spectroscopy of WITec with 532 nm excitation wavelength. The morphology of samples was investigated using SEM of LEO-FESEM with accelerating voltage of 5.00 kV. EDS was performed using JSM-5600LV with accelerating voltage of 20 kV. TEM was performed using JEOL 2010F with accelerating voltage of 200 kV. EDX linescans of TEM samples were performed using JEOL 2010F with dark-field scanning mode and accelerating voltage of 200 kV.

7.2.3. Electrochemical characterization

The prepared samples, Celgard-2300 separators, liquid electrolytes and pure Li metals were assembled in 2032-type coin cells inside an Ar glove box that had O₂ and moisture level of less than 5 ppm. The liquid electrolyte used was 1 M LIPF₆ dissolved in 1:1 by volume of EC and DEC. Since as-deposited Ge and annealed Ge anodes were tested in a half-cell configuration against the Li metal, we refer them to be as-deposited Ge and annealed Ge samples, respectively. Battery cycle life testing was performed using Neware battery tester at the rate of 0.1 C and 0.5 C (1 C = 1624 mA h g⁻¹). The potential window was 1.2 – 0.01 V vs. Li/Li⁺. The specific capacities were

based on Ge mass. The volumetric capacities were based on Ge volume. CV was performed using Autolab machine at the scan rate of 0.1 mV s^{-1} . EIS was performed using Autolab machine at 1×10^5 to 1 Hz frequencies and 0.01 V amplitude.

7.3. Results and discussion

The as-deposited Ge has stable cycle performance when Ge thickness is less than critical thickness. Figure 7-4 shows that at Ge thickness of 72.7 nm and 125.8 nm, the specific capacities were large at 1476.4 and 1304.1 mA h g^{-1} , respectively. The mass loading was only 0.032 and 0.066 mg cm^{-2} for Ge thickness of 72.7 and 125.8 nm, respectively. This resulted in low areal capacity of 0.047 and $0.086 \text{ mA h cm}^{-2}$ for 72.7 and 125.8 nm Ge thickness, respectively. The cycle performance degraded when the Ge thickness was larger than 125.8 nm. As-deposited Ge with thickness of 183, 357.5 and 759.8 nm had poor specific capacities of 594.9, 150.0 and 56.6 mA h g^{-1} , respectively, at the rate of 812 mA g^{-1} for 50 cycles. In the following study, we investigated the effect of annealing to 759.8 nm Ge thickness with mass loading of 0.377 mg cm^{-2} .

Figure 7-4 – The specific capacity vs. cycle of as-deposited Ge at different thickness.

Figure 7-5 - The (a) XRD and (b) Raman spectra of as-deposited Ge and annealed Ge.

The annealed Ge sample was characterized and compared with control sample of as-deposited Ge. There was a little difference between annealed Ge and as-deposited Ge, based on XRD and Raman spectra in Figure 7-5a and Figure 7-5b, respectively. The XRD shows broad peak at $\sim 27^\circ$ which corresponds to amorphous Ge for both as-deposited and annealed Ge. The Raman peak at about 273 cm^{-1} corresponds to amorphous Ge for both as-deposited and annealed Ge. [138]

Figure 7-6a and Figure 7-6b shows the top-view SEM of as-deposited and annealed Ge, respectively. Since the SS was not polished, the Ge surface on both sample follow the rough contour of SS surface. Figure 7-6b shows that the annealed Ge has more charging under the SEM electron beam. It indicated

that the annealed Ge has more oxide than the as-deposited Ge. Due to the annealing process in air, the EDS qualitatively evidenced that intensity of O $K\alpha$ at 0.525 keV is higher in annealed Ge sample than as-deposited Ge sample, as shown in Figure 7-7. However, the Ge was still dominant in both as-deposited and annealed Ge samples.

Figure 7-6 - The top-view SEM images of (a) as-deposited Ge and (b) annealed Ge.

Figure 7-7 - The EDS spectra of as-deposited Ge and annealed Ge.

