Mechanical properties of Uncoated and Core-shell Silicon Nanowire Arrays for the application of Lithium Ion Batteries

By Jeffrey Ho

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Abstract

Three types of silicon nanowires arrays: 1) Uncoated silicon nanowires; 2) Alumina-coated silicon nanowires and 3) Polymer-coated silicon nanowires have been studied with a newly developed Atomic Force Microscopy (AFM) based mechanical testing protocol regarding three mechanical properties, including: i) stress-strain slope (or slope of stress-strain curve); ii) energy dissipation and iii) strain-to-failure.

It is found that the alumina-coated silicon nanowires possessed the highest stress-strain slope, energy dissipation and strain-to-failure. The high stress-strain slope was attributed to the dominating elastic properties of the alumina coating, whereas the high energy dissipation and strain-to-failure were very likely to be due to the shearing of the alumina-silicon interface and the high friction coefficient of the alumina coating. It is concluded that short alumina-coated SiNW was the most suitable material to be used as LIB anode among the three materials tested since it can potentially tackle the mechanical issues during charging and discharging cycles.
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Chapter 1: Introduction

1.1 Importance of lithium ion batteries
In today’s world, electronic devices are necessities for human beings. Lithium ion batteries (LIB) are becoming more important as LIB are the power sources for a wide variety of electronic goods, including smart phone, laptops, digital camera and tablet. In particular, several countries including Japan and USA have been investing heavily on improving the performance of LIB since it has a great potential to be used in hybrid electric vehicles (HEV) which can potentially alleviate global warming issues and it is forecasted that the market share of LIB will increase more than $40 billion by 2021 (See Figure 1(a) and 1(b)) [1].

Figure 1: (a) The growing market share of LIB (b) Hybrid electric vehicles sales are constantly growing [1]
The anodes of LIB are typically made of carbonaceous materials such as graphite whereas the cathodes are usually made of a composition of transition metal-oxide and lithium ion [2]. However, it has long been proven that the anode material of a typical LIB have several limitations that would pose a negative impact on the lifetime and the performance of LIB. For instance, the charge capacity of graphite is only 370 mAh$^{-1}$ while the charge capacity of other materials, such as silicon (Si), can reach up to 4200 mAh$^{-1}$ [3]. Hence, scientists have been trying hard to develop a silicon anode that can replace conventional graphite anodes.

Apart from the limitation of low charge capacity of graphite anodes, a solid electrolyte interphase (SEI) layer typically formed on the anode surface during the charge and discharge cycling. This SEI layer consumes a huge amount of lithium ions upon the first charging cycle which results in a loss of charge capacity [4]. Furthermore, the anode material can experience significant volume expansion during the charging cycle (See Figure 2) when lithium ions are inserting into the anode, and experiences a large contraction during discharging cycle when lithium ions are extracted from the anode. Accordingly, this volume expansion and contraction cycles can induce large local strains within the anode material, which makes that the anode prone to mechanical degradation and pulverization. As a consequence, these limitations can greatly hinder the performance and reduce the lifetime of LIB. Accordingly, developing a new anode material that is one-directional and can be incorporated into LIB is of great essence in order to meet the increasing needs of LIB in today’s society.

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*Figure 2: Silicon nanoparticles underwent huge volume expansion during charging (lithiation) cycles which would eventually lead to the anode pulverization [5]*
1.2 Objectives

The ultimate goal of this project is to improve the efficiency and lifetime of lithium ion batteries through the application of Silicon nanowires arrays as the anode material since individual Si nanowires have been proven to have great potential to tackle the mechanical issues during charging and discharging cycles and exhibit dramatically improved charge capacity as compared to traditional graphite anodes (Refer to sections 2.4 and 2.5). Since numerous researches have been studied on single nanowire, it should be noted that the objective of this work is to evaluate the mechanical properties of nanowires arrays as it can be deduced that an array of nanowires, rather than a single nanowire, are going to be incorporated into future LIB as anode. Furthermore, it is aimed that the manufacturing cost of these nanowires should be as low as possible so that they can be mass-produced economically to replace current bulk graphite anodes.

In particular, the objectives of this work include the following:
1) Develop a new mechanical testing protocol to measure the slope of stress-strain curve, energy dissipation and strain-to-failure during compression of nanowire arrays samples since the assumptions required for conventional mechanical testing models are not appropriate for the nanowire arrays.
2) Conduct Atomic Force Microscopy (AFM) nanoindentation on three types of silicon nanowires (SiNW) arrays: 1) Uncoated SiNW 2) Alumina-coated SiNW and 3) Polymer-coated SiNW.
3) Compare experimental results to computational simulation on the mechanical behaviour of the silicon nanowires samples.
4) Identify the relationships between core-shell structural parameters (including shell material and nanowire length) on the mechanical properties of core-shell silicon nanowires.
2.1 Material selection for LIB anodes

As mentioned in Chapter 1, the majority of anodes used in LIB are made of graphite which has a specific charge capacity of 372 mAhg\(^{-1}\) that actually fails to sustain the daily usage of the electronic devices as many consumers need to recharge their devices very frequently [6]. Hence, it is very crucial to develop new materials that can replace conventional graphite anode in order to improve the performance and lifetime of LIB.

There are several factors that should be taken into consideration when selecting the right anode materials:

1) The materials need to have high charge capacity so that the battery can be long-lasting when it is discharging.
2) The materials should have a low potential so that the overall potential of the electrochemical device is high (as Potential\(_{\text{cell}}\) = Potential\(_{\text{cathode}}\) - Potential\(_{\text{anode}}\)).
3) The materials should possess high strain-to-failure since the anode would experience local strain formation and numerous cycles of volume expansion and contraction during charging and discharging cycles and thus the materials are very likely to fracture.
4) The materials should be non-toxic and have a fairly high electrical conductivity.
5) The materials should be highly abundant and cheap so that the overall production cost of future LIB can be kept low.

N. Nitta et al. analyzed several materials and they concluded silicon (Si) and Tin (Sn) were two suitable candidates to be used as LIB anode given that they have high capacity (Note: Silicon has an extremely high capacity of 4200 mAhg\(^{-1}\) which is 10 times higher than that of graphite), high availability, low potential and low toxicity [6]. Yet, they agreed that one should also pay heed to other materials. For example, Germanium (Ge) has caught the researcher's attention in recent years because of its superior conductivity. Some research showed that an electrochemical device with the use of Ge can be fully charged in 1.5 minutes [6]. However, due to the high cost of Ge, manufacturers might not be interested in putting Ge into LIB. According to the US Department of the Interior, the prices (all in US dollar) of Ge, graphite and Si were $1300-1900/kg, $0.4-1.9/kg and $2.70/kg respectively (See Table 1) [7]. Obviously, Si has a great potential to replace conventional graphite since it is only slightly more expensive than graphite, but with a 10 times higher charge capacity. Accordingly, future research should carry out mechanical and electrochemical testing on silicon to improve LIB performance in an economical way.

<table>
<thead>
<tr>
<th>Material</th>
<th>Germanium</th>
<th>Graphite</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price ($/kg)</td>
<td>1300-1900</td>
<td>0.4-1.9</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table 1: The cost of Ge, graphite and Si for the year 2014 (All in US dollar)
2.2 Lithium Ion Battery mechanism

LIB is a chemical cell that consists of three major components: a cathode, an anode and an electrolyte where there is ionic transportation between the electrodes during charging and discharging cycles (Figure 3). The anode is typical made of graphite whereas the cathode is usually made with a compound containing metal oxide and lithium ions, such as LiCoO₂.

![Figure 3: The major components of a LIB, which consists of a cathode (typically made of LiCoO₂), a graphite anode and an electrolyte which is a solution of lithium salt [8, 1]](image)

The two main chemical reactions that occur at the electrodes are as follows [8]:

1) \[ \text{C} + x\text{e}^- + x\text{Li}^+ = \text{Li}_x\text{C} \text{ (anode)} \]

2) \[ \text{LiCoO}_2 - x\text{e}^- - x\text{Li}^+ = \text{Li}_{1-x}\text{CoO}_2 \text{ (cathode)}, \text{ where } x < 0.5 \text{ to make the two reactions reversible} \]

However, there is a serious problem that has long been deteriorating LIB performance which is the formation of the Solid Electrolyte Interphase (SEI) on the anode surface. The SEI formation is mainly due to the decomposition of the electrolyte upon the first charging cycle, and hence the SEI is composed of both organic and inorganic components (See Figure 4). Ideally, the formation of this SEI layer can help stabilize the performance of LIB since the SEI layer can act as a passive layer that only allows ionic, but not electronic, transportation which can prevent the electrolyte from further degradation, and ensure good cyclability of LIB [4]. However, the formation of the SEI layer is affected by two main factors: i) Voltage and ii) Temperature. For instance, the SEI layer can start to be formed at various voltage, ranging from 0.8 V to 1.7 V, while lithium ion transportation would start at 0.3 V. As a result, a large amount of lithium ions would be consumed to form the SEI layer which can greatly reduce the charge capacity [4].

Battery temperature is another factor that can affect the SEI components and the stability of LIB. Some of the components of the SEI undergo transformation which results in a more stable SEI when the battery temperature reaches 60°C to 105°C. However, when the battery temperature keeps
elevating to 120°C, some active materials inside the battery would react with either the electrolyte or the SEI layer. For example, the lithium ions on the anode would be allowed to react directly with the electrolyte which further reduces the charge capacity of LIB.

Ideally, the thickness of the SEI layer would stop increasing upon the first charging cycle where the SEI is first formed. But with the elevating temperature and changing voltage applied, the SEI thickness would indeed increase since the SEI layer can decompose during discharging cycle and would form again upon subsequent charging cycles. The previously formed SEI debris would increase the thickness of the newly formed SEI layer (See Figure 5). As a result, the ionic transportation path would become longer which reduces the efficiency of LIB [9]. All in all, the unstable transformation of the SEI layer would greatly impact the LIB performance since the thickness of the SEI would become thicker with the increasing numbers of charging and discharging cycles. Regarding this unable transformation of SEI, some researchers have studied the use of various nanostructures such as thin films and nanowires as anodes which can help stabilize the formation of SEI and is able to prolong the LIB lifetime (See Section 2.5).

Figure 4: SEI layer formed on the anode surface during lithiation where the SEI consists of various organic and inorganic components [4]

Figure 5: SEI layer becomes thicker gradually since the SEI would decompose and would form again upon charging and discharging cycles [9]
2.3 Electrochemical testing

The purpose of conducting electrochemical testing is to obtain two pieces of important information regarding LIB performance: 1) Cycle stability, which refers to the final capacity of the LIB after running certain numbers of charging and discharging cycles; 2) Coulombic efficiency, which is the ratio of delithiation capacity to lithiation capacity.

Before implementing the electrochemical testing, it is important to obtain some basic understanding of the parameters with respect to the battery performance. Charge rate, C, which comes with the unit of charge per mass (mAh g\(^{-1}\)) is a significant parameter since it states how long it takes for the battery to be fully charge/discharged [6]. For instance, a charge rate of 1C implies that the battery can be fully charged/discharged in 1 hour; 2C means the battery can be fully charged/discharged in 30 minutes; 0.5C indicates that the battery can be fully charged/discharged in 2 hours [6]. It should be noted that if a battery is discharged with a higher charge rate, the capacity loss will become higher which results in a lower discharge capacity. Also, the formation of SEI would lead to permanent loss of lithium ions and thus lower the capacity [6].

