HIGH CAPACITY ANODE MATERIALS FOR LITHIUM - ION BATTERIES

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ABSTRACT

HIGH CAPACITY ANODE MATERIALS FOR LITHIUM - ION BATTERIES

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Huge energy demand in the world has caused depletion in non - renewable energy sources, and global climate change due to the consumed fuel exhausts. Renewable energy sources are eco - friendly alternatives. Electrochemical energy storage systems (EESS) are useful tools to store the energy, which is harvested from the renewable sources. Lithium - ion batteries are currently the most popular EESS owing to their several advantages over other systems. However, for their use in high energy demanding applications like electric vehicles, new electrode materials with higher capacities are required. Here, we demonstrate two anode materials with high capacities, aluminum and silicon. We address problems regarding their commercial applications and offer solutions. To improve the properties of aluminum, we fabricate aluminum - copper thin films via sputtering, then we apply age hardening to the alloy. We observe that age hardening indeed increase stability of aluminum anodes. In the second work, we synthesize silicon nanoparticles via laser ablation, whose sizes are smaller than 20 nm, and embed them into carbon nanofibers (CNFs) via electrospinning. The electrochemical battery tests are conducted with only CNFs, CNFs with commercial Si nanoparticles and CNFs with laser ablased Si nanoparticles. The cyclic stability of these composites are observed along with their rate capabilities.

Keywords: Lithium - ion batteries, anode materials, high capacity, high energy density, electrospinning, age hardening, silicon, aluminum.

ÖZET

LİTYUM İYON PİLLERİ İÇİN YÜKSEK KAPASİTELİ ANOT MALZEMELERİ

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Dünyada yükselen enerji ihtiyacı, yenilenemez enerji rezervlerinin azalmasına, harcanan fosil yakıtların da küresel iklim değişimine yol açmasına sebep olmaktadır. Yenilenebilir enerji kaynaklarından elde edilen enerjiyi saklayabilien elektrokimyasal enerji depolama sistemleri (EESS), fosil yakıtlara çevre dostu bir alternatif oluşturmaktadır. Diğer sistemlere göre çeşitli yönlerden avantaj sağlayan lityum iyon pilleri, an itibariyle en popüler EESSdir. Fakat, elektrikli araçlar gibi yğksek enerji tüketen uygulamalarda kullanılabilmeleri için, daha yüksek kapasiteli elektrot malzemeleri gerekmektedir. Bu çalışmada, aluminyum ve silikon gibi iki farklı yüksek kapasiteli anot malzemesini sunulmaktadır. Ticari kullanımlarına engel olan problemler işaret edilip, çözüm önerileri sunulmaktadır. Aluminyumun özelliklerini geliştirmek için, sputtering metodu ile aluminyum bakır ince filmleri üretilip, daha sonra yaşlandırarak sertleştirme metodunu uygulanmaktadır. Yaşlandırarak sertleştirme metodunun gerçekten de aluminyum anot malzemesinin stabilitesini arttırdığı gözlemlenmiştir. Diğer çalışmada ise, lazer ile aşındırma yşntemini kullanarak, 20 nmden küçük silikon nanoparçacıklar üretilip, elektro lif çekimi yöntemiyle hazırlanmış karbon nanoliflerin (KNL) içine gömülmüştür. Elektrokimyasal pil testleri; yalnız KNL ile, ticari silikon & KNL kompoziti ile, ve lazer ile aşındırma yöntemi ile üretilmiş silikon & KNL kompoziti ile gerçekleştirilmiştir. Bu kompozitlerin kapasite stabiliteleri ve değişik akımlardaki performansları gözlenmiştir.

Anahtar sözcükler: Lityum iyon pilleri, anot malzemeleri, yüksek kapasite, yüksek enerji yoğunluğu, elektro lif çekimi, yaşlandırarak sertleştirme, silikon, aluminyum.

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Chapter 1

Introduction

1.1 Electrochemical Energy Systems

Expectations from electrochemical energy systems like fuel cells, supercapacitors and batteries have raised further due to quick depletion of fossil fuels, and the pollution and global climate change which are caused by combustion reaction of variety of engines powered by them, in the past few decades [1-3]. Particularly, there has been a boost of attraction to batteries, which have high energy and power density, owing to their use in portable consumer electronic devices such as cellular phones, laptop computers, digital cameras and implantable medical applications. In fact, their worldwide market value was pronounced by ten billion dollars per annum in 2008. However, current performances of commercial batteries are still not sufficient for their proper utilization in advanced applications such as future electric vehicles. Batteries, which are to be used in electric vehicles, are expected to provide quick charging, high energy and power density for long travel distances. The search for advanced batteries is particularly focused on lithium ion batteries (LIBs) since they were made commercially available by Sony in early 1990s, owing to their superiority in terms of power density (5-6 times higher) and energy density (2-3 times higher) compared to other rechargeable battery systems such as nickel - metal hydride, nickel - cadmium and lead - acid batteries [4–6].

Although some different electrochemical energy systems like supercapacitors and lithium - air batteries are more advantageous in terms of power density and energy density, respectively, they have their own drawbacks. To illustrate, supercapacitors offer poor energy density while lithium - air batteries suffer from poor cycle life, hence LIBs still remain more popular. [7–11]

The essence of predominance of LIBs is associated to the employment of nonaqueous electrolytes because they allow the battery to perform in harsh conditions such as high cell potentials ($\sim 4 \text{ V}$), and high operating temperatures. Along with relatively higher energy density, LIBs offer long cycle life and low self - discharge. Furthermore, there is no limitation on partial charging since so - called "memory" effect" does not exist in LIBs. [1,2,4–6] On the other hand, although they possess many advantages over other rechargeable battery systems, commercial LIBs of today could offer only 163 km travelling distance if they are used as energy storage devices in electric vehicles. [12] The standard for an electrochemical energy storage device to be conveniently used in an electric vehicle has been issued by The United States Advanced Battery Consortium (USABC), which claims that the device should provide more than 200 Wh/kg and 300 Wh/L energy density at a discharge rate of C/3 (C indicates the discharge rate at which the device is completely charged/discharged in 1 hour), and at least 80% of its initial capacity should be retained after 1000 cycles. [13, 14] Therefore, there is still much room for improvement in the performance of LIBs.

1.2 Working Mechanism of LIBs

Typically, commercial LIBs are primarily composed of a reductant negative electrode (anode), an oxidant positive electrode (cathode), and a non-aqueous electrolyte. In operation of the battery, Li^+ (Li⁺) shuttle between the electrodes (where the name "rocking - chair cells" comes from). During discharge, Li^+ leave the anode, travels through the electrolyte and intercalate into the cathode. The movement of Li⁺ are reversed in charging process while the electrons are transferred via an external circuit during both of the operations [15, 16]. The energy acquired/required from/for the ion motion is harvested/stored electrochemically in the battery (see Figure 1.1).



Figure 1.1: Schematic representation of the working mechanism of commercial LIBs

The chemistry happening in LIBs is elaborated in Figure 1.2 further. Open circuit potential of a battery is defined by potential difference between electrochemical potentials of μ_{Anode} and $\mu_{Cathode}$ (anode's and cathode's Fermi energies). On the other hand, energy levels, which correspond to lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of electrolyte, determines the working potential window of the electrolyte [17]. If an anode material of a battery has a higher electrochemical potential than LUMO of the battery's electrolyte, the electrolyte is reduced by the anode and a passivization layer, also known as solid - electrolyte interface (SEI), will be formed. Similarly, if a cathode material, which has lower electrochemical potential than HOMO of the electrolyte, is hired in a battery, the electrolyte will be oxidized. Since SEI leads to undesired effects such as blocking the electron transfer during battery operation, designing electrode materials, whose electrochemical potentials are positioned in range of working potential window of the electrolyte, is crucial [18, 19].