The electrochemical performance of annealed Ge is significantly better than the as-deposited Ge. The as-deposited Ge had specific capacity of 1514.1 mA h g⁻¹ and 1226.3 mA h g⁻¹ during first lithiation and delithiation, respectively. The coulombic efficiency of as-deposited Ge was 81 %. The annealed Ge had specific capacity of 1374.8 mA h g⁻¹ and 1247.6 mA h g⁻¹ during first lithiation and delithiation, respectively. The coulombic efficiency of annealed Ge was 90.8 %, which was higher than the as-deposited Ge and comparable with the highest coulombic efficiency reported so far. [89] The as-deposited Ge had poor cycle performance, with only 56.6 mA h g⁻¹ specific capacity after 50 cycles. In contrast, the annealed Ge had improved cycle performance with 1186 mA h g⁻¹ after 50 cycles at 0.5 C rate as shown in Figure 7-8.

Figure 7-8 -The specific capacity vs. cycle at the rate of 0.5 C of 759.8 nm annealed Ge and as-deposited Ge.

To test the rate capability, different lithiation and delithiation rates were used as shown in Figure 7-9a. Annealed Ge shows an excellent specific capacity of 1308.8, 1261.2, 1215.4, 1153.5, 1043.3 mA h g⁻¹ at 0.1 C, 0.5 C, 1 C, 2C, 4C, respectively. In contrast, the as-deposited Ge could only withstand a maximum of 2 C rate. As-deposited Ge had a specific capacity of 186.4,

51.3, 22.6, 8.1 mA h g⁻¹ at 0.1 C, 0.5 C, 1 C, 2C, respectively. When the rate was tuned back to 0.1 C, the annealed Ge showed significant recovery with specific capacity of 1302.1 mA h g⁻¹, while as-deposited Ge only show specific capacity of 60.0 mA h g⁻¹. Figure 7-9b shows the annealed-Ge was able to be cycled at 1 C rate with a specific capacity of 1178.5 mA h g⁻¹ for 100 cycles.

Figure 7-9 - (a) The rate capability of 759.8 nm annealed Ge and as-deposited Ge. (b) The cycle performance at the rate of 1 C of 759.8 nm annealed Ge.

Since our structure had Ge density of 4.96 g cm⁻³ which is close to bulk density of Ge of 5.3234 g cm⁻³, we were able to achieve a high volumetric capacity of annealed Ge of 5887.4 mA h cm⁻³ at rate of 0.5 C for 50 cycles, see Figure 7-10. The volumetric capacity of annealed Ge exceeded that of as-deposited Ge of 288 mA h cm⁻³. The volumetric capacity of annealed Ge also

surpassed the theoretical volumetric capacity of graphite of 830 mA h cm^{-3} and outperformed the experimental volumetric capacity of Si [145-155], Ge [78, 87, 143, 156] and other active materials [157-160], see Figure 7-11.

Figure 7-10 -The volumetric capacity vs. cycle at the rate of 0.5 C of 759.8 nm annealed Ge and as-deposited Ge.

Figure 7-11 - Volumetric capacity vs. rate of annealed Ge and literature [1, 78, 87, 143, 145-160].

The annealed Ge sample had areal capacity of $0.47 \text{ mA h cm}^{-2}$. Typically, areal capacity of above 1 mA h cm^{-2} is needed to achieve practical application. A way to increase the areal capacity would be to deposit thicker Ge. Annealed Ge with 1530 nm thickness had areal capacity of $0.93 \text{ mA h cm}^{-2}$ at 0.1 C for 50 cycles. Another approach would be to use the layer-by-layer

approach, similar to reference [145]. We demonstrated the layer-by-layer approach of annealed Ge, as shown in Figure 7-12, with areal capacity of 0.47, 0.99, 1.40 mA h cm⁻² for 1, 2 and 3 layers, respectively, at 0.1 C for 20 cycles.

Figure 7-12 -The areal capacity vs. cycle at the rate of 0.1 C for 1, 2 and 3 layer annealed Ge film.

Figure 7-13 -The voltage profile of 759.8 nm (a) annealed Ge and (b) as-deposited Ge.