E. Teo et al. carried out electrochemical testing on a LIB which consisted of an anode made of carbon nanotube, nickel and silicon (CNT-Ni-Si) NW [10]. The test was conducted over a potential range of 0.01 V to 1.2 V at 0.2C. It is measured that the initial delithiation capacity was 2527 mAh g\(^{-1}\) and was maintained quite stable throughout the test. It is found that the capacity was 1960 mAh g\(^{-1}\) after 110 cycles which was very close to its initial capacity, meaning that the battery had a very stable cycling (Figure 6a). E. Teo et al. then implemented another test in which they increased the charge rate every 10 cycles. It is shown that the capacity was able to go back to 2246 mAh g\(^{-1}\), which was very close to its initial capacity of 2527 mAh g\(^{-1}\), once the charge rate was switched back to its original value (Figure 6c). These results indicated that the battery with the use of CNT-Ni-Si anode exhibited excellent cycle stability, rate capability and reversible capacity. Apart from these significant results obtained from electrochemical testing, it is noteworthy that the use of Ni and CNT could optimize LIB performance (Figure 7). The reason is that Ni is an inactive metal so it is not going to react with the lithium ions and thus it can relieve volume expansion and avoid capacity fading. Besides, the “brush-like” shape of the Ni can allow the silicon NW to firmly attach to it. As for CNT, it has superior mechanical strength and hence it can effectively accommodate the local strain formed during charging and discharging cycles, and prevent the anode from degradation [3].
Figure 6: Result showing that the use of CNT-Ni-Si anode resulted in a high rate capability and reversible capacity, as well as stable cycling [10].

Figure 7: The structure of CNT-Ni-Si NW [10].

All in all, electrochemical testing can definitely be applied to all kinds of nanowires and should be carried out on in future studies in order to understand the capacity behaviour of different types of nanowires upon charging and discharging cycles.
2.4 Mechanical testing

Apart from the electrochemical testing of the nanowires, it is very critical to understand the mechanical behaviour of different types of nanowires and nanowires array. As mentioned before, the anode of the LIB would often undergo volume expansion due to the local strain formation during charging and discharging cycles, which would ultimately lead to pulverization (i.e. the electrode will break down). Therefore, by measuring the tensile strength, strain-to-failure and Young’s modulus of the anode materials, one can predict which type of nanowire can increase the durability of LIB.

A.Kushima et al. performed mechanical testing on lithiated SiNW using AFM, where tensile stress was applied to the SiNW by a controlled displacement to pull the NW away from the cantilever [11]. They obtained the stress vs. strain graph by calculating several parameters, including the force acting on the NW, the cross-sectional area, displacement and elongation of the NW. With all these parameters, they were able to measure the Young’s modulus of the NW. A.Kushima et al. wrapped up the experiment by stating that both the tensile strength and Young’s modulus of the lithiated NW were lower than that of the pristine NW [11]. This type of mechanical testing was indeed very important since it could allow the researchers to measure the largest stress the nanowire can withstand as well as the stiffness of the nanowire.

Some research groups observed size effect on nanowire that were made of different materials. For instance, M.J. Gordon et al. made use of a new, multipoint protocol in AFM to study the failure mechanism and the mechanical properties of single SiNW [12]. They figured out the Young’s modulus would increase slightly with decreasing diameter, whereas the fracture strength would increase by 2-3 orders of magnitude with decreasing diameter [12].

Apart from single nanowires studies, it is crucial to investigate the mechanical properties of nanowire arrays since future LIB anodes are very likely to be made of an array of nanowires. A similar studies has been conducted by C. Cao. et al. where they measured the Young’s modulus of carbon nanotubes (CNT) array using nanoindenter [13]. In C. Cao’s work, the Young’s modulus of unbuckled CNT arrays was measured to be 13.2±0.3 MPa where the Young’s modulus of the pre-buckled CNT arrays was 11.5 – 15.8 MPa. The increase of the Young’s modulus of the pre-buckled CNT arrays may be attributed to the fact that the CNT were firmly held together after buckling and the existence of interfacial force between the CNT would provide additional resistance to the load. In addition to the above experimental work, it is always beneficial to use simulation tools to study the mechanical behaviour of the nanowires since one can understand the atomic movement, layers movements, bond structure and the changes in the bond length under different loading conditions. Thanks to the above tools and results, researchers can perform similar mechanical testing and simulation on different material systems in an attempt to be more familiar with their mechanical properties. Lastly, it is very crucial that the experimental researcher can work closely with the simulation experts in hopes of verifying their own results.
2.5 Mechanical properties of nanostructures and SiNW

With the above mechanical testing equipment and procedures, many researchers found that nanomaterials in general exhibit a higher strength and ductility as compared to traditional bulk material which can potentially relieve the problems of mechanical degradation during charging and discharging cycles. Also, the extreme small size of nanomaterials can provide extra space to accommodate volume expansion. According to the weakest link theory, the probability of a nanomaterial having a critical defect is much lower than that of a bulk material [14]. Also, the nano-sized grains of a nanostructured material generally leads to higher strength and higher ductility [15]. Therefore, nanomaterials have great potential to replace traditional bulk material as the anode in LIB.

In particular, nanowires possess exceptional mechanical properties. Since nanowires exhibit an extremely large surface-to-volume ratio, the surface energy of nanowires is higher than other nanomaterials. As a consequence, the surface atoms would need to rearrange themselves to lower the excessive surface energy. To achieve this, the bond length would contract which results in an increase in the binding energy between atoms. Hence, the stiffness and fracture strength of nanowires are higher than that of bulk materials [16]. F. Xu et al. conducted in-situ SEM tensile and buckling testing on individual ZnO nanowire to measure its Young’s modulus and fracture strength. It is found that the Young’s modulus of a single ZnO nanowire was higher than a bulk ZnO when the diameter was less than 80nm (Figure 8). F Xu et al. further conducted computational simulation using a core-surface model and a core-shell model which met their experimental data well. They concluded the experiment that the Young’s modulus of the ZnO nanowire was dominated by the elastic property of the surface where the surface atoms reconstruction would result in a higher modulus.

![Figure 8](image)

**Figure 8:** (a) In-situ SEM tensile and buckling showed that the Young’s modulus of a single ZnO nanowire was higher than that of a bulk ZnO when the diameter was less than 80nm. Simulation results using a core-surface model (solid lines) and a core-shell model (dashed line) matched well with the experimental data (b) Fracture strength of a single ZnO nanowire from in-situ SEM tensile test [16]
F. Xu et al. also conducted in-situ SEM tension test on single SiNW where they obtained several observations from the experiment [17]. Firstly, it was found that the Young’s modulus of SiNW decreased with decreasing diameter which was due to surface effect, meaning that the oxide layer that possessed a lower modulus than that of the silicon core would lead to a decrease in the overall Young’s modulus (Figure 9). Secondly, SiNW exhibited an extremely high strain-to-failure as compared to bulk silicon. Bulk silicon generally possessed a failure strain from 0.4% to 2.2% whereas F. Xu et al. found that the failure strain of SiNW could reach 12% [18]. It is believed that the extreme small size of nanowire would have a lower probability of containing defects which resulted in a higher failure strain. Lastly, even though SiNW exhibited such a high strain-to-failure, SiNW was found to be linear elastic until fracture, meaning that SiNW was not able to undergo plastic deformation (See Figure 10).

Figure 9: Young’s modulus of single SiNW was found to decrease with decreasing diameter [17]
2.6 Charge/dischage behaviour of nanostructures and Si structures

Some previous research had demonstrated that certain kinds of Si nanomaterials were vulnerable to charge capacity fading and mechanical degradation due to volume expansion and local strain formation during charging and discharging cycles. For instance, M. Green et al. made use of sub-micrometer Si pillars as the anode where cracks were initiated on the pillars surface after 50 cycles of charging and discharging cycles (Figure 11) [19]. J. Gretz et al. made use of Si nanocrystalline particles with diameter of 12nm and Si thin film with 100nm thickness as the anodes in LiB, where the charge capacity was reduced to 1100 mAhg\(^{-1}\) after 50 charging and discharging cycles, meaning that the charge capacity reduced to only one fourth of the theoretical capacity of bulk Si (Figure 12) [20].
Figure 11: (a) Si surface before charging (b) Cracks formed after 50 charging/discharging cycles of charging cycles with charge current of 415 μA cm\(^{-2}\) and a discharge current of 41.5 μA cm\(^{-2}\) (c) Cracks formed after 50 charging/discharging cycles of charging cycles with charge current of 1016 μA cm\(^{-2}\) and a discharge current of 101.6 μA cm\(^{-2}\) [19]
Figure 12: Charge capacity reduced to 2000 and 1100 mAh\textsuperscript{1} after 50 charging and discharging cycles for Si thin film and nanoparticles respectively [20]

Yet it is found that Si nanowires have the potential to overcome the above mechanical and electromechanical issues. The extreme small size of the nanowires plays an important role in improving the battery performance. Due to the small size of the nanowires, they can better accommodate the volume expansion which could hinder cracks initiation. Secondly, with the high surface to volume ratio, nanowires could have a larger contact with the current collector, meaning that each nanowire can contribute to the overall charge capacity of the battery. Thirdly, since nanowires are one-dimensional (1D) materials, the lithium ions can transport in a shortest and straightest path which in turn facilitates the ionic transportation rate leading to an overall increase in the charge capacity and cycle life (Figure 13) [20].

Figure 13: SiNW have a better resistance to mechanical degradation and exhibit high ionic transportation rates under charging and discharging cycles [20]
2.7 Core-shell nanowires

2.7.1 Core-shell nanowires advantages
Recently, core-shell nanowires have been proposed as an advanced material to replace traditional graphite anode since the shell provides an additional protective layer to dissuade the anode from breaking and provide an artificial SEI layer. Y. Liu et al. studied the behavior of an aluminum nanowire (AlNW) anode with a naturally oxidized Al₂O₃ layer subjected to charging and discharging cycles. They found that the AlNW were broken into numerous nanovoids upon numerous charging and discharging cycles (Figure 14). Also, the AlNW experienced a volume expansion of more than 100%. Yet, this volume expansion and transformation of AlNW did not hinder the battery performance. The reason is that the Al₂O₃ layer had been transformed into a stable Li-Al-O glasstube which helped the AlNW remained functional (Figure 15). Even better, this Li-Al-O glasstube could facilitate the ionic conductivity which increased the efficiency of the battery [21].

Figure 14: It is found that AlNW was broken into numerous nanovoids upon charging cycles [21]
Another recent study utilized double-walled silicon nanotube (DWSiNT), where the inner core was silicon and the outer shell was silicon oxide, as the anode material [9]. The advantage of using DWSiNT was that the silicon oxide shell could act as a barrier to avoid the inner silicon from contacting the electrolyte, meaning that the SEI formation was very stable and the SEI thickness could not increase after the first charging cycle (Figure 16). Even better, the silicon oxide shell could allow lithium ions to penetrate and react with the inner silicon. Moreover, the outer silicon oxide is so rigid that it could only allow the inner silicon to expand and contract in a very confined space, which in turn prevented the huge amount of volume expansion and local strain formation. Overall, using a core-shell NW could increase the ionic transportation and provide a protective layer to the anode which was very likely to improve the LIB cyclability.
Figure 16: The silicon oxide shell (mechanical clamping layer) could help resist the volume expansion while allowing Li$^+$ ions to penetrate into the anode [9]

2.7.2 Core-shell nanowires fabrication

Since core-shell nanowires have great potential to tackle the mechanical issues of an anode, it is imperative to obtain an understanding of how the shell is coated on the nanowires. Furthermore, having a coating with uniform thickness is extremely important since the coating might alter the mechanical properties of the SiNW. Atomic Layer Deposition (ALD) is a very common technique to deposit thin film in a wide variety of applications since ALD can operate at a wide temperature range, from room temperature to 400°C, and can be applied on very large substrates [22]. The most common ALD materials are metal oxide and metal nitrides where a pair of precursor gases (typical precursor gases include trimethylaluminium and H$_2$O) are required to deposit the coating on a substrate [23]. The $1^{st}$ precursor gas will first react with the substrate and any excessive precursor gases and by-product will be pumped away prior to the reaction of the $2^{nd}$ precursor gases and the substrate (Figure 17).