In today's commercial LIBs, $LiCoO_2$ is the most widely used cathode material while graphitic carbon is a material of choice for the anode side. Electrochemical reactions that take place in commercial batteries are demonstrated below:



Figure 1.2: Schematic representation of energy levels of components in LIBs Cathodic reaction:

$$LiCoO_2 \iff Li_{1-x}CoO_2 + xLi^+ + xe^-$$
 (1.1)

Anodic reaction:

$$xC_6 + xLi^+ + xe^- \iff xLiC_6 \tag{1.2}$$

Overall reaction:

$$LiCoO_2 + xC_6 \iff Li_{1-x}CoO_2 + xLiC_6$$
 (1.3)

Before LIBs' commercialization, lithium metal was used as anode in lithium batteries, which caused several problems. When lithium is employed in the anode side, parasitic reactions are observed during the operation due to the chemical reaction between lithium and non - aqueous electrolyte. As a result, SEI forms on lithium electrode and prevents further corrosion of the electrode; however, Li⁺ forms dendrites on the layer that cause short circuit [1]. The dendrite region is then faced local overheating, which cause serious safety issues [20, 21]. To overcome these issues, lithium insertion compounds have been used as lithium ion battery electrodes. For example, graphite is now the most excessively used anode material that can provide better safety, but it comes with several drawbacks such as low capacity (372 mAh/g), low Li⁺ ion diffusion coefficient, high volume change (~ 9%) during operation and low operating potential (<0.2 V vs Li/Li⁺ electrode) [22,23].

There are different lithium transition metal oxides which are conventionally employed as cathode materials (LiMO_x, where M is a transition metal) for LIBs [6]. The problem related to transition metal oxides is that they release oxygen from their lattice at high temperatures [24]. Materials having polyanion groups offer relatively higher stability at elevated temperatures [6, 25, 26]. However, although they propose improved safety, they generally suffer from low ionic and electric conductivity, which lead to poor energy and power density [27,28]. There are some ways to overcome conductivity related problems in electrode materials and the methods will be discussed thoroughly in the upcoming sections.

Electrolytes for LIBs are classified according to their physical state at room temperature, which are referred to as solid, liquid and gel electrolytes. Each type is useful for different applications. Liquid electrolytes are generally preferred in portable electronic devices owing to their superior ionic conductivity [29], which leads to better performance at high power applications. Even though solid electrolytes possess poor ionic conductivity at room temperature, they greatly enhance the battery stability and safety. In addition to hindering SEI layer formation in the electrolytes, on the other hand, are introduced to combine the advantages of solid and liquid electrolytes to form an electrolyte with high ionic conductivity, flexibility and safety [31].

1.3 Pathway to High Performance Anode Materials

Having mentioned the current challenges in lithium - ion battery field, it is clear that anode materials need progression along with the other components. Since this thesis is dedicated to anode materials, they will be the primary focus from this part on. One needs to be careful about some key parameters such as material selection, and the material's structural formation before offering a new anode material to the field. Hence, these parameters will be elaborated in this section.

Table 1.1: Properties of some of the high capacity anode materials for LIBs

Materials	Li	С	Si	Sn	Sb	Al	Mg
Density (g/cm^3)	0.53	2.25	2.3	7.3	6.7	2.7	1.3
Lithiated Phase	Li	LiC_{6}	$\rm Li_{4.4}Si$	$\rm Li_{4.4}Sn$	${\rm Li}_3{\rm Sb}$	LiAl	${\rm Li}_3{\rm Mg}$
Theor. Cap. (mAh/g)	3862	372	4200	994	660	993	3350
Volume Change $(\%)$	100	9	420	260	200	96	100
Potential vs Li/Li^+ (V)	0	0.05	0.4	0.6	0.9	0.3	0.1

Depending on the material to be used as anode; lithium - ion storage capacity of material, energy density of battery and stability of electrode change [32]. The capacity of an electrode is determined by recording the electrochemical reaction's current and the reaction time during its Li⁺ ion uptake. Optionally, gravimetric and volumetric capacities of the electrode could be obtained by taking its weight and volume into account, respectively. Furthermore, energy density of a material is obtained by multiplying the capacity with the potential difference between the anode and the cathode. Thus, a good anode material should offer both high capacity and low electrochemical potential. Some of the possible elements to be used as high capacity anode materials for LIBs, and their properties are listed in Table 1.1 [33]. Nevertheless, materials with electrochemical potentials, which are not in the working potential window of the electrolyte, are susceptible to side reactions, which cause instability in SEI. There are different solutions to this problem such as coating electrode material, or forming various structures to embed the material into some protective environment, which should have no hindering effect on the cell operation mechanism.

Secondly, ionic and electronic conductivities of electrode material are crucial limiting factors because any hindering effect on electronic and/or ionic movement causes overpotential, and reduces reversibility and energy density. Nevertheless, long intercalation distance of Li^+ ion and low electronic conduction could be fixed by applying some strategies such as forming nano morphologies, doping and/or coating the active material with various type of materials. Particularly, implementing nanochemistry enhances electric conductivity while reducing the diffusion distance for Li^+ ions. Consequently the battery life and its energy density is improved [34,35].

Furthermore, volume changes during cell operation could result in pulverization of the electrode, which is often observed in high capacity materials. As a result, active material falls off from current collector and does not contribute to electrochemical reaction, which results in large irreversible capacity losses [36]. Pulverization could be prevented by employing strategies that are similar to the ones, which are hired in occasions where stability and conductivity problems are present.

Although size reduction and coating offer a promising pathway for reversible anode materials with high energy density, one should be careful with its design parameters [37–39]. For example, decreasing the active materials' size leads to higher surface area. Provided that the uncoated surfaces of electrode materials are prone to side reactions and SEI formation, poorly modified nano structure could easily produce large irreversible Li⁺ ion consumption, increase in the electrode resistance due to electrically insulating SEI layer, and poor Coulombic efficiency [40–42]. At this point, coating the surface of active material can improve the electrode's reversibility, however, it would form a dead weight in the anode which does not contribute to the redox reaction, hence the gravimetric energy density is compromised [22]. In addition, particle size of an anode material is inversely proportional to its volumetric energy density [43]. Hence, it is critical to optimize the parameters of nano morphology and coating of anode materials.

1.4 Anode Materials According to Their Chemistry

As mentioned previously, working principle of lithium - ion materials is primarily based on intercalation of Li⁺ ions to host electrode materials. Moreover, the importance of morphology is emphasized and optimization of structure parameters is suggested in the former sections. According to lithiation mechanism, anode materials are classified as insertion based anode materials, alloying based anode materials and conversion reaction based anode materials. Each mechanism comes with a set of advantage and its limitation, which will be discussed in detail in the subsections.

1.4.1 Insertion Based Anode Materials

In insertion based anode materials, Li⁺ ion intercalation is proceeded through vacancies, which are already present in the structure. This mechanism is mostly observed in transition metal oxide electrodes, which are generally hired as cathodes, but it is also observed some materials that are used in anodes, such as carbon and titanium based materials (i.e. LTO) [22,44]. Characteristically, these materials are stable and safe due to their moderate reaction potentials and low volumetric change. In addition, they offer good power density and reaction kinetics as they contain obstacle free one and two dimensional diffusion paths [45,46]. On the other hand, the main disadvantage of these anodes is that they provide low or moderate capacities [47].