Figure 7-13a and Figure 7-13b show the voltage profile of annealed Ge and as-deposited Ge, respectively. The annealed Ge had more stable specific capacity than as-deposited Ge. Figure 7-14a shows the CV of annealed Ge sample had cathodic peaks at 0.22 and 0.07 V and anodic peak at 0.61 V in the first cycle. In the 2nd and 3rd cycles, the cathodic peaks shifted to 0.34 and 0.15 V, while the anodic peak kept at 0.61 V. Figure 7-14b shows the CV of as-deposited Ge. The current of as-deposited Ge significantly decreased from 1st to 3rd cycle. It indicated that the performance of the Ge based anode degraded with cycle number probably because the pulverization and detachment of Ge film that cut the electrical pathway to the current collector.

Figure 7-14 -The CV of (a) 759.8 nm thick annealed Ge and (b) 759.8 nm thick as-deposited Ge.

Figure 7-15 -The top-view SEM images of 759.8 nm as-deposited Ge after (a) 1, (b) 2 and (c) 50 cycles. The top-view SEM images of 759.8 nm annealed Ge after (d) 1, (e) 2 and (f) 50 cycles.

Figure 7-15 show the SEM images of samples after cycling in the delithiated state. Figure 7-15a, Figure 7-15b, and Figure 7-15c show the as-deposited Ge after 1 cycle, 2 cycles, and 50 cycles. Figure 7-15d, Figure 7-15e, and Figure 7-15f show the annealed Ge after 1 cycle, 2 cycles, and 50 cycles. After one cycle, most of the thick Ge film in the as-deposited Ge sample was detached from the SS substrate, see Figure 7-15a. Although there existed cracks in the Ge film of annealed Ge sample, most of the Ge film in the annealed Ge sample was still attached onto the SS substrate as shown in Figure 7-15d. After 50 cycles, most of Ge film was detached in the as-

deposited Ge sample. In contrast, the Ge was still attached to SS substrate in the annealed Ge sample.

Figure 7-16 shows the SEM image of annealed Ge after 2 cycles and its EDS mapping. The island-like-objects were indeed Ge. The annealed Ge sample had improved cycle performance than as-deposited Ge because majority of the Ge film was not detached from the SS current collector. The detachment of Ge film increases the charge-transfer resistance as shown in the Figure 7-17b.

Figure 7-16 - The top-view SEM image and EDS mapping of 759.8 nm annealed Ge after 2 cycles.

Figure 7-17 shows that after 2 cycles, the charge-transfer resistance of as-deposited Ge of $\sim 53.9 \Omega$ was similar to annealed Ge of $\sim 44.2 \Omega$. After 50 cycles, the charge-transfer resistance of as-deposited Ge increased to $\sim 157 \Omega$, much higher than that of annealed Ge of $\sim 19.6 \Omega$.

Figure 7-17 - The Nyquist plots of 759.8 nm thick annealed Ge and as-deposited Ge after (a) 2 and (b) 50 cycles.

Figure 7-18 shows the cross-section TEM (X-TEM) image of annealed-Ge sample at the top interface. During TEM preparation, Cu and Pt protective layers were deposited on top of Ge film to protect the Ge film during FIB milling. There was ~8 nm oxide layer on top of the Ge layer, probably formed during annealing process in air.

Figure 7-18 -The X-TEM images of 759.8 nm thick annealed Ge near the top surface.

Figure 7-19 - The cross-section STEM images of the 759.8 nm thick (a) as-deposited Ge and (b) annealed Ge samples and their corresponding EDX linescans. (c) The EDX linescan of the 759.8 nm thick as-deposited Ge. (d,e,f) The EDX linescans of the 759.8 nm thick annealed Ge.

Figure 7-19a and Figure 7-19b show the cross-section Scanning Transmission Electron Microscopy (STEM) images of as-deposited Ge and annealed Ge samples, respectively. The EDX linescans were performed to investigate the concentration profile near the SS/Ge interface. Figure 7-19c shows that the as-deposited Ge sample had no inter-diffusion at the interface. In contrast, the EDX linescans in Figure 7-19d and Figure 7-19e confirmed the

inter-diffusion at the interface of the annealed Ge sample. The inter-diffusion suggested the formation of intermetallic phases, which can be clearly seen from the contrast difference in the inter-diffusion zone, see Figure 7-19b. Figure 7-19f shows no inter-diffusion at the interface. These findings suggest that the formation of intermetallic phase is not uniform.