Figure 17: The sequence of the ALD where Precursor gas A would complete its reaction with the substrate first, followed by the reaction with Precursor gas B [22]

It is important to note that the sequential surface reactions are self-limited which leads to several advantages: 1) The two precursor gases would not react with each other to produce any unwanted products; 2) The precursor gases are able to react with any uncoated surface which results in a smooth, continuous and pinhole-free surface; 3) Due to the self-limited reactions, one can have a very precise control on the coating thickness at Ångstrom or monolayer level which is extremely important for nanomaterial fabrication [22]. Depending on one’s own desired thickness, one cycle of ALD (i.e. both precursor gases have completed their reactions with the substrate) would produce one monolayer thickness. Therefore, using ALD can produce a very uniform coating thickness on the
substrate. Lastly, some researchers have recently used organic precursor gas to replace H₂O which can produce a polymer thin film. This technique is known as molecular layer deposition (MLD). It should be noted that the working mechanism of MLD is the same as that of ALD where two precursors are required and the chemical reactions are also self-limited [23]. The only difference is the precursors being applied.

2.8 Strengthening mechanisms of nanomaterials
Since the goal of this project is to enhance LIB performance by improving the mechanical properties of the anode material, it is beneficial to understand of the strengthening mechanism that can improve the mechanical properties of nanomaterials.

First of all, some researchers figured out that certain defects can strengthen the mechanical properties of nanowires. C. Jagadish et al. conducted in-situ TEM mechanical testing to study the properties of three Gallium Arsenide (GeAs) nanowire with different crystal structures, including cubic zinc-blende (ZB), hexagonal wurtzite (WZ) and hexagonal wurtzite with stacking faults defects (WZ-SF) [24]. The three nanowires were tested under compression and it was measured that the they failed at three different loads. ZB NW failed at a load of 10µN, WZ NW failed at 15µN while WZ-SF NW failed at 22 µN (Figure 18). Hence, it can be seen that nanowires with stacking faults exhibited the highest strength. They also measured the ultimate compressive stress of the three nanowires. Again, it is found that WZ-SF NW had the highest compressive stress of 9.0 GPa. ZB NW had an ultimate compressive stress of 5.4 GPa, whereas the ultimate compressive stress of WZ NW was 6.2 GPa [24]. C. Jagadish et al. verified their results by conducting a simulation modeling which was found to match the in-situ TEM mechanical testing results very well. Therefore, they concluded that the high density of stacking fault defects could increase the Young’s modulus of the materials. More importantly, the stacking faults could not only resist bending, but they could also inhibit crack propagation. This strengthening mechanism is very vital since one can now know that the introduction of defects is not only applicable in bulk materials, but also in nanomaterials.
Figure 18: GeAs NW with different crystal structures withstand different level of forces [24]

In addition to the insertion of defects into nanowires, R.A. Webb et al. found that electron beam irradiation (EBI) can strengthen the nanowires [25]. R.A. Webb et al. carried out the uniaxial buckling test on individual Zinc Tin (ZTO) nanowires (Figure 19) where they first measured the Young’s modulus of the NW without any EBI. Afterwards, they started to apply EBI on the nanowires for different time intervals and it is observed that the Young’s modulus of the ZTO NW increased by 40% after 120 minutes of EBI where the modulus was saturated (Figure 20). Still, the increase of the Young’s modulus can be attributed to the fact that EBI would cause bond contraction which increased the binding energy and thus the Young’s modulus.
2.9 Summary & Conclusion

Traditional graphite anodes of LIB have long been shown that they are subjected to several mechanical issues during charging and discharging cycles, including volume expansion, SEI formation and capacity fading. It is believed that silicon is an appropriate material to replace graphite anodes since silicon not only has a 10 times higher charge capacity than graphite, but it is also very abundant and hence its price is lower than many other materials. Also, it has been shown by previous research that individual nanowire exhibits high surface-to-volume ratio and possesses high Young’s modulus and fracture strength. To makes things better, it is proved that core-shell nanowires have the potential to form a stable SEI which can lessen the problem of capacity fading. Hence, researchers and engineers have been trying strenuously to make use of both Si nanowires and core-shell Si nanowires as the LIB anodes in hopes of leveraging their high charge capacity.

Yet, further research should be enforced to study the mechanical properties of Si nanowire arrays as future LIB anodes are very likely to be composed of arrays of nanowires, rather than a single nanowire. Besides, researchers should conduct more experimental work to ensure the use of silicon nanowires arrays could actually lead to higher cyclability and efficiency before they can incorporate the nanowires into commercial LIB. For instance, mechanical testing on the nanowires to measure the Young’s modulus and strain-to-failure is needed since an anode with higher modulus and strain-to-failure can better resist the volume expansion issue. Implementing electrochemical testing is an equally important task since it can reveal the LIB performance by giving out information such as the rate capacity, cycle stability and reversible capacity upon thousands of charging and discharging cycles. In addition, it is mentioned that metal oxides coating and polymer coating can be deposited on a substrate using atomic layer deposition and molecular layer deposition respectively. Accordingly, researchers would have much more opportunities to study different nanowires systems. For instance, they can compare the mechanical properties of metal-oxide coated and polymer-coated nanowires since metal-oxide generally exhibits higher strength and modulus while polymer possesses higher ductility, where strength, modulus and ductility are all the keys to improving the endurance of LIB anodes.
Apart from the above testing, it is imperative to figure out some strengthening mechanisms that can improve the mechanical properties of the nanowires. For example, the insertion of stacking fault defects in the nanowires can inhibit crack propagation and thus increase the strength. All in all, future research should be focusing on mechanical and electrochemical testing on different types of nanowires in an attempt to find ways to improve both the nanowires mechanical properties and LIB performance. Some possible experiments may include inserting some ductile metals molecules, such as copper and aluminium, into ceramic nanowires and to see if they can raise the toughness of the nanowires. At last, only by working on continuous experiments and testing can one develop new materials and mechanism that will improve the performance of LIB.
Chapter 3: Theoretical background and Experimental setup

3.1 Atomic Force Microscopy

Atomic Force Microscopy (AFM) belongs to the family of Scanning Probe Microscopy (SPM) which is a critical tool that has been used extensively since the 1980s to study nanostructures of various kinds of materials. The advantage of SPM is that it does not only allow one to study the crystalline surfaces of a material, but it can also reveal the distribution of point defects, adsorbents and structural defect [26]. Furthermore, SPM is able to measure the force between atoms and molecules which enables one to obtain a detailed understanding of the material properties under atomic scale. The first developed tool of SPM is known as Scanning Tunneling Microscope (STM) where there is a sharp metallic tip scanning over a conductive surface at a distance of less than 1nm. In other words, the STM can allow the tip to scan in an atomic scale which can help researchers understand the atomic structure of a material. However, the STM can only image a material that contains a conducting surface which is not helpful when it comes to polymer and insulating materials studies.

In 1986, Binnig, Quate and Gerber invented the AFM that can measure the topography of any material that has or does not have a conducting surface [27]. The main function of the AFM is to measure the force between the tip and the sample where this force is dependent on the spring constant of the cantilever and be described in accordance with Hooke’s Law [28]. There are several components inside the AFM that help measure the force, including a cantilever, a 4-quandrant photodiode detector, piezoelectric scanner and a light beam (Figure 21). A sharp tip (Figure 22) which is typically made of silicon or silicon nitride is mounted on the cantilever and is scanning over the sample surface where the cantilever will bend due to the interactive force between the tip and the sample. The piezoelectric scanner which comprises a hollow tube made of a piezoelectric material will expand and contract depending on the voltage applied. Thus, this piezoelectric scanner is able to control the movement of the tip in the x,y,z directions with sub-Angstrom accuracy [27]. The movement of the tip and the deflection of the cantilever are monitored by a laser beam which is emitted on the rear side of the cantilever where the beam is reflected towards the 4-quandrant photodiode detector. The top and bottom halves of the photodiode detector is then able to measure the deflection of the cantilever and give out information regarding the force measured [27].
In this experiment, all the mechanical testing was carried out in the Asylum MFP-3D AFM. Figure 23 below displayed the basic setup of the MFP-3D AFM where it consists of three main components: a head, a scanner and a controller [29]. The head comprises the z piezo, z Linear Variable differential transformer (LVDT), the optical beam deflection system and the cantilever where the Z piezo and the optical beam deflection system are used to control the detection of the cantilever. LVDT are the position sensors which physically attached to the piezo and are able to detect the position of each piezo. Each axis has a position sensor to detect the piezo position which constitutes a close loop control system. The scanner will be moving the sample in the x,y directions with the x, y piezo and the positions of the two piezo are detected with the x and y LVDT [29].
3.2 Operation mode and types of forces measured by the AFM

There are 3 primary operation modes in the AFM, namely: 1) Contact mode (tip-sample distance <0.5 nm) 2) Tapping mode (tip-sample distance = 0.5 – 2nm) and 3) Non-contact mode (tip-sample distance = 0.1 – 10 nm) (Figure 24) [28]. Depending on the sample that is being studied, each operation mode has its own advantages and disadvantages. When operated in contact mode, the changes in the cantilever deflection will be monitored and recorded where the deflection is caused by the changes of the height of the sample. A feedback circuit inside the AFM is able to maintain a constant deflection which completes the imaging process. During contact mode operation, when the tip is scanning over a large change of height, the deflection may become so large that it would cause a lot of wearing on the tip and may break tip in the worst case scenario. Hence, the disadvantage of contact mode is that the tip can easily damage soft sample such as biological tissues.

When operated in tapping mode, the cantilever is oscillating at or slightly below its resonance frequency with an amplitude of 20nm to 100nm [27]. Similar to contact mode, the feedback circuit is able to control the vibration amplitude constantly based on the amplitude setpoint [27]. In contrast with contact mode, tapping mode would allow the tip to slightly tap the sample surface during scanning, contacting the surface area at the bottom of its swing [28]. An image will then be obtained by maintaining constant oscillating amplitude between the cantilever and the sample. The advantage of tapping mode is that it allows the capture of a high resolution image of a sample that is easily damaged by the sharp tip or a sample that is loosely attached to a surface. Still, as the tip only has an intermittent contact with the surface, the scanning speed will be lower for the purpose of obtaining a better image. Non-contact mode also requires the oscillation of the cantilever where the cantilever is oscillating at a frequency that is slightly higher than the resonance frequency. Since the tip does not contact the sample, the cantilever resonance frequency will become lower due to
the presence of attractive Van der Waals force and other long range forces. Therefore, the amplitude of oscillation will be decreasing while the tip is scanning over the surface [27]. The advantage of non-contact mode is that the tip is only exerting a very low force on the sample which increases the endurance of the cantilever. However, since the tip does not contact the sample surface, the adsorbed layer (i.e. contaminants) present on the sample surface will limit image resolution. Therefore, an ultra-high vacuum (UHV) environment is often required to improve the image quality. Generally speaking, an even lower scan speed is needed for non-contact mode to obtain clearer images [27].

![Figure 24: The different operation modes of the AFM][28]

Given that there are different operation modes of AFM, it is important to understand what forces are being measured when the tip is scanning over the sample surface. Indeed, different types of forces would exist between the tip and the samples during the scanning. In contact mode, since the tip-sample distance is very close, the dominating interactions are short range forces such as the repulsive Van der Waals force. As for tapping made and Non-Contact mode, long ranges forces would dominate, including attractive Van der Walls force, capillary force, electrostatic and magnetic forces [26].

### 3.3 Calibration of AFM cantilevers

AFM measures the force between the tip and the sample surface by measuring the cantilever deflection and calculating the force using the spring constant of the cantilever. Therefore, it is very crucial to first determine the spring constant of the cantilever prior to any mechanical testing. The spring constant, \( k \), of a rectangular cantilever can be determined from the geometrical parameters of the cantilever as follow [30]:

\[
k = \frac{M \rho_c b h L}{\omega_{\text{vac}}^2}
\]  

(3.1)
Where $M_e$ is the effective cantilever mass, $\rho_c$ is the cantilever density, $b, h, L$ are the cantilever width, thickness and length respectively and $\omega_{vac}$ is the resonant frequency of the cantilever in vacuum.