According to the variation in electrode potential during the intercalation, the insertion mechanisms are sorted as homogeneous or heterogeneous insertions. The potential remains constant throughout the reaction in heterogeneous insertions while it is continuously changed in the homogeneous insertions. Homogeneous insertions are considered to be advantageous over the heterogeneous counterparts as the kinetics are faster, the electrode remains more stable and it is possible to

monitor state of charge of the anode [16, 48].

1.4.2 Alloying Based Anode Materials

As it is inferred from the name, the function of alloying based anode materials, which are generally metals and semi - metals such as aluminum, tin and silicon, is that they form alloys with lithium upon the intercalation. These type of alloys draw attention of the researchers primarily owing to their very large energy densities. In addition to their excellent capacity (up to 4.2 Ah/g) and low operating potentials, these materials are highly abundant and cheap. Nevertheless, they are prone to the pulverization effect, which was mentioned in the previous sections, since large number of Li⁺ ion uptake causes huge volumetric changes up to 300-400 vol% in the electrode. The change consequently damages the connection between active material and current collector [49–51]. There are numerous strategies to reduce the damage occuring on the electrode and to increase the electrodes' stability, and they will be discussed in detail in the following sections.

1.4.3 Conversion Reaction Based Anode Materials

Conversion reaction based anode materials are generally composed of compounds of transition metals and O, S, N, and P. During cell reaction, Li⁺ ions reduce the transition metal to its metallic state and form a new compound with the anion. Although this kind of reaction was not foreseen earlier, it was found out that it was possible to obtain very high capacity values with this type of reaction [52]. Their electrode potential is proportional to bond strength of the bond between the metal and the anion, and it varies generally from 0.5 V to 1 V vs Li/Li⁺ [53]. Notwithstanding, in addition to their moderate stability, they also have large overpotential, which leads to poor energy efficiencies [54]. The overpotential is proportional to electronegativity of the anion while it is inversely proportional to the compound's ionic conductivity, and disorder of its crystal structure [55, 56].

1.5 Motivation

In this thesis work, we aim to propose strategies to increase electrochemical performances and stabilities of two alloying based anode materials, which are silicon and aluminum, for LIBs. As shown in Table 1.1, both the materials offer very high Li⁺ ion storage capacities, and low operating potentials. Although they promise high energy densities in theory, they face some serious problems, which make their commercial usage unfeasible, during operation. In the following sections, each material will be introduced in more detail, complications regarding their operation will be explained, and possible pathways to enhance the materials' performance will be addressed. Furthermore, materials and methods that were hired for these studies will be presented along with results that were obtained.

Chapter 2

Materials & Methods

2.1 Materials

Commerical silicon nanopowders (>99% purity, AVP = ~ 100 nm) were purchased from Alfa Aesar. P - type silicon wafer had 99.999% purity, 0.1 ohm.cm resistivity and its surface was composed of silicon (100) plane. Polyacrylonitrile (PAN, Mw = ~ 150000) was purchased from Scientific Polymer Products. Sputtering target for aluminum and copper were bought from Kurt J. Lesker Company, and purity for both was 99.99%. Stainless steel that was used as current collectors, and sputtering substrates was 310 grade, which corresponds to austenitic stainless steel. Lithium metal, lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), isopropanol (IPA), N,N-Dimethylformamide (DMF), battery grade ethylene carbonate (EC), and dimethyl carbonate (DMC) were purchased from Sigma-Aldrich and were used without further treatment. Celgard C480 membrane was purchased from Celgard. Glass microfiber filter (GF/C) was purchased from Whatman.

2.2 Methods

2.2.1 Synthesis of Silicon Nanoparticles

Silicon nanoparticles (<20 nm) were synthesized by employing laser ablation on p - type silicon wafer, whose thickness was 500 μ m. The wafer was cleaned in ultrasonic bath for 5 minutes in each of acetone, ethanol and water, subsequently. Nufern NuQ fiber laser (NUQA-1064-NA-0030-F1) was hired for the ablation, whose parameters were as follows: A laser of 1064 nm wavelength, a 100 ns pulse width duration, a repetition rate/frequency of 30 kHz, a pulse energy of 60 mJ, a spot size of ~3.8 mm at a focal length of 200 mm, and a fluence amount of 30 mJ/cm² at room temperature. The cleaned target was dipped in 1 cm thick DMF solution. The ablation was carried out for 20000 cycles. 35 mL of silicon nanoparticle solution is obtained during each operation. Resulting solution is shown in Figure 2.1.



Figure 2.1: a) Photographic image of the silicon nanoparticles which were synthesized by laser ablation

2.2.2 Electrospinning of Silicon & Carbon Nanofiber Composite

In preparation of silicon & DMF solutions, commercial silicon nanoparticles (SiNP), and concentrated solutions (SiNPA1, SiNPA2), which were prepared by evaporating a portion of DMF solvent at 60 °C for 2-3 days, were used. In densification of SiNPA1, DMF in 35 mL of silicon nanoparticle solution was evaporated to yield a 15 mL solution. Highly dense SiNPA2 solution was obtained by reducing the volume of DMF from 105 mL to 7.5 mL. Finally, the solutions were sonicated for 30 minutes before mixing them with the polymer precursor.



Figure 2.2: Photographic image of the silicon nanoparticle & PAN solutions with a) Silicon nanoparticles as synthesized, b) SiNPA1 and c) SiNPA2

The bead-free and uniform silicon & carbon nanofiber composite materials were produced by using DMF as solvent. The homogenous electrospinning solutions were prepared by dissolving PAN in silicon & DMF solution in different percentages, and magnetically stirring for two days at room temperature (see Figure 2.2). It was observed that below 8% PAN content, homogeneity in the fibers was lost (see Figure 2.3).



Figure 2.3: Photographic image of bead formation in inhomogeneous electrospun fibers after carbonization, which contains 6 % PAN in its electrospinning precursor



Figure 2.4: Schematic representation of homogeneous electrospinning silicon nanoparticles & carbon nanofiber composite

Table 2.1: Parameters and proportions used in electrospinning precursor preparation and electrospinning (The "*" values are unknown since yield of the synthesis procedure was not clear)

Electrode Name	SC1	SC1'	SC2	SC3	SC4	SC5
Si Precursor	-	-	SiNP	SiNPA1	SiNPA1	SiNPA2
%wt of PAN	10	8	10	10	8	8
Si:PAN ratio	0	0	1:6	*	*	*
Potential (kV)	15	12	15	15	12	12
Needle distance (cm)	15	15	18	18	15	18
Flow rate (ml/h)	0.75	0.75	0.75	1	0.85	0.5



Figure 2.5: Photographic image of the electrospun fibers

After clear solutions were obtained, they were loaded in syringes, which had metallic needle tips with 0.6 mm inner diameter. The syringes were positioned horizontally on a syringe pump (model KDS-101, KD Scientific, USA). One of the electrodes of high-voltage power supply (Spellman, SL30, USA) was clamped to the metallic needle. On the other side, plate aluminum collector, which was the substrate for fiber deposition, was grounded (see Figure 2.4. The processes were carried out at ~25 °C and ~20% relative humidity. The collected nanofibers were dried over night at room temperature in a fume hood. The electrospinning parameters and the solution proportions are given in Table 2.1. Furthermore, a representative picture of the electrospun fibers is given in Figure 2.5.