The inter-diffusion at SS/Ge interface might be responsible to the improvement of the battery performance of annealed Ge. To validate this, we tested other samples where we intentionally hinder the inter-diffusion of SS and Ge by introducing a diffusion barrier layer.

The improved adhesion of the Ge film to SS substrate was investigated by having a control samples of as-deposited TiN/Ge and annealed TiN/Ge. Ti was used as adhesion layer between TiN and SS substrate. TiN was used as a diffusion barrier layer between Ge film and SS substrate. The Ti/TiN layer did not negatively affect the cycle performance as it has been used in references [50, 136] as a barrier layer for Ni catalyst for MWCNT growth.

Figure 7-20a shows the electrochemical performance of 125.8 nm thick Ge with and without TiN diffusion barrier as well as with and without annealing. At 125.8 nm, the as-deposited Ge was stable over 50 cycles. Figure 7-20a also shows the TiN diffusion barrier did not negatively affect the cycle life of Ge film. The Ti/TiN layer enabled better performance of as-deposited TiN/Ge than as-deposited Ge probably because of the usage of Ti adhesion layer. The annealed Ge showed the best performance. The annealed Ge has better performance than annealed TiN/Ge because TiN diffusion barrier layer prevented the inter-diffusion of Ge and SS during annealing in air. This effect become more obvious when thicker Ge was used.

Figure 7-20b shows at 759.8 nm Ge thickness, the annealed Ge had the best cycle performance in comparison with the annealed TiN/Ge, as-deposited TiN/Ge and as-deposited Ge. This shows that when the inter-diffusion at the SS/Ge interface impeded, the cycle performance degraded, probably because the inter-diffusion improves the adhesion of Ge film to the SS substrate.

Figure 7-20 - (a) The cycle performance of 125.8 nm thick as-deposited Ge, as-deposited TiN/Ge, annealed TiN/Ge and annealed Ge. (b) The cycle performance of 759.8 nm thick as-deposited Ge, as-deposited TiN/Ge, annealed Ge and annealed TiN/Ge.

The oxide in the Ge film might also be important to the cycle performance of annealed Ge samples. We observed that the annealed Ge sample had improved cycle performance only when annealing was performed in air. However, over anneal in air could decrease the specific capacity. The mass loading of Ge might be decreased due to over-oxidation. Figure 7-21

shows that annealing for 2 hours decreased the specific capacity to 1050.7 and 913.8 mA h g⁻¹ in the first and 50 cycles, respectively, much lower than the corresponding capacities for 1-hour annealed Ge sample.

Figure 7-21 - The cycle performance of 759.8 nm thick annealed Ge with annealing time of 1 and 2 hours.

7.4. Summary

As-deposited Ge had a poor cycle performance when Ge thickness was larger than 125.8 nm. However, thicker Ge was needed to increase the areal capacity for practical application. We have fabricated annealed Ge with a thickness of 759.8 nm with specific capacity and volumetric capacities of 1186 mA h g⁻¹ and 5887.4 mA h cm⁻³, respectively. The areal capacity of annealed Ge was 0.47 mA h cm⁻², and can be increased using thicker Ge and/or layer by layer approach.

Annealed Ge had better performances than as-deposited Ge because: 1) improved adhesion of Ge layer to SS, as evidenced by SEM after cycles and 2) a little oxygen impurities in the Ge layer. The improved adhesion was due to the inter-diffusion of Ge and SS during high temperature annealing in air. Oxygen impurity in Ge film is important to the cycle performance, but the amount of impurity must be controlled carefully. We presented an improved performance of thick Ge film anode by a simple process of annealing in air.

Chapter 8 : Conclusions and recommendations

8.1. Conclusions

We have designed and developed four types of Li-ion anodes from Chapter 4 to Chapter 7. Novel technique to fabricate NiO-C composite on 3D substrate was reported in Chapter 4. Although most literature had shown high specific capacities, the loading of active anode materials and thus their areal capacity were limited. To increase areal capacity, large mass loading was used but faced the problem of poor cycle performance. By having graphitic and amorphous carbon composite, NiO-C structure maintained stable cycle performance while achieving acceptable areal capacity

NiO was deposited on vertically-aligned MWCNT arrays and achieved a stable cycle performance in Chapter 5. The MWCNT arrays play a role of minimizing pulverization and agglomeration problems of NiO.