However, it is typically not convenient to obtain the spring constant using the above equation due to several reasons. First of all, the thickness of the cantilever needs to be acquired by using scanning electron microscope which is time consuming. Secondly, the density and the mass of the cantilever are hard to obtain as the cantilever is usually coated with a layer of gold films. Thirdly, the cantilever is usually placed in air rather than in a vacuum environment, and thus the above equation is not able to give out the most accurate spring constant [30].

In this experiment, the spring constant is determined by the method suggested by Sader et al. [30, 31]. The equation for determining the spring constant, $k$, is as follow:

$$k = 0.1906\rho_f b^2 L Q_f (\omega_f) \omega_f^2$$  \hspace{1cm} (3.2)

Where $\rho_f$ is the density of the fluid medium, $b$ is the cantilever width, $L$ is the cantilever length, $Q_f$ is the quality factor, $\Gamma_i$ is the imaginary part of the hydrodynamic function, $\omega_f$ is the resonant frequency of the fluid medium.

Sader et al. found that the resonant frequency is strongly dependant on both the density and viscosity of the surrounding medium. Moreover, it is not suitable to use the resonant frequency of the cantilever in a vacuum medium since most of the cantilever is placed in air. Also, the resonant frequency would vary a lot in different media. For example, the resonant frequency can reduce significantly in vacuum and hence one needs to obtain an accurate resonant frequency based on the environment of the cantilever, whether it is in air, fluid or vacuum. Regarding these challenges, Sader et al. successfully eliminated the requirements of knowing the density and thickness of the cantilever as well as using the resonant frequency in a vacuum environment. In Sader’s equation, it not only considers the geometry of the cantilever (i.e. the length and width, but not the thickness), but it also takes the actual surrounding medium of the cantilever into account. Accordingly, Sader’s equation can allow the cantilever to be placed in any medium as long as the density and viscosity are known. All in all, Sader’s equation is applicable for most of the experiment that takes place in ambient condition as one can easily obtain the spring constant of the cantilever without worrying the surrounding medium.

In this experiment, all mechanical testing was conducted in the AFM (Model: Ayslum MFP-3D™) in an ambient environment where the software can perform thermal tune to obtain the resonant frequency and quality factor of the cantilever. Afterwards, the spring constant for each cantilever used was determined by applying the Sader’s equation.
3.4 Nanoindentation and the Oliver-Pharr model

With the growing needs of miniaturization of components of electronic devices, such as nano-SIM card, nano-sized computer chips, being able to measure the mechanical properties of very small objects become more and more important [32]. Traditional mechanical testing tools such as tensile testing machine is not suitable for carrying out the tensile testing on such a small material. Hence, the concept of nanoindentation emerged 30 years ago. The advantage of nanoindentation is that it can record the very small load and indenter displacement and generates a force vs. indentation depth graph. Researchers would then apply various engineering models to determine the mechanical properties, such as hardness and Young’s modulus, of the sample. Nanoindenter and AFM are two most common equipment to conduct nanoindentation, where a force is applied on an indenter to compress the sample. Nanoindenter is generally used to study the bulk properties of a material. In our experiment, it is aimed to study the stress-strain slope and strain-to-failure of the nanowires where it should be noted that the properties of the nanowires would very likely be affected some nano-scale features present in the samples such as electrostatic force and Van der Waal’s force and may also be subjected to problems like sink-in and pile up. Hence, using AFM can allow us to observe closely the surface topography and the local properties of the nanowires during indentation.

Several engineering models are typically used to interpret the force vs. indentation depth graphs obtained from the AFM in order to measure the mechanical properties of the samples. For instance, Oliver-Pharr model is applicable in the samples that exhibit high strength and high ductility where the deformation can be both elastic and plastic [33]. The first step of the Oliver-Pharr model is to fit a power law equation, \( P = A(h-h_i)^m \) on the unloading curve, where \( P \) is the force applied, \( h-h_i \) is the elastic displacement, \( m \) and \( A \) are the constants determined by curve fitting and are dependent on the indenter shape (Figure 25) [34]. Subsequent steps require the calculation of several parameters including the unloading stiffness, contact depth and contact area in order to obtain the hardness [35]. It should be noted the contact area hinges on the shape of the indenter since the contact area functions are different for different indenter shapes [36]. Typical indenter shapes include spherical, Berkovich, Vickers and cone [36]. However, even though the Oliver-Pharr model takes plastic deformation into account, it is subjected to several limitations. Firstly, the contact area function is not always correct since the tip would wear in reality upon numerous nanoindentation testing. Secondly, the surface roughness might affect the contact area, especially for the sample in this experiment where the length of the individual nanowire varies a lot. Thirdly, the pile-up or sink-in phenomena of the sample during indentation would underestimate and overestimate the contact area respectively. Hence, a new approach was developed, as will be outlined in Chapter 5, to better simulate the contact area to calculate more accurate stress-strain slope and strain-to-failure of the nanowires arrays for this experiment.
3.5 Contact mechanics models

In addition to the Oliver-Pharr model mentioned previously, continuum level contact mechanics models are generally used to interpret the force vs. Indentation depth graphs. Contact mechanics was first introduced by Hertz in 1880 who studied the problem of elastic deformation for two spheres being pressed into contact (Figure 26) [37]. Hertz developed a model which is known as the Hertz Model demonstrating that when two spheres of radii $R_1$ and $R_2$ are pressed into contact with a loading force $F_{\text{applied}}$, the region around the contact deforms with the center displacing by an amount of $\delta$, forming a circular contact areas, $A$, with a radius, $r$, where the equations are as follows:

$$r = \left(\frac{3F_{\text{applied}}R_{\text{eff}}}{4E^*}\right)^{1/3}$$  \hspace{1cm} (3.3) \\
$$\delta = \left(\frac{9F_{\text{applied}}^2}{16R_{\text{eff}}E^*}\right)^{1/3}$$  \hspace{1cm} (3.4) \\

Furthermore, the effective radius $R_{\text{eff}}$ and effective modulus $E_{\text{eff}}$ are defined as

$$R_{\text{eff}} = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)^{-1}$$  \hspace{1cm} (3.5) \\
$$E_{\text{eff}} = \left(\frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2}\right)^{-1}$$  \hspace{1cm} (3.6)
Hertz model is a very common technique to determine the mechanical properties of a material subsequent to nanoindentation testing. Yet it should be noted that the Hertz model is subjected to several assumptions [37]:

1) The two contacting bodies are homogeneous where each body is monolithic material without any surface coating or films
2) Adhesion force between the two bodies are negligible
3) The materials are isotropic which exhibits linear elastic behaviour
4) The surfaces have to be frictionless
5) The surfaces are perfectly smooth
6) Deformation are small where $\delta \ll R_1, R_2$

It is obvious that the Hertz model does not perfectly reflect the real mechanical properties of a material since friction must be present when the two bodies are compressing each other. Also it is almost implausible to have two perfectly smooth surfaces. Therefore, the Hertz model is only appropriate when one needs to obtain a first approximation of the Young's modulus of the sample.

In an actual experiment, the materials would experience some level of adhesion since the tip-sample distance is so close. This adhesion may be due to interatomic force, electrostatic force and capillary force acting on the contacting surfaces [37]. Hence, some scientists developed more realistic models that took adhesive forces into consideration. The two most popular models are known as the Derjaguin-Muller-Toporov (DMT) and Johnson, Kendall-Roberts (JKR) models. In the DMT model, the adhesive forces are assumed to be weak or long range and the material is so stiff that the contact interfaces do not experience significant amount of deformation, resulting to a contact area that is similar to that of the Hertz model [37]. The equation of the radius and deformation are the same as that in the Hertz model, whereas the only difference is the force applied, $F_{\text{app}}$, is replaced by $F_{\text{total}}$, where $F_{\text{total}} = F_{\text{adhesive}} + F_{\text{applied}}$, $F_{\text{adhesive}} = 2\pi R_{\text{eff}} W_{\text{adh}}$, and $W_{\text{adh}}$ is the work of adhesion.
As for the JKR model, it is assumed that the adhesive force is so strong that the contact interface would experience a huge amount of localized deformation, resulting in a larger contact area compared to that of the Hertz model [37]. The adhesive force equation is as follow:

\[ F_{\text{adhesive, JKR}} = \frac{3}{2} \pi R_{\text{eff}} W_{\text{adh}} \]  

(3.7)

However, even though the DMT and JKR models are more realistic in a way that they both consider adhesion of the tip-sample contact, they are still subjected to the assumptions of the Hertz model which are: 1) The surfaces need to be homogenous and isotropic and 2) The materials need to exhibit linear elastic behaviour. In this experiment, the samples are all silicon nanowires arrays where the SiNWs are of various length, heights and thicknesses. As a consequence, the contact between the tip and the sample can in no way be smooth, frictionless and linear elastic. In order to accurately measure the mechanical properties of the SiNW arrays, a new testing protocol was developed.

### 3.6 Sharp tip versus Colloidal tip

Conventional nanoindentation requires the use of a diamond tip for compressing the sample whereas AFM tips are typically made of silicon or silicon nitride [28]. Since the conventional AFM tip radius is very small (the tip radius is usually around 10-100nm), it can lead to several problems regarding the determination of the mechanical properties of the sample. First of all, given that the tip radius is very small, a very high contact stress will be generated even though the applied force is very small [38]. Accordingly, the Young’s modulus obtained with the sharp tip may not be representative of the realistic pressures experienced by the sample as the sample wound be more profound to plastic deformation. Secondly, since the goal of this experiment is to study the mechanical properties the nanowires arrays, using a sharp tip might only be able to indent one or two nanowires, instead of a large area of a nanowires array (Figure 27). Therefore, the sharp tip needs to be modified in order to obtain an accurate measurement of the mechanical properties of the nanowires arrays.
In this experiment, two types of micro beads were attached on a silicon tip: 1) 28 μm glass bead 2) 20 μm Borosilikatglas bead. The 28 μm bead was attached on tip manually along with the use of epoxy and a micromanipulator whereas the 20 μm bead was commercially available (NanoandMore, USA). Figure 28 are the SEM images of the two colloidal probes. It can be seen that the 28 um glass bead was not perfectly centered but it was still applicable in nanoindentation testing, while the 20 um bead was perfectly aligned at the center.

Figure 27: A schematic diagram showing the two types of tips. (a) A colloidal tip can compress hundreds of nanowires (b) A sharp tip might only be indenting one or two nanowires or the holes between nanowires

Figure 28: The SEM image of the types of beads after attaching on the tip a) 28um glass bead b) 20um Borosilikatglas bead [39]
Chapter 4: Sample characterization- Uncoated Silicon Nanowire and Core-shell Silicon Nanowire

Three types of samples were investigated in this experiment: 1) Uncoated SiNW; 2) Alumina-coated SiNW and 3) Polymer-coated (polymer made of trimethylaluminium and glycerol) SiNW. All three samples were prepaid by Prof. Andy Sun and his research group at the University of Western Ontario. The uncoated SiNW were grown on a silicon substrate and was synthetized by chemical etching. The reason for using chemical etching is that it is a relatively cheap and simple fabrication method to produce nanowires as compared to alternatives such as chemical vapour deposition (CVD) which requires expensive facilities and equipment [40]. In addition, chemical etching can produce large areas of SiNW which met the objectives of mass-producing these SiNW and incorporate them into LIB economically in the future [41]. Figure 29 below shows SEM images of SiNW fabricated by chemical etching and CVD. It can be seen that the nanowires grown by chemical etching are very irregular with varying thicknesses and heights while the nanowires grown by CVD were very ordered and had regular height and thickness.