2.2.3 Heat Treatment Steps of Silicon & Carbon Nanofiber Composite

Stabilization of the electrospun fibers was obtained by heating the samples to 280 $^{\circ}$ C with 5 $^{\circ}$ C/min heating rate, then leaving the sample at the high temperature for 2 hours. The stabilization procedure took place in open atmosphere. Later on, the samples were heated to 800 $^{\circ}$ C with 5 $^{\circ}$ C/min heating rate, and similar to the stabilization, they were held for 2 hours. Continuous argon flush was applied after the stabilization. In Figure 2.6, an image of electrospun fibers after carbonization was shown.



Figure 2.6: Photographic image of the electrospun fibers after carbonization

2.2.4 HF treatment of SC5

To remove the oxide layer on the silicon nanoparticles of SC5, 0.1 M HF solution was employed. Carbonized samples were dipped into the HF solution, and kept in the solution for 5 minutes. Afterwards, the samples were collected and dipped into DI water, and kept for 1 minute. The procedure with DI water was repeated twice. For further purification, the samples were put in ethanol for 5 minutes and then dried in vacuum oven overnight.

2.2.5 Thin Film Deposition of Aluminum and Aluminum - Copper

Aluminum and aluminum - copper thin films were deposited on stainless steel (SS) substrates by VAKSIS NanoD-4S RF magnetron sputtering system using RT and RT - DC, respectively. Prior to deposition, SS substrates were cleaned with acetone, ethanol and DI water, subsequently. The depositions took place at room temperature and 20 mTorr pressure with 50 sscm constant Ar flow while 50 mm of constant target-to-substrate distance was maintained. 320 nm of aluminum was continuously deposited using an RF power of 125 W. For the deposition of aluminum - copper alloy, both DC and RF sources of the sputtering system were exploited to avoid air exposure and oxidation. To maintain 4 wt% copper ratio, required copper thickness on the substrate was calculated to be 4 nm. To prevent exposure of the thin copper layer, it was sandwiched between two aluminum layers, whose thicknesses were 160 nm each. During the deposition, the same parameters, which were previously indicated in the aluminum deposition, were applied for aluminum with RF source while a DC power of 150 W was hired for copper deposition.

2.2.6 Heat Treatment Steps of Aluminum and Aluminum - Copper

Aluminum - copper thin films were heated to 540 °C with 5 °C/min heating rate using a tube furnace, and held there for 2 hours in open atmosphere. Then, the samples were quenched by using ice - DI water solution. Aging process was started when the temperature of the samples reduced to room temperature. For aging, the samples were heated to 170 °C with 5 °C/min heating rate using the same tube furnace, and held there for 14 hours in open atmosphere. Afterwards, they were left to cool at room temperature. To compare the effect of the heat treatment process, some of the aluminum thin film samples were also put through the same heat treatment steps. Images of SS, aluminum and aluminum - copper



Figure 2.7: Photographic image of (from left to right) SS, aluminum thin film after deposition, aluminum - copper thin film after deposition, aluminum - copper alloy after age hardening

thin films after deposition, and age hardened aluminum - copper alloy are shown in Figure 2.7.

2.2.7 Characterization

Different tools such as FEI Tecnai G2 F30 Transmission Electron Microscopy (TEM), FEI Quanta 200 FEG Environmental Scanning Electron Microscope (SEM), Thermo Scientific X-ray Photoelectron Spectrometer (XPS) using Al K α radiation, PAN analytical XPert X-ray Diffractometer and PRO MRD diffractometer using Cu K α radiation (XRD and GIXRD, respectively), TA Instruments TGA Q500 (TGA) using dry air (H₂O <1.5 ppm), and WITEC Alpha 300 Raman Microscope using a laser with 532 nm wavelength were exploited for the characterization of the electrode materials.

For characterization of silicon nanoparticles after the synthesis, DMF solution that contained the nanoparticles were dropped over copper and silica substrates in XPS, Raman Spectroscopy, respectively. For TEM measurements, the solution was diluted with acetone to yield 5:1 acetone:solution ratio, then dropped over a film carbon grid and dried in oven at 60°C and open atmosphere for a couple of minutes. Furthermore, for TG measurements, previously carbonized materials were used.

To characterize the electrodes after electrochemical testing, the batteries were carried in and disassembled in glovebox. The electrodes were washed with 3 mL acetonitrile to clean electrolyte residues. To avoid their contact with air, they were sealed in glovebox and then moved to instruments.

2.2.8 Lithium - Ion Battery Preparation

The electrode materials were vacuum dried at 70 °C overnight, then rapidly put into argon filled glovebox (O₂ <0.5 ppm, H₂O <0.5 ppm) to prevent air exposure. Swagelok type cells were used to build lithium half cells where lithium metal electrodes were used as anode materials (see Figure 2.8). Stainless steel current collectors were hired for both electrodes. Celgard C480 separators were utilized at anode while separators of the cathodes were glass microfiber filter (GF/C). The electrolyte solutions of the cells were composed of 280 μ L of 0.5 M LiTFSI dissolved in EC:DMC (1:1) solution. The cells were sealed after the assembly to prevent interaction with the atmosphere, and rested at room temperature for 11 hours prior to testing.



Figure 2.8: a) Photographic image of the Swagelok battery cell b) Schematic representation of the components in the battery assembly

2.2.9 Electrochemical Characterization

Biologic Instruments SP - 150 Potentiostat was hired for CV and impedance measurements of all the samples (see Figure 2.9a). For the aluminum samples, 0.5 mV/sec of scan rate was applied between 0.01 V - 1.5 V. For the silicon & carbon nanofiber composite electrodes, same potential interval was used, however, the scan rate was determined to be 0.1 mV/sec to differentiate the peaks of silicon and carbon. Furthermore, for impedance measurements of the silicon & carbon nanofiber composite electrodes, a frequency interval of 0.01 Hz to 1 MHz was hired at OCV, with 10 mV potential oscillation amplitude.

For the galvanostatic measurements, Landt CT2001A multichannel potentiostat/galvanostat was employed (see Figure 2.9b). Different current rates (100 mA/g, 200 mA/g, 500 mA/g and 1000 mA/g) were applied to all the samples in the voltage range of 0.01 V - 1.5 V.

For the aluminum samples, the sequence for galvanostatic measurements was as follows: 10 cycles at 100 mA/g, 50 cycles at 200 mA/g, 10 cycles at 100 mA/g, 10 cycles at 200 mA/g, 10 cycles at 500 mA/g, and 10 cycles at 1000 mA/g. For the aluminum - copper alloy, 10 additional cycles at 100 mA/g were applied after the tests were finished.

Sequence for the silicon & carbon nanofiber composite electrodes was altered to observe their rate capability behavior earlier than their cyclic stability like the following: 10 cycles at 100 mA/g, 10 cycles at 200 mA/g, 10 cycles at 500 mA/g, and 10 cycles at 1000 mA/g, 10 cycles at 100 mA/g, and 50 cycles at 200 mA/g.

Average electrode weights for the aluminum samples were 0.1 mg - 0.2 mg while it was ~ 1.3 mg for the silicon & carbon nanofiber composite.



Figure 2.9: Photographic image of a) Biologic Instruments SP - 150 potentiostat, and b) Landt CT2001A multichannel potentiostat/galvanostat
Chapter 3

Silicon Based Anode Materials for Li - ion Batteries

In this chapter, fabrication and characterization of silicon carbon nanofiber composite anode materials were presented and discussed after introducing silicon as an anode material for lithium - ion batteries. The methods that have been used through out the study were also explained.