The effect of crystallographic nature of Ge, whether amorphous or polycrystalline, to the performance of Ge-based anode was investigated in Chapter 6. Vertically-aligned MWCNT arrays were used as a platform for both MWCNT/a-Ge and MWCNT/c-Ge. Amorphous Ge might be a better candidate for anode material than polycrystalline Ge as amorphous Ge is more flexible in accommodating the volume changes during lithiation and delithiation.

Finally, the effect of annealing to the performance of amorphous Ge film anode was examined in Chapter 7. By annealing Ge film at optimal conditions, the cycle performance of thick Ge film was significantly improved.

The main features of the four anodes developed in this PhD project are summarized in Table 8-1.

Table 8-1 - Comparison of technical specifications of investigated anodes

	NiO-C composite	MWCNT/NiO	MWCNT/a-Ge	Annealed Ge film
Novelty	Demonstrated a stable cycle performance of large mass loaded anode by incorporation of graphitic and amorphous carbon composite.	Demonstrated the importance of MWCNT to minimize pulverization of conversion-type anode.	Investigated the systematic comparison of a-Ge and c-Ge on same MWCNT platform. Recommended amorphous Ge for anode active material.	Demonstrated a stable cycle performance of thick amorphous Ge film by annealing treatment in air.
Cost of material	Low	Low	Medium	Medium
Cost of processing	Low	Medium	Medium	Medium
Specific capacity	389.16 mA h g ⁻¹ at 359 mA g ⁻¹ for 102 cycles	864.8 mA h g ⁻¹ at 143.6 mA g ⁻¹ for 50 cycles	1096.1 mA h g ⁻¹ at 162.4 mA g ⁻¹ for 100 cycles	1186 mA h g ⁻¹ at 812 mA g ⁻¹ for 50 cycles
Mass loading	4.54 mg cm ⁻²	0.90 mg cm ⁻²	0.37 mg cm ⁻²	0.377 mg cm ⁻²
Areal capacity	1.76 mA h cm ⁻² at 359 mA g ⁻¹ for 102 cycles	~0.42 mA h cm ⁻² at 143.6 mA g ⁻¹ for 50 cycles	0.41 mA h cm ⁻² at 162.4 mA g ⁻¹ for 100 cycles	0.47 mA h cm ⁻² at 812 mA g ⁻¹ for 50 cycles
Volumetric capacity	~2615 mA h cm ⁻³ at 359 mA g ⁻¹ for 102 cycles	~702.5 mA h cm ⁻³ at 143.6 mA g ⁻¹ for 50 cycles	1623 mA h cm ⁻³ at 162.4 mA g ⁻¹ for 100 cycles	5887.4 mA h cm ⁻³ at 812 mA g ⁻¹ for 50 cycles
Initial Coulombic efficiency	52.74% at 359 mA g ⁻¹ 62.41% at 79 mA g ⁻¹	75.3% at 143.6 mA g ⁻¹	~73.5 % at 162.4 mA g ⁻¹	90.8 % at 812 mA g ⁻¹
Potential profile of 2 nd cycle onwards	Lithiation plateau mainly at 1.18 V Delithiation plateau mainly at 2.25 V	Lithiation plateau mainly at 1.1 V Delithiation plateau mainly at 2.25 V	Lithiation plateau at 0.16 and 0.34 V Delithiation plateau mainly at 0.42 V	Lithiation plateau at 0.15 and 0.34 V Delithiation plateau mainly at 0.61 V

The NiO-C composite had the advantages of low costs of material and processing. Ni can be easily oxidized to achieve NiO. In addition, the processing of NiO-C composite does not need a vacuum environment. In contrast, MWCNT/NiO, MWCNT/Ge and annealed Ge film are processed using vacuum-based systems. Therefore, these materials are fabricated at higher costs than NiO-C.