![SEM images of SiNW](image)

*Figure 29: (a) SiNW fabricated by chemical etching (b) SiNW fabricated by CVD. It can be seen that the SiNW fabricated by CVD was very ordered (Image provided by Ms. Shiming Su at the University of Toronto).*

Before conducting mechanical testing on the sample, it is important to determine the dimensions and the chemical compositions of the nanowires. Therefore, high resolution SEM (Model: S5200, Hitachi) and AFM had been used to obtain the morphology of the samples while Energy-Dispersive X-Ray Spectroscopy (EDS) was utilized to study the chemical compositions of the nanowires.
4.1 Uncoated SiNW

Figures 30 below demonstrated the SEM top view image of the uncoated SiNW where some holes between the nanowires could be seen. Figure 31(a) – (f) were the SEM side view images of the uncoated SiNW where it can be seen that the nanowires were quite irregular as their length and thickness vary considerably. From Figure 31(e) and (f), it can be observed that some very short nanowires, with length between 100 to 200nm, and some broken nanowires, which maybe due to transportation issues, were found at the bottom of the array. Figure 32(a) was the AFM top view image of the uncoated SiNW whereas Figure 32(b) was the height profile obtained from the AFM. It can be seen that the nanowires had length of approximately 800nm.

Figure 30: SEM images of the top view of the uncoated SiNW
Figure 31: (a) – (b) SEM images of the side view of the uncoated SiNW (Edge). (c) – (d) SEM images of the side view of the uncoated SiNW (Center). It can be seen that the nanowires are very irregular where their length and thicknesses vary considerably. (e) and (f): Very short nanowires and broken nanowires could be found on the substrate.
The lengths of the nanowires were measured to be in the range of 300nm to 1800nm. It should be noted that the diameter of the NWs varied considerably since the reactions happened very fast during chemical etching [40]. Area coverage of NW was also determined with the use of the software, ImageJ, and it is found that the area covered with nanowires was approximately 60-80%. With all these dimensions, the maximum number of nanowires being indented by the AFM tip would be approximately 200.

Figure 33 below demonstrated the EDS images of the uncoated SiNW. It is shown that the chemical composition was mainly silicon with a small amount of silver since silver was a very common catalyst for chemical etching fabrication of SiNW.
Figure 33: (a) EDS mapping of the top view of the uncoated SiNW (b) Chemical composition of the uncoated SiNW showing that it is mostly consisted of silicon. A small amount of silver was detected since silver was a common catalyst of chemical etching for the fabrication of SiNW.
4.2 Alumina-coated core shell SiNW

Figure 34 (a) and (b) showed the SEM top view image of the alumina-coated SiNW and the EDS result respectively. It should be noted that the alumina coating was fabricated by 20 cycles of atomic layer deposition at 150°C with a thickness of about 2nm. From the SEM top view image, there was not any significant difference between the surface morphology of the alumina-coated SiNW and the uncoated SiNW which was expected since the alumina coating was only 2nm. From Figure 34(b), it can be observed that there was a significant amount of aluminium in addition to silicon. Figure 35(b) further proved that the alumina coating was uniformly deposited on the SiNW.

Figure 34: (a) EDS mapping of the top view of the alumina-coated SiNW (b) Chemical composition of the alumina-coated SiNW showing that the composition was mainly silicon where aluminium concentration increased significantly
Figure 35: (a) EDS mapping of the side view of the alumina-coated SiNW (b) Aluminium and oxygen were the major compositions, suggesting alumina coating was uniformly deposited along the silicon nanowire.
4.3 Polymer-coated SiNW

Figures 36(a) and (b) were the SEM top view image and the chemical compositions of the polymer-coated SiNW respectively. It should be noted that the polymer coating was fabricated by 10 cycles of molecular layer deposition at 150°C with a thickness of 5 nm while the precursor gases comprised trimethylaluminium and glycerol with a repeating unit of \( \text{Al-(O-CH}_2\text{-CH}_2\text{-O)}_3 \). It can be seen that silicon and aluminum were the major compositions of the structure since the core was made of silicon and trimethylaluminium was one of the precursor gases. The oxygen composition was significantly higher than that of alumina-coated SiNW which was due to the additional OH groups from the glycerol precursor gas. Figure 37 proved that the entire core-shell structure was covered with aluminium, oxygen and carbon which were all the compositions from the two precursor gases.

![Figure 36](image_url)

*Figure 36: (a) EDS mapping of the top view of the polymer-coated SiNW (b) Chemical composition of the alumina-coated SiNW showing that the composition were mainly silicon and aluminium where the oxygen concentration was higher than that of the alumina-coated SiNW, which was due to the additional OH groups from the glycerol precursor gas.*
Figure 37: EDS mapping of the side view of the polymer-coated SiNW (b) It can be seen that the polymer coating which consisted of aluminum, oxygen and carbon were covering the entire core-shell structure.
Chapter 5: Mechanical Testing Protocol Development

As mentioned in the Chapter 3, even though standard contact mechanics models, such as the Hertz model and JKR model, have been widely used to interpret the force vs. indentation depth graph, they are not the most appropriate model to measure the mechanical properties of the SiNW arrays samples due to their discrete nature. Therefore, a new protocol has been developed to interpret the force vs. indentation depth graph where it makes use of the fundamental concept of the Young’s modulus for uniaxial loading, which is defined as follow [15]:

$$\text{Young’s Modulus} = \frac{\text{Stress}}{\text{Strain}}$$  \hspace{1cm} (5.1)

Figure 38: Young’s modulus (as known as modulus of elasticity) can be determined from the slope of a Stress vs. Strain graph [15]

Generally speaking, Young’s modulus is determined from the slope of a stress vs. strain graph for uniaxial loading in tension or compression. From the AFM used in this experiment, one can easily obtain the force vs. indentation depth graph. Hence, the only challenge is to convert the force vs. indentation depth graph into a stress vs. strain graph. Regarding this, it would be appropriate to divide the mechanical testing protocol into 2 parts: 1) Stress and 2) Strain.
5.1 Stress computation
An equation that can be used to relate stress and force is defined as follow:

\[
\text{Stress} = \frac{\text{Applied force}}{\text{Contact area}}
\]  
(5.2)

From this equation, it can be seen that two components are needed to compute the stress of the material under nanoindentation which are the 1) Applied force and 2) Contact area of the two contacting bodies. In this protocol, it is assumed the stress is increasing uniformly and can be treated as an average stress. The applied force can be collected automatically from the AFM during nanoindentation process. However, the contact area cannot be determined directly from the AFM. Also, the area functions from the Oliver-Pharr model are not very convenient to be used here since those functions are restricted to particular tip shapes. Thus, a MATLAB code developed by Dr. Guillaume Colas at the University of Toronto was adopted to compute the contact area (detailed code is listed in Appendix 8.1). Colas’s code is able to estimate the actual material interacting with the tip during nanoindentation and thus one can approximate the contact area between the tip and the sample for any tip shape. It should be noted that due to the discrete nature of the SiNW array samples under study, the contact area is assumed to be constant during indentation which was similar to other studies on the measurement of Young’s modulus of nanomaterials arrays [42].

Figures 39-45 demonstrated the steps to construct the stress vs. strain graph. Step 1 was to locate a spot for nanoindentation and to measure the height of the nanowires as shown in Figure 39. Step 2 was to apply a force to compress the nanowires array. As mentioned in the beginning of this chapter, 10 cycles of indentation were enforced on the same spot where the force applied was 2μN for all the nanoindentation testing in this experiment.
Step 3 was to determine the indentation depth compressed by the tip. In this experiment, the indentation depth was determined from the upper portion of the force vs. indentation depth graph where a sharp change of the slope on the loading curve could be noticed. From Figure 40, it can be seen that Slope 2 was much steeper than Slope 1, indicating that actual indentation initiated at Point B where the tip might only be softly scratching the nanowires before it reached Point B. The indentation depth was the distance between Point B and Point C which was measured to be 20.47nm.
Figure 40: Force vs. indentation depth graph obtained directly from the AFM. It can be seen that Slope 2 was much greater than Slope 1 and a sharp change of the slope occurred at Point B. Point B would be selected as the origin where the indentation started to happen and BC was the indentation depth.

Step 4 required the determination of the contact area between the tip and the nanowires array with the use of Colas’s code. There are three main input parameters for Colas’s code, including 1) (x,y) coordinates of the nanoindentation location; 2) Indentation depth and 3) Tip radius. Figure 41 showed the result from the code where the indentation depth and the contact area were 20.47nm and 2.1667 μm² respectively. However, it should be noted that this contact area was not the actual contact area and it could be explained by the contact area vs. indentation depth graph (Figure 42) which was also generated from Colas’s code.

As shown in Figure 42, the tip started compressing the nanowires array when there was a sharp change in the slope which was Point B. The actual contact area was calculated to be 1.2 μm². Indeed, the contact area before the sharp change in the slope might indicate that the tip was only softly scratching the nanowires arrays instead of compressing them. Hence, those area should not be considered in the final calculation of the contact area. After determining the actual contact area, the equation Stress = Applied force/Contact area could be applied to compute the changes of the stress throughout the nanoindentation process.
Figure 41: Results from Colas’s code where the indentation depth was 20.47 nm and the contact area was 2.1667μm²

Figure 42: Contact area vs. indentation depth graph. The contact area before Point B should not be considered in the determination of the contact area. The actual contact area was 1.2 μm²
5.2 Strain computation

Strain was the second component needs to be determined which can be calculated using the following equation:

\[
\text{Strain} = \frac{l_i - l_o}{l_o}
\]  

(5.3)

Where \(l_i\) and \(l_o\) are the final and initial length of the nanowire respectively [15].

\(l_i - l_o\) can be seen as the indentation depth which can be collected from the AFM. \(l_o\) needed to be measured from the AFM images before and after each of the nanoindentation. In the above case, \(l_o\) would be the nanowire height as shown in Figure 39(b) which was 715nm.

5.3 Stress vs. Strain graph

After calculating the stress and strain changes throughout the nanoindentation testing, the stress vs. strain graph could be established. Figure 43 below demonstrated stress vs. strain graph for one of the nanoindentation testing for the alumina-coated SiNW.

![Stress vs. Strain graph](image)

*Figure 43: A stress vs. strain curve for the alumina-coated SiNW at the 10th cycle. The contact area was 1.2\(\mu\)m\(^2\) which was calculated previously.*

The slope of the unloading curve would be one of the mechanical properties being investigated in our work since this slope revealed the elastic behaviour of the nanowires after compression. Curve-fitting was applied on the unloading curve to determine the slope. Figure 44 was the stress vs. strain graph with curve-fitting applied on the unloading curve. It is shown that the stress-strain slope was 89 MPa. It should be noted that it was decided to entitle this measurement as “slope” rather than “Young’s modulus” because Young’s modulus is used to describe an intrinsic property of a material. However, as the nanowires would interact with the tip differently during each cycle (for instance some nanowires might be broken while some may buckle), the contact area would also vary during each indentation cycle. Therefore, it was more appropriate to name this measurement as slope of stress-strain graph or stress-strain slope.
Figure 44: A stress vs. strain graph for the alumina-coated SiNW at the 10th cycle. By applying curve-fitting on the unloading curve, it was found that the slope of stress-strain graph was 89 MPa.

Apart from the stress-strain slope, energy dissipation was another mechanical property that could be determined from the stress vs. strain graph. As shown in Figure 45, the area between the loading and unloading curves was defined as the energy dissipation which was referred to the energy being lost to surrounding as heat due to plastic deformation. Detailed interpretation of the stress-strain data would be explained in the next chapter.

Figure 45: Energy dissipation, which was the area between the loading and unloading curves, was calculated to be 0.005 J/cm³
5.4 Limitation of the code

The MATLAB code developed by Colas allowed one to estimate the contact area for any sample and any tip shape. Yet it should be noted here that the code itself did not consider the force applied to deform the sample and the determination of the contact area was based on geometry only where the AFM tip was placed at a certain depth of the nanowire arrays. This is considered to be a reasonable approach given the discrete nature of the nanowire arrays under study. However, to obtain a better understanding of the interaction between the sample and the tip, in-situ SEM should be used in future work.
Chapter 6: Mechanical properties of Uncoated Silicon Nanowires and Core-shell Silicon Nanowires

The mechanical testing protocol described in Chapter 5 was applied on all the three nanowires samples: 1) Uncoated SiNW; 2) Alumina-coated SiNW and 3) Polymer-coated SiNW. A summary of the samples parameters and testing conditions was included in Appendix 8.2. It is found that the shapes of the stress vs. strain graphs obtained in this experiment were quite different from the traditional stress vs. strain graph in a way that the loading and unloading curves were very uneven (Figure 46(b)). This can be attributed to the fact that all three SiNW array samples consisted of very irregular nanowires. Since the nanowires were all of different length and thicknesses, it can be predicted that the number of nanowires being compressed by the AFM tip would be different during each nanoindentation testing. Also, some nanowires might break while some might buckle (See schematic Table 2) and hence the loading and unloading curves were not smooth. Detailed images of the stress vs. strain graphs for all three samples could be found in Appendix 8.3.