3.1 Silicon as an Anode Material for Lithium -Ion Batteries

Silicon is a very popular alloying based anode material for lithium - ion batteries as mentioned previously. In addition to being the second most abundant element on the earth, it also offers a very large capacity. After full lithiation, $\text{Li}_{15}\text{Si}_4$ (yielding 3579 mAh/g theoretical capacity) and $\text{Li}_{22}\text{Si}_5$ (yielding 4200 mAh/g theoretical capacity) alloys are formed at room temperature and at 415 °C, respectively. [57]. Furthermore, it offers a very high energy density provided that it has an average discharge potential of ~370 mV vs. Li/Li^+ [58]. Thermodynamically, silicon should go through a series of phase transformations before it ends up with fully lithiated state as follows: Si to $\text{Li}_{12}\text{Si}_7$, $\text{Li}_{12}\text{Si}_7$ to $\text{Li}_{14}\text{Si}_{16}$, $\text{Li}_{14}\text{Si}_{16}$ to $\text{Li}_{13}\text{Si}_4$ and $\text{Li}_{13}\text{Si}_4$ to $\text{Li}_{22}\text{Si}_5$. In practice, these transformations are only observed as multiple potential plateaus at elevated temperatures (i.e. 450 °C) while at room temperature, crystalline silicon is transformed into amorphous silicon at ~100 mV vs. Li/Li^+ and continues cycling in that state [59, 60]. Furthermore, formation of metastable $\text{Li}_{15}\text{Si}_4$ phase is observed under 50 mV potential vs Li/Li^+ upon lithiation [61].

The problems related to employing silicon as electrode material could be indicated in three main topics: Low intrinsic electrical conductivity, pulverization and electrical contact loss, and unstable SEI formation.

Firstly, silicon is well - known for its semiconducting electrical properties. When electric conductivity of an electrode material is low, it gives rise to overpotential, which is especially pronounced at high current rates. Energy efficiency of an electrode is dramatically reduced in presence of a large overpotential.

Secondly, high lithium uptake of silicon cause large volume changes ($\sim 400\%$) during lithiation and delithiation, forming massive stresses. As a result, crack formation is observed in bulk silicon, even during first electrochemical cycles. Those cracks then lead to loss of electrical contact with current collector and within the electrode, eventually form inactive dead weight. This phenomenon is referred to as pulverization, and it is partially responsible for capacity loss in silicon anodes [62]. On the other hand, electrical contact loss does not always occur due to cracking. While volume of silicon contracts during delithiation process, some particles can lose their contact with each other and some gaps can form between them, which has similar consequences with pulverization [33].

Finally, it is important for SEI film to be stable for electrode materials as mentioned previously. In the literature, it was confirmed with HRTEM, FTIR, and XPS that SEI films in silicon electrodes are composed of Li₂CO₃, Li₂O, LiF, various lithium alkylcarbonates (RCO₂Li), and non-conductive polymers [63–66]. Note that the SEI of silicon is originally stable, however, the main problem of it is that because of the pulverization problem mentioned above, new surfaces are exposed to electrolyte upon cycling. Thus, SEI formation proceeds and leads to continuous capacity loss.

To circumvent these challenges, different applications of nanotechnology were hired. First and foremost, reducing size increases surface to volume ratio, enhance electric conductivity, and shorten diffusion distances of lithium ions [67]. One could consequently obtain an electrode with lower overpotential, better rate capability, and higher capacity. Furthermore, nanoparticles are less prone to stresses formed due to volumetric changes. In a study, it was proposed that particles with lower diameter than 10 nm would not experience pulverization according to the calculation of misfit stress energies of partially delithiated (lithiated core - delithiated shell) particles with different sizes [68]. Although nanoengineering enhances general properties of an electrode; stability, reversibility and energy density of an electrode are highly dependent on nanostructure. Various morphologies were investigated in the literature such as nanoparticles, nanotubes, porous spheres, core - shell structures, and nanocomposite structures etc.

As mentioned above, silicon nanoparticles could withstand large volumetric strains upon cycling; however, supplying and keeping electrical connection with current collector and within electrode stands a problem [69]. Convensional slurry methods including conductive carbon and binder addition did not prove effective for silicon. Therefore reaching the full capacity and cyclic stability is problematic for the nanoparticles. Silicon nanowires, on the other hand, are advantageous over the nanoparticles as they provide one - dimensional electronic pathways and each of them are connected to current collector. Hence, they supply robust electric conductivity without requiring usage of conductive additive or binder. Furthermore, the empty space between neighbour nanowires enable accomodation of volume changes upon cycling. Combination of advances in electric conductivity and buffer zone for volumetric change enhances capacity and cyclic stability of silicon nanowires. In the literature, core - shell nanowire structures, where core is an electrically conductive layer and shell is electrochemically active silicon, with increased rate capability and cyclic stability were also reported [64]. On the other hnad, core - shell structures are not inherent in the nanowires, they are also used

in nanoparticles. Silicon nanoparticles are coated with amorphous carbon, which helps buffering volumetric changes and provide electrical conductivity. Moreover, it prevents direct contact of electrolyte to silicon, and forms a more stable SEI [70,71]. It is also possible to form a structure with more than one shells to increase the material's properties. Luo et al. reported that they synthesized a core shell - shell nanoparticle structure with silicon - amorphous carbon - crystalline TiO₂, respectively [62]. Crystalline TiO₂ was used to form a better SEI layer and improve mechanical properties of the nanoparticles. Additionally, thin film silicon anodes were also tested at the initial stages of silicon research [72]. The advantage of thin films is that the critical fracture stress is inversely proportional to the film thickness according to the Griffith - Irwin relation [68]. Although some cracks are observed after initial cycle, capacity fade is comparatively lower than bulk silicon since cracked particles are still attached to current collector [73].

3.2 Electrospinning

Electrospinning is a method to generate exceptionally long and uniformly thick one - dimensional nanofibers with solid or hollow interiors. With the method, it is possible to form nanofibers with various compositions. Electrospinning technique makes use of the uniaxial elongation of a polymer solution or melt, which acts as a viscoelastic jet. Instead of hiring mechanical force for elongation, electrostatic repulsion, which is obtained by applying a potential difference between two surfaces, is exploited. When compared to mechanical drawing, electrospinning can provide much thinner fibers (considerably thinner than a human hair) [74,75]. It is particularly useful in electrode preparation as it is possible to form silicon & carbon nanofiber composites by simply combining polymer solution and silicon containing solution, then using the mixture as electrospinning precursor. Electrospun composites combine the advantages of size reduction with stability and conductivity of carbon nanofibers throughout the electrode.

3.3 Silicon & Carbon Nanofiber Composite

Having mentioned different morphologies for silicon anodes, electrospinning offers some advantages in electrode formation as it is a simple, cheap, and scalable method for continuous silicon containing nanofiber production. Furthermore, electrospun electrodes are composed of free - standing, ductile and conductive nanofibers. They do not require conductive additive or binder addition to be used as electrodes. Furthermore, the fact that they are able to free - stand eliminates the requirement of slurry preparation. There are different morphologies of electrospun silicon & carbon nanofiber composites reported in the literature such as continuous, core - shell, and porous structures [76–81]. Generally, commercial silicon nanoparticles having diameter of \sim 50 - 100 nm are employed in the composites.

In the continuous nanofibers, silicon particles are partially exposed to electrolyte due to their large size, which results in SEI formation and capacity loss upon cycling. In a continuous nanofiber composite study, commercial silicon nanoparticles (~50 nm size) and PAN solution were electrospinned and then carbonized [81]. An initial specific discharge capacity of 1620 mAh/g and Coulombic efficiency of 66.6% were obtained at 0.1 C current rate in a potential range of 0.01 V to 1.5 V. It was reported that after 100th cycle, 850 mAh/g of capacity was obtained with 52.5% capacity retention.