The annealed Ge film had the best specific performance. At a high rate of 812 mA g^{-1} , annealed Ge film achieved a specific capacity of 1186 mA h g^{-1} at for 50 cycles. Although the areal capacity of annealed Ge was only 0.377 mg cm^{-2} , it can be increased using thicker film or multilayer methods. Annealed Ge with 1530 nm thickness had an areal capacity of $0.93 \text{ mA h cm}^{-2}$ at 162.4 mA g^{-1} for 50 cycles. A three-layer annealed Ge films had an areal capacity of $1.40 \text{ mA h cm}^{-2}$ at 162.4 mA g^{-1} for 20 cycles.

The NiO-C composite had the largest mass loading of 4.54 mg cm^{-2} and areal capacity of $1.76 \text{ mA h cm}^{-2}$ at 359 mA g^{-1} for 102 cycles. Assuming the same density with NiO of 6.72 g cm^{-3} [144], the volumetric capacity of NiO-C composite is calculated to be $\sim 2615 \text{ mA h cm}^{-3}$.

The annealed Ge film had the best volumetric capacity performance of $5887.4 \text{ mA h cm}^{-3}$ at 812 mA g^{-1} for 50 cycles. This is due to the nature of its dense film. NiO-C composite, MWCNT/NiO and MWCNT/Ge used porous structures, leading to lower volumetric capacities. Generally, porous structures are good for cycle performance at high rate, but at the expense of lower volumetric capacity.

The annealed Ge film also had the best initial Coulombic efficiency of 90.8% at 812 mA g^{-1} . The initial Coulombic efficiency is important when the

anode is paired with LiCoO_2 cathode. The higher the Coulombic efficiency means the lower the Li ion loss due to irreversible capacity.

The delithiation plateau of 2nd cycle onwards of MWCNT/a-Ge at 0.42 V was the lowest than that of annealed Ge of 0.61 V, NiO-C composite of 2.25 V and MWCNT/NiO of 2.25 V. Generally, Ge-based anode had lower delithiation potential than that of NiO-based anode.

8.2. Recommendations for future work

As outlined in the scope, we have tested the samples using half-cell configuration so far. In the future, full battery configuration can be tested by pairing the anode samples with LiCoO_2 cathode.

Important know-how has been gained from Chapter 4 to Chapter 7.

- a) 3D Ni foam current collector allows a large surface area.
- b) Vertically-aligned MWCNT arrays could improve the specific capacity, cycle performance and rate capability of NiO and Ge.
- c) Annealing treatment enables high specific and volumetric capacities of thick Ge films.

In the future, one can do more characterizations to better understand the mechanism: 1) the role of oxygen impurities to improve the performance of a-Ge and 2) the direct evidence of vertically-aligned MWCNT platform in absorbing compressive/tensile stress experienced by NiO.

One can investigate the annealed thick Ge film on 3D SS foam instead of planar current collector. MWCNT/Ge on 3D Ni foam is also worth to be studied. One can also investigate the effect of annealing treatment of MWCNT/thick-Ge.

One might improve the annealed Ge film anode by studying the effect of different type of substrates. One could also investigate the feasibility of using solution-based Ge deposition instead of vacuum-based Ge deposition to significantly decrease the material and processing costs of annealed Ge.

NiO might suffers from a low energy density when paired with LiCoO_2 cathode since NiO has a high delithiation plateau of ~ 2.25 V and lithiation plateau of ~ 1.18 V. A more suitable application for NiO might be as a cathode material for thin-film Li microbattery. NiO can be paired with Li metal or pre-lithiated Si. NiO paired with Li metal can achieve a working potential of 1.18 V. Today's transistors require less supply voltage than before, for example CMOS $0.09\text{ }\mu\text{m}$ technology requires ~ 1 V supply voltage which is smaller than that of $0.5\text{ }\mu\text{m}$ technology of ~ 5 V supply voltage. [161] Usually when using a high voltage battery of ~ 3.9 V, an inefficient dc-dc converter is used to match the potential requirement of the circuit. Using NiO-Li microbattery, the inefficiency of dc-dc converter can be avoided.

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