Figure 46: (a) Traditional stress vs. strain graph consists of very smooth loading and unloading curves [43] (b) It can be found that the loading and unloading curves obtained from the stress vs. strain graphs in our experiments were very uneven.
Table 2: Schematic diagram of various sources of energy dissipation of the nanowires during nanoindentation [44]

<table>
<thead>
<tr>
<th>Sources of energy dissipation</th>
<th>Sliding</th>
<th>Fracture</th>
<th>Plastic deformation</th>
<th>Shear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

The three SiNW arrays samples have undergone a number of nanoindentation testing where each testing consisted of 10 cycles of nanoindentation. Three major mechanical properties were studied: 1) Stress-strain slope; 2) Energy dissipation and 3) Straining ability. Section 6.1 described the stress-strain slope behaviour of the uncoated SiNW whereas section 6.2 discussed the stress-strain slope for all three samples. Section 6.3 comprised a detailed explanation of the energy dissipation of the three samples. Section 6.4 explored the straining ability of the different SiNW arrays while section 6.5 included a comparison of the experimental results with computational simulation results.

Before going into the detailed results from our experiment, it would be appropriate to obtain a basic understanding the mechanical properties of the core and the shell materials of the three samples since it is expected that the coating material would play a role in changing the properties of the entire core-shell structure. Table 3 below summarized various mechanical properties that have been previously reported for silicon (core), alumina (shell) and polymer (shell). These will be used to aid in the interpretation of the results reported in the following sections.

Table 3: Previously reported mechanical properties of silicon and the two coating materials: alumina and polymer

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (GPa)</th>
<th>Friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk silicon</td>
<td>129-187 [15]</td>
<td>0.43 [45]</td>
</tr>
<tr>
<td>Alumina</td>
<td>198±8 [46]</td>
<td>0.55-0.82 [47]</td>
</tr>
<tr>
<td>Polymer</td>
<td>21±8 [46]</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Several notes should be stated here regarding the above mechanical properties. First of all, the Young’s moduli of the alumina and polymer were obtained from an alumina thin film (fabricated by atomic layer deposition) and a polymer thin film (fabricated by molecular layer deposition) respectively [46]. It should be noted that the precursor gases used for molecular layer deposition in our experiment and the experiments from the references were different. The precursor gases used in our experiment consisted of trimethylaluminium and glycerol whereas the precursors from the
references comprised trimethylaluminium and ethylene glycol. The only difference is that glycerol contains one more hydroxyl group than ethylene glycol and hence it is still appropriate to study these references. In addition, the friction coefficients of bulk silicon and alumina were both obtained by macro-scale ball-on-disc test for the sake of the fairness of the comparison.

6.1 Stress-strain slope of Uncoated SiNW

From Figure 47 below, it can be seen that the largest stress-strain slope of the uncoated SiNW array was approximately 200MPa. However, there was a huge discrepancy between our results and the result from those mechanical testing of single nanowire. F. Xu et al. conducted in-situ SEM tensile test on single SiNW where they found that the Young’s modulus of a single SiNW with 60nm diameter was about 180GPa which was similar to that of bulk silicon [17]. Yet, our result was indeed similar to several other studies on carbon nanotubes arrays where the carbon nanotube arrays had been compressed by triboindenters and nanoindenters [42]. A single carbon nanotube is well-known for its extremely high Young’s modulus which has a range of 100GPa to 4.15 TPa. However, when the carbon nanotubes arrays were compressed, it was found that their Young’s moduli were only 0.12MPa to a maximum of 60 MPa [42]. Therefore, it is reasonable to predict that the failure mechanism of the SiNW arrays might be similar to that of the carbon nanotubes array.

1) Folding of the SiNW and Si substrate (Si-Si) interface and 2) buckling of the nanowires were believed to be the two main causes of the low stress-strain slope of the uncoated SiNW as compared to the Young’s modulus of bulk silicon. During indentation, the AFM tip would first contact the top part of the nanowires and thus the top part was supposed to be compressed. However, it was very likely that the top part of nanowires would only slide and rotate when they were compressed as there was no adhesion sticking the nanowires together. Therefore, the bottom part of the nanowire and the Si-Si interface would in turn bear most of the load. Also, it is likely that the Si-Si interface was a weak contact point and thus the interface would be prone to breakage and folding, resulting in a low stress-strain slope as compared to the bulk Si Young’s modulus. Moreover, SiNW were very likely to buckle when they were compressed where there is a possibility that the both top part and bottom part (which was close to the Si-Si interface) would buckle. This dual buckling would then lead to a lower stress-strain slope than the bulk Si Young’s modulus since bulk Si was less prone to buckling.
Figure 47: Relationship between average slope of stress-strain graph of the nanowires and their length. It is seen that alumina-coated SiNW exhibited the highest slope when the nanowires were of the same length. Besides, the stress-strain slope of alumina-coated SiNW was found to decrease with increasing length.

6.2 Stress-strain slope of Uncoated, Alumina-coated and Polymer-coated SiNW

As mentioned in Chapter 2, some researchers have already shown that core-shell single nanowire not only possessed high Young’s modulus, but it could also limit the growth of the SEI layer which better conserve the charge capacity and prolong the lifetime of LIB [16]. Therefore, our work here was to study the stress-strain slope of uncoated and core-shell SiNW arrays to see if the shell material would also increase the stress-strain slope of the entire array. Besides, as nanoindentation has been conducted on nanowires with different length, it is possible to study the relationship between nanowire length and the stress-strain slope. Figure 47 revealed the relationship between the average stress-strain slope and the nanowire length for all three samples. It should be noted some data points were removed due to systematic experimental errors that were identified during analysis (See Appendix 8.4).

From Figure 47, it can be seen that alumina-coated SiNW exhibited the largest stress-strain slope when the three types of nanowires were compared in the same length. This may be attributed to the fact that the alumina coating would experience the largest stress and strain as compared to the silicon core under compression [16]. F. Xu et al. conducted in-situ SEM buckling test and measured the Young’s modulus of a single ZnO NW, where they found that the Young’s modulus of ZnO NW was higher than that of a bulk ZnO when the diameters was less than 80nm. They concluded that the Young’s modulus of the ZnO NW was dominated by the elastic property of the surface as the surface would experience the largest stress and strain under buckling. Hence the surface atoms would need to reconstruct themselves and undergo bond contraction to reduce the excessive surface energy, leading to a higher Young’s modulus. F Xu et al. also conducted another in-situ SEM tensile test on single SiNW where they found that the Young’s modulus of SiNW would decrease
with decreasing diameter. It was concluded that surface effect was still dominating the SiNW where the oxide layer, which had a lower Young’s modulus than the silicon core, would result in a decrease of the Young’s modulus of the SiNW when the diameter decreased. In our experiment, it is believed that surface effect would play a role in altering the stress-strain slope of the nanowire since it can be deduced that alumina coating would experience the largest stress and thus the interatomic spacing of coating would decrease. Accordingly, the alumina molecules at the surface would need to reconstruct themselves to lower the excessive surface energy through bond contraction, meaning that the elastic properties were dominated by alumina coating. Since alumina coating has a very high Young’s modulus (Table 1), it can be deduced that the stress-strain slope of the entire alumina-coated SiNW would become higher.

Furthermore, the rule of mixture might give us an additional clue for the high stress-strain slope of alumina-coated SiNW even though it did not take surface effect in consideration. Rule of mixtures is defined as [15]:

$$E_c = E_m V_m + E_p V_p$$  \hspace{1cm} (6.1)

Where E and V are the Young’s modulus and volume fraction respectively, the subscripts c, m and p refer to composite, matrix and particulate phase respectively.

Using the rule of mixtures equation and combining the Young’s moduli of alumina and polymer in Table 1, it can be deduced that the stress-strain slope of alumina-coated SiNW would be higher as the alumina coating itself exhibited very high modulus.

Besides, friction coefficient of the coating material might play a role in changing the stress-strain slope of the nanowire arrays. From Table 1, it can be seen that the friction coefficient between two alumina surfaces ranged from 0.55 to 0.82 whereas the friction coefficient between two silicon dioxide contacts has shown to be approximately 0.43. During nanoindentation, it can be estimated that SiNWs would slide against each other. Given that the friction coefficient of alumina was greater than that of silicon oxide, it can be deduced that a larger force would be required to slide the alumina-coated SiNW, which could also led to a higher stress-strain slope.

Moreover, it is found that the stress-strain slope of alumina-coated SiNW was decreasing with increasing length. This size effect might be explained by several engineering theories. Firstly, according to the weakest link theory, it is said that a material with longer length would have a higher probability of containing a critical defect to cause failure [14]. In other words, the long nanowires would easily break when they were compressed by the AFM tip which resulted in a lower stress-strain slope. Secondly, it is expected that the longer nanowires would experience significant buckling than shorter ones. An equation that relates the force required to induce buckling and the material length is defined as [48]:

$$P = \frac{\pi^2 E l}{L}$$  \hspace{1cm} (6.2)
Where \( P \) is the critical load to buckle a column, \( L \) is the material length, \( E \) is the Young’s modulus of the material, \( I \) is the moment of inertia of the cross section.

From this equation, it can be deduced that the longer nanowire are more prone to buckling than the shorter ones and would give rise to a lower stress-strain slope. However, the stress-strain slope of polymer-coated SiNW showed an opposite trend which was not conceivable and further research should be conducted to study the mechanical behavior of the polymer coating.

### 6.3 Energy dissipation of Uncoated SiNW, Alumina-coated SiNW and Polymer-coated SiNW

During nanoindentation, it is very likely that the nanowires would be compressed which lead to various sources of energy dissipation. Table 3 demonstrated several types of sources of energy dissipation. Theoretically speaking, a perfectly elastic material could store 100% of its mechanical energy into strain energy when it is loaded (either in compression or in tension). The material is then able to release 100% of the strain energy when the load is removed [43]. However, many materials would behave elastically at low strain only. When the materials are subjected to high strain, they are no longer elastic and would deform plastically. Since the area under the loading curve and the unloading curves represents the energy absorbed and energy released respectively, the difference between the two curves can be interpreted as the energy lost as heat [43]. Accordingly, the energy dissipation could be calculated from the area between the loading and unloading curve of a stress vs. strain graph. Figure 4 below showed the relationship between the average energy dissipation (i.e. the average energy dissipation of the 10 nanoindentation cycles) and the nanowire length.

![Average Energy Dissipation vs. Nanowire length graph](image)

*Figure 48: Average energy dissipation vs. Nanowire length graph. It can be seen that the energy dissipation was decreasing with increasing nanowire length. Also, nanowires with length below 900nm would deform plastically.*

From Figure 48, it can be seen that the energy dissipation was decreasing with increasing nanowire length for all three samples. In addition, it is observed that the average energy dissipation was very
low for all three samples when the nanowire length exceeded 900nm. It should be noted that the energy dissipation of the samples were related to the strain level which was covered in section 6.4. Therefore, it can be said that all three types of nanowires were deforming elastically when their length exceeded 900nm whereas they were deforming plastically with length below 900nm. Moreover, when nanowires with the same length (e.g. 200nm) were compared, it can be seen that alumina-coated SiNW exhibited the highest energy dissipation while the uncoated SiNW showed the lowest energy dissipation. Hence, this result suggested that alumina-coated SiNW might contain more sources of energy dissipation than the other two samples. Interestingly, it was also found that the energy dissipation of alumina-coated SiNW was decreasing with nanoindentation cycles for some testing (Appendix 8.5). However, the reason for causing this decreasing trend is still not known and further studies could be focused on alumina-coated SiNW.