In the core - shell structures, various type of studies were conducted. Xiao et al. suggested a structure which is composed of PVDF membrane core. On top of that, a conductive inert nickel shell and electrochemically active amorphous silicon shell were coated via aqueous electroless plating and magnetron sputtering, respectively [76]. In their galvanostatic measurements, they preferred to use 0.05 V - 1.2 V potential interval vs Li/Li⁺. Their anode yielded 3210 mAh/g initial specific discharge capacity at 0.2 C while the capacity was reduced to 1821 mAh/g after 1000 cycles, providing 56.9% capacity retention. In a different example, a core - shell - shell structure (using PAN - silicon - PAN precursors, respectively) was designed by dual nozzle co - axial electrospinning, which was

followed by carbonization [77]. In half cell measurements between 0.01 V - 3 V potential range, their electrode provided 1479.8 mAh/g specific discharge capacity with 82.7% Coulombic efficiency at 50 mA/g current rate. After 50 cycles, their capacity was decreased to 886.5 mAh/g with a capacity retention of 72.4% capacity retention.

Porous fiber electrodes, on the other hand, provide larger surface area, shorter Li^+ ion diffusion path and increased silicon content to the composite. In an example, Li et al. proposed electrospinning silicon nanoparticles with PAN and PMMA precursor [80]. After carbonization, PMMA leads to formation of pores in the structure. Their electrode offered 3109 mAh/g first overall discharge capacity with 61% Coulombic efficiency when the half cell was cycled in between 0.05 V - 1.2 V at 0.05 C current rate. A discharge capacity of 950 mAh/g was obtained 80th cycle with 30.6% capacity retention.

In this study, we aimed to propose a free - standing, cheap and scalable continuous silicon & carbon nanofiber composite electrode with high capacity and stability. To do that, we synthesized smaller silicon nanoparticles than what were used in previously reported studies with different synthesis routes, then we homogeneously embedded and distributed the particles inside the carbon nanofibers. With the help of size reduction, we tried to achieve complete coating of the particle to prevent electrolyte exposure, buffer the volumetric changes, and enhance the ion diffusion kinetics. Polyacrylonitrile (PAN) was determined to be the polymer source as it is a frequently used polymer in electrospinning and its carbon yield after carbonization is relatively higher than other polymers. Furthermore, we avoided to use metal or metal - oxide coating to decrease the cost and enhance the ease of production.

3.4 Results & Discussion



Figure 3.1: a) Regional XPS scan for Si 2p of, b) Raman spectra of, c) TEM image of silicon nanoparticles, which are synthesized via laser ablation



Figure 3.2: Regional XPS scans for a) C 1s, b) O 1s, c) N 1s of SC1 before carbonization (black), and after carbonization (red)

Figure 3.1a represents regional XPS scan for Si 2p of silicon nanoparticles, which were synthesized via laser ablation. According to the results, there are two peaks located at 103.5 eV and 99.4 eV, which came from silicon in silica and Si NPs, respectively. Since XPS is a surface characterization technique, and peak intensity of Si - O bond is respectively higher than peak intensity of Si - Si bond, it was concluded that silicon core is coated with a silica layer, which has a few nm thickness. Presence of silicon was further proven with Raman spectroscopy, see Figure Figure 3.1b. The only peak that was observed lies between 500 cm⁻¹ and 530 cm⁻¹, which is the strongest characteristic peak of silicon [82]. In Figure 3.1c, TEM image of the synthesized silicon nanoparticles having ~20 nm average size were shown. In high - resolution TEM mode (see Figure A.1a), it was observed that the particles contain crystalline silicon cores, which were surrounded by a native - oxide shell, whose presences were proven by EDX in Figure A.1b.

Regional XPS scan for C 1s of only carbon nanofiber (CNF) electrode (SC1) was given in Figure 3.2a. It was noticed that intensity of the peak at 284.8 eV, which corresponds to graphitic carbon, was increased after carbonization while the peak at 285.5 eV, which indicated C in C = N groups, was diminished. Oxygen peak, which is located in between 532 eV - 533 eV, signifies the presence of organic C - O and C = O groups in the fibers, and its intensity was slightly increased after carbonization, see Figure 3.2b. It was probably originated from functional groups, which were formed during the stabilization process of the fibers before carbonization. Finally, in Figure 3.2c, it was observed that the nitrogen peak diminished after carbonization, indicating that the nitrogen groups were almost fully eliminated. It was inferred from the XPS results that the carbonization of the fibers was successfully achieved.

When SEM images of SC1 before and after carbonization were investigated, it was concluded that the fibers were homogeneously electrospun, see Figure 3.3a and 3.3b. Diameter of the fibers before carbonization was 198 ∓ 18 nm while after carbonization the diameter was decreased to 140 ∓ 15 nm. A reduction was expected in the volume as well as the weight due to decomposition of side groups and loss of nitrogen. The Raman spectrum in Figure 3.3c demonstrates both the D band (1440 cm⁻¹) and the G band (1580 cm⁻¹), which indicates that the fibers were partially transformed into amorphous carbon, and there were some defects on their structure. Since the carbonization temperature (800 °C) was not too high, total carbonization of the fibers was not anticipated. Furthermore, TG analysis of the fibers indicate that almost all the material was burned at 600 °C in presence of O₂, as predicted, see Figure 3.3d.



Figure 3.3: SEM images of SC1 a) Before carbonization, b) After carbonization, c) Raman spectrum and d) TG curve of SC1

Regional XPS scan for Si 2p of SC2 in Figure 3.4a reveals that commercial silicon nanoparticles were present with carbon nanofibers to form a composite. There is a peak located at 99.4 eV, which came from silicon in the nanoparticles. Furthermore, the peaks, which are distributed in between 101 eV and 105 eV, indicate that there is a SiO_x layer around the nanoparticles. The graphitic carbon peak located at 284.8 eV proves that the structure was not affected after the silicon addition, see Figure 3.4b.

In Figure 3.5a, it was observed from the SEM image that the homogeneity of the fibers was lost after commercial silicon nanoparticle addition. Diameter of the fibers varied from ~ 100 nm to ~ 250 nm and some beads were visible. After carbonization, the fiber diameter was reduced to ~ 100 nm, see Figure 3.5b. Furthermore, agglomerated silicon nanoparticles, which had a few hundred nm



Figure 3.4: Regional XPS scan of SC2 for a) Si 2p and b) C 1s, after carbonization

in size, were observable on top of the fibers. The inhomogeneity in particle distribution and the particle agglomeration were expected to cause critical drop in performance of the electrodes. Presence of the nanoparticles after carbonization was further proven by using Raman spectrum as shown in Figure 3.5c. Characteristic silicon peak at $\sim 520 \text{ cm}^{-1}$ was present along with the D and the G bands in the spectrum. Similarity of the D and the G bands of this spectrum to the spectrum of SC1 supports preservation of the amorphous carbon structure with the silicon addition. According to the TG curve of SC2, the nanoparticle content was measured to be $\sim 35 \text{ wt}\%$, see Figure 3.5d. Increase in the weight after ~ 600 °C was due to further oxidation of the nanoparticles.