From Figure 49 below, it can be predicted the nanowires would be compressing each other during lithiation since the nanowires would undergo volume expansion. Therefore, it can be said that compression would be the dominating mechanism as compared to tension when it came to battery application. When the nanowires were compressed, there was a likelihood that the nanowires would buckle. Since the nanowire arrays were made of the same kind of nanowire, the force required to buckle one single nanowire would be the same for every nanowire on the array. However, since the nanowires were all of different length and thickness in our samples, it was very likely that one nanowire would buckle first and then other nanowires would be loaded. As a result, the nanowires would be shearing. From Figure 48, it can be seen that alumina-coated SiNW exhibited the highest energy dissipation which suggested that the interface between the alumina shell and silicon core were likely to be more subjected to shearing as shearing was a source of energy dissipation.

![Figure 49](image-url)

*Figure 49: SiNW would be compressing each other during lithiation. Therefore, it is very likely that the nanowires would be shearing, sliding and deforming upon charging cycles [20]*

In addition, it is shown in Table 2 that sliding of the nanowires was also a source of energy dissipation. In fact, SiNW were very likely to slide against each other during AFM indentation since the nanowires might buckle and would entangle with one another. Therefore, given that the friction coefficient of alumina was high (see Table 3), it was possible that the alumina-coated SiNW would
slide hard against each other which generated more heat and resulted in a higher energy dissipation than the other two samples as shown in Figure 48.

6.4 Straining ability of Uncoated SiNW, Alumina-coated SiNW and Polymer-coated SiNW

Knowing that alumina-coated SiNW exhibited both high stress-strain slope and energy dissipation, it would be appropriate to compare the three samples to see which one exhibited the greatest straining ability to resist the volume expansion issue during charging and discharging cycles. Figures 50 and 51 below were the nanowire length vs. strain graph and average energy dissipation vs. strain graph respectively. From Figure 50, it can be seen that shorter nanowires would strain more than longer nanowires for all three samples. This is expected as the indentation depth was similar for all indentation tests performed. This also indicates that shorter nanowires had a higher likelihood of plastic deformation. Also, when looking at the same nanowire length, e.g. 150nm, it can be found that alumina-coated SiNW strained the least and the polymer-coated SiNW strained the most, which agreed with our previous result that alumina-coated were the stiffest material among the three samples.

![Nanowire length vs. Strain graph](image)

*Figure 50: Nanowire length vs. strain graph where it can be seen that the shorter the nanowires, the higher is the strain. Besides, alumina-coated SiNW strained the least when the three nanowires were of the same length (e.g. 150nm), suggesting that alumina-coated SiNW was the stiffest among the three samples.*

From Figure 51, the energy dissipation was found to increase with increasing strain for all three samples, where alumina-coated SiNW showed the highest energy dissipation at the same strain level, suggesting that alumina-coated SiNW were more prone to energy dissipation such as sliding and shearing.
Figure 51: Relationship between average energy dissipation and strain. It can be seen that at the same strain level, e.g. 0.065, alumina-coated SiNW exhibited the highest average energy dissipation.

6.5 Comparison with computational simulation of the mechanical properties of Uncoated SiNW and Alumina-coated SiNW

We have compared our experimental results to Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) along with Molecular Dynamic (MD) modelling carried out on different types of SiNW in the research group of Prof. C.V. Singh in the Department of Materials Science and Engineering at the University of Toronto. In Singh’s study, three types of individual SiNW: 1) Uncoated SiNW (thickness =4nm); 2) Silica (SiO\textsubscript{2})-coated SiNW (Si thickness=4nm, SiO\textsubscript{2} thickness=0.5nm) and 3) Alumina (Al\textsubscript{2}O\textsubscript{3})-coated SiNW (Si thickness=4nm, Al\textsubscript{2}O\textsubscript{3} thickness=0.5nm) had been pulled to failure under tensile testing at 0K. Even though the testing condition of the simulation and the dimensions of the nanowires were different from our experimental condition, some similar trends have been observed. From Figure 52, it can be seen that the alumina-coated SiNW exhibited the highest ductility among the three nanowires, meaning that alumina-coated SiNW would experience highest energy dissipation under tension and compression. In other words, when the alumina-coated SiNW was compressed during nanoindentation, it would lose more energy that might be due to shearing at the interface, nanowires buckling and sliding, which matched our experimental result.
Figure 52: MD Simulation on the tensile testing of uncoated SiNW and core-shell SiNWs conducted by Ms. Ijya Srivastava in Prof. C.V. Singh’s research group at the University of Toronto. Results showed that at the same strain level, Al₂O₃-coated SiNW exhibited the largest ductility which implied that Al₂O₃-coated SiNW had the greatest ability to undergo plastic deformation, leading to a higher energy dissipation under nanoindentation (Figure courtesy of Ijya Srivastava).

6.6 Summary & Conclusion

In this study, three types of nanowires: 1) Uncoated SiNW; 2) Alumina-coated SiNW and 3) Polymer-coated SiNW, have been investigated regarding their stress-strain slope, energy dissipation and straining ability with AFM indentation testing. Firstly, it is found that uncoated SiNW possessed a much lower stress-strain slope than the Young’s modulus of a single Si nanowire which may be due to the fact the SiNW would buckle during nanoindentation.

Secondly, alumina-coated SiNW has been shown to exhibit the highest stress-strain slope at the same length and same strain level among the three samples. The high stress-strain slope of alumina-coated SiNW is believed to be attributed to the fact the alumina coating, which had a very high Young’s modulus, was dominating the elastic properties of the entire core-shell structure. Also, it is estimated that the high friction coefficient of alumina would make the sliding between alumina-coated SiNW more difficult which led to a higher stress-strain slope. Furthermore, it is found that the stress-strain slope of alumina-coated SiNW decreased with increasing length since longer nanowires had a higher probability of containing critical defects that lead to fracture and were more subjected to buckling and as compared to shorter ones.

Thirdly, the energy dissipation of the alumina-coated SiNW is found to be the highest which indicated that alumina-coated SiNW consisted of more sources to lose energy during
nanoindentation. For instance, the alumina shell- silicon core interface might be more prone to shearing. Besides, the high friction coefficient of the alumina coating suggested that the sliding of the nanowires under nanoindentation would generate more heat which was also a source of energy dissipation.

Lastly, a comparison with computational analysis conducted by Prof. C.V. Singh and his research group at the University of Toronto has been conducted on uncoated SiNW and alumina-coated SiNW to verify the experimental result where it is found that alumina-coated SiNW was more ductile than uncoated SiNW, proving that alumina-coated SiNW would lose more energy during compression and thus show a higher energy dissipation, which matched our experimental result.

All in all, in order to tackle the mechanical issues during charging and discharging cycles, the anode materials should be stiffer and exhibit higher strain-to-failure. From our results, it is found that short alumina-coated SiNW would be the most suitable material to replace conventional graphite anode as alumina-coated SiNW showed the highest stress-strain slope and strain-to-failure among the three samples.
Chapter 7: Conclusion and Future Work

7.1 Conclusion

The objectives of this work were to evaluate the stress-strain slope, energy dissipation and straining ability of three types of SiNW array samples: 1) Uncoated SiNW; 2) Alumina-coated SiNW and 3) Polymer-coated SiNW using AFM nanoindentation in order to study the relationship between structural parameters (including nanowire length and coating materials) and to identify a design guideline to synthesize core-shell SiNW that can improve the mechanical properties of future LIB anode and hence the lifetime of LIB.

Prior to conducting AFM nanoindentation, a new mechanical property testing protocol has been developed since typical contact mechanics models such as the Hertz model, DMT and JKR modes, which are the most common techniques to interpret AFM results, are subjected to a number of unrealistic assumptions for the materials under study here. This new protocol made use of the fundamental concepts of Young’s modulus and can better simulate the contact areas which could measure the stress-strain slope and the energy dissipation of the three nanowires samples under nanoindentation more accurately.

Our results showed that alumina-coated SiNW exhibited the highest stress-strain slope at the same length and same strain level among three samples. It is believed that alumina coating, which possessed a very high Young’s modulus, was dominating the elastic properties of the entire core-shell nanowire which gave rise to an increase to the stress-strain slope. In addition, the friction coefficient of alumina was so high that it would hinder the sliding between alumina-coated SiNW which meant more force would be required to deform the nanowire and was very likely to result in a higher stress-strain slope. Furthermore, it is demonstrated that the stress-strain slope of alumina-coated SiNW decreased with increasing length which is due to the fact that longer nanowires had a higher probability of containing critical defects and were more subjected to buckling.

It is also found that alumina-coated SiNW exhibited the highest energy dissipation at the same length and same strain level during nanoindentation. This is believed to be attributed to the fact that alumina-coated SiNW were subject to more sources of energy dissipation, such as core-shell interfacial shearing and hard sliding of the nanowires.

Our experimental result was compared with a computational analysis making use of molecular dynamics modelling that studied the mechanical behavior of uncoated SiNW and alumina-coated SiNW. It is shown by the simulation that alumina-coated SiNW demonstrated higher ductility than uncoated SiNW, implying that alumina-coated SiNW would lose more energy under compression and would show a higher energy dissipation under nanoindentation, which matched our experimental result.
To summarize, it has long been shown that conventional graphite anodes of LIB are subjected to several mechanical and electromechanical issues, such as local strain formation, volume expansion, SEI formation and capacity fading, which greatly deteriorate the LIB performance and lifetime. Therefore, it is very imperative to develop a new type of anode material that possesses high stiffness and strain-to-failure to cope with all these issues. From our study, it is shown that short alumina-coated SiNW would be the most suitable material as it showed the highest stress-strain slope and energy dissipation during nanoindentation testing.

7.2 Future work
Given the results presented in this work, several future studies should be focused:

1) The study of mechanical properties of polymer coating
It has been shown that the stress-strain slope of polymer-coated SiNW was increasing with increasing length. However, longer nanowire should be more prone to buckling which would result in a lower stress-strain slope. Therefore, it is estimated that the polymer coating might have altered the mechanical properties of the entire core-shell structure. Accordingly, further studies should be focused on the polymer coating.

2) Stress-strain slope and energy dissipation studies on lithiated nanowires arrays
It has been mentioned that current graphite anodes of LIB are subjected to several mechanical and electromechanical issues upon charging and discharging cycles. Therefore, the stress-strain slope, energy dissipation and strain-to-failure of the lithiated nanowires arrays should also be studied in order to ensure that the use of these nanowires arrays can potentially improve the mechanical properties of the anodes and hence the performance of LIB.

3) In-situ SEM studies
Our results were all obtained from AFM and computational simulations where we were able to measure the mechanical properties, such as stress-strain slope and strain-to-failure, of the nanowires arrays. However, we were not able to visualize the interaction between the nanowires and the AFM tips. It is estimated that the nanowires might break and buckle. Yet using in-situ SEM could allow us to verify our assumptions and ensure that our measurement is completely accurate. Therefore, in-situ SEM studies are extremely important in order to prove that the nanowires arrays are applicable in future LIB.
Chapter 8: Appendix

8.1 Dr. G. Colas’s MATLAB for the determination of contact area

```matlab
% disp('******************************************************************************')
% disp(' Program Data Treatment AFM ')
% disp(' Version 1 - UofT ')
% disp(' (c) G. COLAS - NanoM2 - October 2014 ')
% disp('******************************************************************************')
% % ////////////////////////////////////////////////////////////////////////////////////////////////////////////////////////////////
% % disp('')
% % disp('******************************************************************************')
% % disp(' Image Data treatment procedure ')
% % disp('******************************************************************************')
% % === Chargement du fichier Pedeba ===
% % [NomFichAFM,path] = uigetfile('.txt','Select the file .txt ');
% % cd(path);
% % load(NomFichAFM);
% % AffichNomFich = NomFichAFM(1:end-5);
% %
% % disp(' ')
% % dim = input('What is the image size in micron? ');
% % disp(' ')
% % nbpt = input('What is the number of point per fast-scan line? ');
% % disp(' ')
% %
% % D = importdata(NomFichAFM);
% % g = min(min(D));
% % D(:,:,:) = D(:,:,:) - g;
% %
% % Data = transpose(D*1000000);
% % l = min(min(Data));
% % h = max(max(Data));
% %
% % X = transpose(0:dim/nbpt:dim-dim/nbpt);
% %
% % figure;
% % hold on;
% % grid on;
% % surf(X(:,),X(:,),Data(:,,:));
% % title(AffichNomFich,'Fontsize',16);
% % xlabel('microns','Fontsize',12);
% % ylabel('microns','Fontsize',12);
% % zlabel('microns','Fontsize',12);
% % caxis manual;
% % caxis([l,h]);
% % colorbar;
% % saveas(gcf, [AffichNomFich,'_surface'], 'tiff');
% % saveas(gcf, [AffichNomFich,'_surface'], 'fig');
```
% hold off;
% d = input('What is the bead diameter? ');
% diam = num2str(d);
% disp(' ')
% disp('What is the position of the contact with the bead? ')
% ab = input('x = ');
% ord = input('y = ');
% c = min(Data(fix(ord*nbpt/dim),fix(ab*nbpt/dim)),Data(round(ord*nbpt/dim),round(ab*nbpt/dim)))+d/2;
% Azim = 90;
% Elev = 90;
% figure;
% hold on;
% grid on;
% surf(X(:,X(:,Data(:,::)))) ; hold on;
% [x,y,z] = ellipsoid(ab,ord,c,d/2,d/2,d/2,256);
% surf(x,y,z);
% axis ([0 dim 0 dim 1 dim]) ;
% caxis manual;
% caxis([l,h]);
% title([AffichNomFich,'FontSize',16)
% xlabel('microns','FontSize',12) ;
% ylabel('microns','FontSize',12) ;
% zlabel('microns','FontSize',12) ;
% colorbar;
% saveas(gcf, [AffichNomFich,'_surface_and_Bead_'], 'tif');
% saveas(gcf, [AffichNomFich,'_surface_and_Bead_'], 'fig');
% hold off;
%
% S = [];
% for ii = 1:length(X)
% for jj = 1:length(X)
% if (X(jj)-ab)^2 + (X(ii)-ord)^2 + (Data(ii,jj)-c)^2 >= (d/2)^2
% S(ii,jj) = 0;
% else
% S(ii,jj) = Data(ii,jj);
% end
% end
% end
% figure;
% hold on;
% grid on;
% surf(X(:,X(:,S(:,::)));
% axis ([0 dim 0 dim 1 dim]) ;
% caxis manual;
% caxis([l,h]);
% xlabel('microns','FontSize',12);
% ylabel('microns','FontSize',12);
% zlabel('microns','FontSize',12);
% colorbar
% saveas(gcf, [AffichNomFich,'_contact_SB_'], 'tiff')
% saveas(gcf, [AffichNomFich,'_contact_SB_'], 'fig')
% hold off;
%
% disp(' ')
% ind = input('Do you want to emulate indentation? Y/N ', 's');
%
% if ind == 'Y' || ind == 'y'
% disp(' ')
% depth = input('What is the indentation depth in micron? '); 
%
% figure;
% hold on;
% grid on;
% surf(X(:,),X(:,),Data(:,:)); hold on;
% [x,y,z] = ellipsoid(ab,ord,c-depth,d/2,d/2,d/2,256);
% surf(x,y,z);
% axis ([0 dim 0 dim 1 dim]);
% caxis manual;
% caxis([l,h]);
% title([AffichNomFich],'FontSize',16)
% xlabel('microns','FontSize',12);
% ylabel('microns','FontSize',12);
% zlabel('microns','FontSize',12);
% colorbar;
% saveas(gcf, [AffichNomFich,'_surface_and_Bead_ind'], 'tiff');
% saveas(gcf, [AffichNomFich,'_surface_and_Bead_ind'], 'fig');
% hold off;
%
% Sd = [];
% s = 0;
% for ii = 1:length(X)
% for jj = 1:length(X)
% if (X(jj)-ab)^2 + (X(ii)-ord)^2 + (Data(ii,jj)-(c-depth))^2 >= (d/2)^2
% Sd(ii,jj) = 0;
% else
% Sd(ii,jj) = Data(ii,jj);
% s = s+1;
% end
% end
% end
%
% pa = s*(dim/nbpt)^2;
% Projected_area = num2str(pa);
figure;
hold on;
grid on;
surf(X(:,X(:,Sd(:,::)))
axis ([0 dim 0 dim 1 dim])
caxis manual;
caxis([l,h]);
xlabel('microns','FontSize',12)
ylabel('microns','FontSize',12)
zlabel('microns','FontSize',12)
title(['Projected surface area ','Projected_area', ' micron^2']}
hold off
disp('')
%
% if anim == 'Y' || anim == 'y'
% step = input('which indentation step (in micron) do you want to have between every image? ');
% k = 1;
% H = max(max(S));
% if mod(H+d/2-c+depth,step) == 0
% start = H+d/2;
% else
% start = H+d/2 - mod(H+d/2-c+depth,step);
% end
% de = -start+c;
% Area = [];
% for aa = start : -step : c-depth
% sa = 0;
% Sda = [];
% for ii = 1:length(X)
% for jj = 1:length(X)
% if (X(jj)-ab)^2 + (X(ii)-ord)^2 + (Data(ii,jj)-aa)^2 >= (d/2)^2
% Sda(ii,jj) = 0;
% else
% Sda(ii,jj) = Data(ii,jj);
% sa = sa +1;
% end
% end
% end
% num = num2str(k);
\texttt{% psi = sa*(dim/nbpt)^2;}
\texttt{% Projected\_area\_a = num2str(psa);}
\texttt{% ind\_depth = num2str(de);}
\texttt{%}
\texttt{% Area(k,1) = de;}
\texttt{% Area(k,2) = psa;}
\texttt{%}
\texttt{% figure;}
\texttt{% hold on;}
\texttt{% grid on;}
\texttt{% surf(X(:,1),X(:,2),Sda(:,1,:));}
\texttt{% axis ([0 \ dim \ 0 \ dim \ l \ h]);}
\texttt{% caxis manual;}
\texttt{% caxis([l,h]));}
\texttt{% xlabel('microns','FontSize',12);}
\texttt{% ylabel('microns','FontSize',12);}
\texttt{% zlabel('microns','FontSize',12);}
\texttt{% title([{'Indentation depth ',ind\_depth,' micron'};[{'Projected surface area','Projected\_area\_a', 'micron\^2'}]),'FontSize',12);}
\texttt{% colorbar}
\texttt{% saveas(gcf, [AffichNomFich,'_contact_SB_ind\_anim_',num], 'tiff')}
\texttt{% hold off;}
\texttt{% close figure 1;}
\texttt{%}
\texttt{% k = k+1;}
\texttt{% de = de+step;}
\texttt{% end}
\texttt{%}
\texttt{% figure;}
\texttt{% hold on;}
\texttt{% grid on;}
\texttt{% plot(Area(:,1),Area(:,2));}
\texttt{% xlabel('Indentation depth (microns)','FontSize',12);}
\texttt{% ylabel('Projected surface area (microns\^2)','FontSize',12);}
\texttt{% title('Evolution of the projected surface area','FontSize',12);}
\texttt{% saveas(gcf, [AffichNomFich,'_Evolution\_of\_the\_PSA'], 'tiff');}
\texttt{% saveas(gcf, [AffichNomFich,'_Evolution\_of\_the\_PSA'], 'fig');}
\texttt{% hold off;}
\texttt{%}
\texttt{% dlmwrite('psa.txt',Area,'delimiter','\t');}
\texttt{% end$}
### 8.2 Summary of AFM nanoindentation parameters

<table>
<thead>
<tr>
<th>Testing no.</th>
<th>Coating</th>
<th>NW length (nm)</th>
<th>Tip radius (μm)</th>
<th>Tip material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Uncoated</td>
<td>1000.00</td>
<td>28</td>
<td>Glass</td>
</tr>
<tr>
<td>2</td>
<td>Uncoated</td>
<td>1500.00</td>
<td>28</td>
<td>Glass</td>
</tr>
<tr>
<td>3</td>
<td>Uncoated</td>
<td>1824.63</td>
<td>28</td>
<td>Glass</td>
</tr>
<tr>
<td>4</td>
<td>Uncoated</td>
<td>843.60</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>5</td>
<td>Uncoated</td>
<td>150.42</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>6</td>
<td>Uncoated</td>
<td>278.91</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>7</td>
<td>Uncoated</td>
<td>453.21</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>8</td>
<td>Alumina</td>
<td>1219.00</td>
<td>28</td>
<td>Glass</td>
</tr>
<tr>
<td>9</td>
<td>Alumina</td>
<td>899.80</td>
<td>28</td>
<td>Glass</td>
</tr>
<tr>
<td>10</td>
<td>Alumina</td>
<td>716.13</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>11</td>
<td>Alumina</td>
<td>333.93</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>12</td>
<td>Alumina</td>
<td>128.81</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>13</td>
<td>Polymer</td>
<td>1590.99</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>14</td>
<td>Polymer</td>
<td>270.00</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>15</td>
<td>Polymer</td>
<td>960.00</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>16</td>
<td>Polymer</td>
<td>509.93</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
<tr>
<td>17</td>
<td>Polymer</td>
<td>103.09</td>
<td>20</td>
<td>Borosilikatglas</td>
</tr>
</tbody>
</table>

*Table 4: The nanowires length, tip radii and tip materials of each testing*
8.3 AFM images of nanoindentation from 1st cycle to the 10th cycle
Figure 53, 54, 55 below demonstrated the stress-strain behaviour of uncoated SiNW, alumina-coated and polymer-coated SiNW.

Figure 53: Stress vs. Strain curve for all 10 cycles of the uncoated SiNW with height of 150.4 nm and their corresponding contact areas and stress-strain slopes during each cycle.
Figure 54: Stress vs. Strain for all 10 cycles of the alumina-coated SiNW with length of 128nm and their corresponding contact areas and stress-strain slopes during each cycle.
Figure 55: Stress vs. Strain curve for all 10 cycles of the polymer-coated SiNW with length of 103nm and their corresponding contact areas and stress-strain slopes during each cycle.
8.4 Data points removal due to systematic experimental errors

Figure 56: Origin of Figure 47 where two data points, 1 and 2, were circled as outliers.

From Figure 56, two data points were identified as outliers. For point 1, it is found that the AFM tip was actually indenting the wrong location (Figure 57). For point 2, it is found that the contact area was halved which maybe due to some nanowires breakage (Figure 58).

Figure 57: (a) Right before the 1st nanoindentation test where “X” was the location chosen for nanoindentation (b), (c) and (d) were the AFM images after the 2nd, 3rd and 10th nanoindentation cycles respectively. It can be seen that the white area (red circles) remained unchanged after the 10th cycles meaning that it was not compressed by the AFM tip at all. However, some materials (green circle) were removed which implied that the AFM tip was indenting the wrong spot.
Figure 58: (a) AFM image right before 1st cycle of nanoindentation where “X” was chosen to be the nanoindentation location. (b), (c) and (d) were the AFM images after the 2nd, 3rd and 10th nanoindentation cycles respectively where it can be seen that the original white area (red circles) split into half which resulted in a smaller contact area and a higher stress-strain slope. This may be due to the breakage of the nanowires.
8.5 Energy dissipation of alumina-coated SiNW

Figure 59: It was found that the energy dissipation of alumina-coated SiNW was decreasing with nanoindentation cycles for several testing
Bibliography


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[43] D. Roylance, "STRESS-STRAIN CURVES," Department of Materials Science and Engineering, Massachusetts