Regional XPS scans in Figure 3.6 show the effect of changing parameters during the electrospinning process. It was noted that the signal coming from silicon in Si NPs at 99.4 eV was not observable in the regional scans for Si 2p (Figure 3.6a), although it was detected in XPS measurements of the silicon nanoparticle precursor solution (Figure 3.1a). Since XPS is a surface analysis technique, it was inferred that the nanoparticles were embedded inside the fibers, rather than being deposited on their surfaces. Thus, only the oxide layer of the particles was detected in between 101 eV and 105 eV. Furthermore, decreasing PAN ratio in the electrospinning precursor solution from 10% to 8% seemed to increase intensity of the signal coming from silicon, which was anticipated as the fiber thickness was expected to be decreased. Increasing the concentration of the silicon solution



Figure 3.5: SEM images of SC2 a) Before carbonization, b) After carbonization, c) Raman spectrum and d) TG curve of SC2

for the electrospinning precursor seemed to boost the silicon signal intensity one step further in SC5, which was quite anticipated. According to regional scans for C 1s in Figure 3.6b, however, there was no difference in the amorphous carbon structure of the fibers if the amount of silicon or PAN precursor were changed.

Findings of XPS measurements were further supported by SEM, see Figure 3.7a, 3.7b and 3.7c. There was no agglomeration of silicon nanoparticles on the fiber surfaces unlike the observations made in SC2 (Figure 3.5b), so it was confirmed that the particles were embedded inside the fibers. Furthermore, diameter of the fibers in SC3, which was 315 ∓ 49 nm, was comparatively higher than the



Figure 3.6: Regional XPS scans of SC3 (black), SC4 (red) and SC5 (blue) for a) Si 2p and b) C 1s



Figure 3.7: SEM images (after carbonization) of a) SC3, b) SC4, and c) SC5

value of SC2. The increase was affiliated with decreasing silicon - to - carbon ratio. On the other hand, fiber diameter was reduced to 133 ± 22 nm in SC4, when the PAN content of the precursor solution was decreased from 10% to 8%, which could help enhancing the electrode's total gravimetric capacity by increasing its silicon - to - carbon ratio. In addition, SC4 seems to be denser than SC3, which could also contribute to the electrode's overall volumetric capacity. Nevertheless, fiber connection in SC4 seemed to have some disconnections and distortions in its structure, which could cause electric conductivity problems especially at high current rates. Similar structural distortions were also observed in SC5 (see Figure 3.7c). An increase was observed in the fiber diameter to yield 162 ± 22 nm. The increase was associated with the increasing silicon content due to the more concentrated silicon solution, which was utilized in electrospinning procedure of SC5. It was noted that the silicon - to - carbon ratio was inversely proportional with the fiber thickness up to some critical point, which was then followed by a proportional relation. Furthermore, some particles were noticable close to the fibers' surface, which is in correlation with the XPS results as intensity of the silicon was increased in SC5.

TG curves of SC3 and SC4 were given in Figure 3.8. According to the curves, 5.9 wt% and 6.3 wt% of the materials remained after ~600 °C, respectively. Only 0.4 wt\% difference was observed between SC3 and SC4. Hence, it was noted that although the fiber diameter was decreased to almost half when the PAN content in the precursor was reduced from 10% to 8%, it did not effect the silicon - to - carbon ratio, dramatically. Furthermore, it was anticipated that these electrodes cannot provide high lithium storage capacities due to their low silicon content.



Figure 3.8: TG curves (after carbonization) of a) SC3, b) SC4

TG curve of SC5 was given in Figure 3.9a, which indicated that amount of TGA remnant in this material was 16.9 wt% at ~ 600 °C. When it was compared to amount of the remnants of SC3, 10.6 wt% of increase was calculated in SC5. It was inferred from the results that when the silicon solution was densified prior to mixing with the electrospinning solution, along with decreasing the PAN content of the precursor solution from 10% to 8%, it was possible to enhance the silicon content of the materials, greatly. Nevertheless, amount of silicon was measured to be inferior than the value observed for SC2 (see Figure 3.5d). To have a better understanding of silicon to silicon - oxide ratio in the particles, which were



Figure 3.9: TG curves of a) SC5 after carbonization, b) SC5 after HF treatment

embedded in the fibers of SC5, another TGA was performed for HF - treated SC5, and the result was presented in Figure 3.9b. After the oxide layer was etched, amount of the remnants was calculated to be 7.9 wt%, which corresponded to almost half the value of the pristine sample. Hence, it was concluded that approximately half of the particles consisted of SiO_x layers.

Further characterization steps were performed on HF treated SC5 to reveal effect of HF to the material structure. High shift in silicon peak to lower binding energy (see Figure A.2a) indicated that elimination of the oxide layer was successfully achieved. Small deviation in the peak from the Si⁰ peak at 99.4 eV was considered as an effect of size reduction, where presence of surface atoms start to dominate the structure and alter the bonding energy. While there was no difference between the carbon peaks after the HF treatment (see Figure A.2b), Figure A.2c represented presence of F on the surface after the treatment. Furthermore, SEM images of the sample showed correlation with the XPS results, where there was no visible damage on the fibers (see Figure A.3a, and presence of F was confirmed with EDS in Figure A.3b. Moreover, lack of oxygen peak in EDS additionally proved elimination of the oxide layer.

Figure 3.10 presents regional XPS scans for Si 2p and C 1s of SC5 before TG analysis, and remnants of SC5 after the analysis. Expectedly, signals coming from silicon in Si NPs was increased, see Figure 3.10a. Furthermore, SiO_x zones



Figure 3.10: Regional XPS scans of SC5 before (black), and after (red) TGA for a) Si 2p, and b) C 1s

in the material were fully oxidized and resulted in forming a peak at 103.5 eV, which indicates presence of silica. Carbon in the material, on the other hand, was almost fully oxidized and evaporated since the intensity of carbon peaks reduced dramatically, see Figure 3.10b. Oxidization of carbon was further confirmed with the peak with a small intensity, which was formed at \sim 288.5 eV and came from C in O - C = O groups.



Figure 3.11: Raman spectrum of SC5 after carbonization

Structure of the carbonized SC5 was investigated further with Raman spectroscopy, see Figure 3.11. Characteristic peak of silicon was almost fully diminished at $\sim 520 \text{ cm}^{-1}$. It was inferred that either the laser could not reach to the embedded particles or signal coming from the particles was lost in the background. Ratio of D band to G band was observed to be comparatively higher than the ratios for SC1 and SC2, which indicated that there were more defects in fiber structure of SC5 than the other samples. Hence, it was expected for SC5 to perform poorer at high current rates.



Figure 3.12: Cyclic voltammograms of a) SC1, b) SC2, and c)SC5, where the first, the second and the third cycles were indicated with black, red, and blue, respectively

According to cyclic voltammograms, SC1 showed a cathodic peak at ~0.7 V, which corresponds to irreversible SEI layer formation (see Figure 3.12a). After the peak, the current started to increase at ~0.4 V and showed no individually observable peak, which was due to the homogeneous insertion mechanism of amorphous carbon. Furthermore, similar behaviour was observed during the oxidation. In the following cycles, reversibility of the electrochemical reaction was increased as area of the cathodic region gradually decreased and got close to the value of the anodic region. In the voltammogram of SC2 (see Figure 3.12b) showed a different SEI formation profile in its first cycle, where there was no peak to single out. It was inferred that presence of the commercial silicon nanoparticles, which was composed of differently sized particles, on surface of the fibers led to formation of SEI at different potentials. Two cathodic peaks were observed in the first cycle at ~0.2 V and ~0.1 V. The peak at ~0.1 V indicated transition of crystalline silicon to amorphous silicon; however, origin of the peak at ~0.2 V was not clear. Presence of cathodic peaks was diminished in the second and the third cycles. Moreover, anodic peak at ~0.5 V arose from delithiation of amorphous silicon - lithium alloy, whose intensity was continuously raised upon following cycles. Along with the decreasing area of the cathodic side, it was noted that reversibility of the reaction increased gradually. Figure 3.12c shows the voltammogram of SC5, where SEI formation exhibited a similar profile to SC1's. In addition, presenting no sharp cathodic peak suggested a homogeneous insertion mechanism like SC1. On the other hand, an anodic peak with a small intensity was emerged in the second cycle at ~0.5 V. Thus, it was concluded that a small activation of the silicon in the structure was obtained. Lastly, reversibility of the reactions was increased gradually, just like the previous electrodes.



Figure 3.13: Galvanostatic charge/discharge curves of a) First 10 cycles at 100 mA/g_{cathode}, b) Last 10 cycles at 100 mA/g_{cathode}, c) Cyclic stability measurement at 20 mA/g_{cathode} between 40th and 90th cycles, and d) Rate capability measurement between 10th and 40th cycles, of SC1

Electrochemical characterization of electrode materials were further performed galvanostatically, see Figure 3.13. A huge SEI layer formation was observed in

SC1 at ~0.7 V with an initial discharge capacity of 1128 mA/g_{cathode}, and 39.9% charge - to - discharge capacity ratio at 100 mA/g_{cathode} current rate. Stable SEI formation of carbon is already well known and studied [83]. At the end of first 10 cycles, where a homogeneous insertion mechanism dominated the Li₊ ion insertion, the capacity was stabilized at 321 mAh/g_{cathode}, which is close to the theoretical capacity of graphite (372 mAh/g). The following rate capability measurement indicated that the capacities of the electrode were 285 mAh/g_{cathode}, 500 mA/g_{cathode} and 219 mAh/g_{cathode}, respectively. Afterwards, the electrode offered 96.7% capacity retention in 50 cycles with 99.6% average Coulombic efficiency. At the end of the tests, it offered ~280 mAh/g_{cathode} discharge capacity at 100 mA/g_{cathode} current rate. Hence, the results indicated that carbon nanofibers were successfully carbonized and were able to perform decently.

The same characterization steps were also applied to SC1' to observe effects on electrochemical performance of changing PAN content of the precursor solution from 10% to 8%, and the results were presented in Figure A.5. It was expected that reduction in the PAN content would result in some discontinuity in the fiber structure, hence a poorer electric conductivity. Expectedly, the first discharge capacity was reduced to $819 \text{ mAh}/\text{g}_{cathode}$ with 43.7% charge - to - discharge capacity ratio. The capacity was stabilized at $261 \text{ mAh/g}_{cathode}$ after 10 cycles at 100 mA/ $g_{cathode}$. Furthermore, rate capability performance was dropped in SC1'. Only 58.2% of discharge capacity was preserved when the current rate was increased 10 times, while 68.2% of the capacity was sustained in the same conditions. Although initial discharge capacity was lower in cyclic stability measurement (202 mAh/ $g_{cathode}$), 99.3% capacity retention and 99.7% average Coulombic efficiency were obtained, which was even better than the value for SC1. The measurements were ended with 220 mAh/ $g_{cathode}$ discharge capacity at 100 mA/g_{cathode}, which was comparatively lower than the value of SC1 (280) $mAh/g_{cathode}$). As a result, it was noted that the reduction in PAN content reduced discharge capacity and rate capability of electrode, while there was a small increase in capacity retention.

Electrochemical performance of SC2 was diminished quickly, as expected, see



Figure 3.14: Galvanostatic charge/discharge curves of a) First 10 cycles at 100 mA/g_{cathode}, b) Last 10 cycles at 100 mA/g_{cathode}, c) Cyclic stability measurement at 20 mA/g_{cathode} between 40th and 90th cycles, and d) Rate capability measurement between 10th and 40th cycles, of SC2

Figure 3.14. It offered a very high first discharge capacity of 1618 mAh/g_{cathode} with 70.2% charge - to - discharge capacity ratio, which shows correlation to examples from the literature [76–81]. Furthemore, in the first cycle, crystalline silicon nanoparticles turned into amorphous phase upon lithiation at ~100 mV, as mentioned in the introduction section. In the following cycles at 100 mA/g current rate, the electrode yielded a stable discharge capacity of ~1080 mAh/g_{cathode}. When the applied current was increased, however, the capacity values became rather unstable. In average, the electrode yielded average discharge capacities of 982 mAh/g_{cathode}, 530 mAh/g_{cathode} and 145 mAh/g_{cathode}, respectively. Rate capability performance of SC2 was drastically lower than what SC1 offered, which was due to low electric conductivity of large silicon nanoparticles. Then, the

battery was practically failed after cyclic stability measurement for 50 cycles at 200 mA/g_{cathode} current rate, offering only 5.1% capacity retention with 99.5% average Coulombic efficiency. In the following last 10 cycles, the potential profile became very unstable and the capacity was reduced to 61 mAh/g_{cathode} at 100 mA/g_{cathode} current rate.



Figure 3.15: Galvanostatic charge/discharge curves of a) First 10 cycles at 100 mA/g_{cathode}, b) Last 10 cycles at 100 mA/g_{cathode}, c) Cyclic stability measurement at 20 mA/g_{cathode} between 40th and 90th cycles, and d) Rate capability measurement between 10th and 40th cycles, of SC3

Electrochemical performance profile of SC3 quite resembles to SC1, exhibiting a homogeneous insertion mechanism, see Figure 3.15. The first cycle at 100 mA/g_{cathode} yielded 640 mAh/g_{cathode} discharge capacity and 40.8% charge - to - discharge capacity ratio due to the formation of SEI layer at ~0.7 V. The capacity was stabilized at 200.6 mAh/g_{cathode} after 10 cycles. In terms of rate capability, the electrode provided average discharge capacities of 156 mAh/g_{cathode}, 118 mAh/g_{cathode} and 88 mAh/g_{cathode} at current rates of 200 mA/g_{cathode}, 500 $mA/g_{cathode}$ and 1000 $mA/g_{cathode}$, respectively. In terms of cyclic stability, 91.1% of the capacity was preserved at the end of 50 cycles, which is drastically higher than the value obtained in the measurement of SC2. The average Coulombic efficiency during the stability measurement was 99.9%, which indicates that reversibility of the electrochemical reaction is very high. The electrode exhibited 191 mAh/g_{cathode} discharge capacity in the last 10 cycles at 100 mA/g_{cathode} current rate.



Figure 3.16: Galvanostatic charge/discharge curves of a) First 10 cycles at 100 mA/g_{cathode}, b) Last 10 cycles at 100 mA/g_{cathode}, c) Cyclic stability measurement at 20 mA/g_{cathode} between 40th and 90th cycles, and d) Rate capability measurement between 10th and 40th cycles, of SC4

Electrochemical characterization data of SC4 were given in Figure 3.16. It appears from the first potential profile at $100 \text{ mA/g}_{cathode}$ (Figure 3.16a), a high overpotential was observed in the measurement. In the SEM images of SC4 (Figure 3.7b), it was observed that the fibers contained some discontinuity in their morphologies, hence an electrical conductivity problem was foreseen for the electrode.

High overpotential problem as well as bad rate capability performance (Figure 3.16d) indicates that the conductivity of the electrode was, indeed, poor. Thus, electrochemical reactions, which were taking place in the battery, were highly irreversible. Even SEI formation of the electrode occured at a lower potential (~0.5 V) than the previous samples, yielding 321 mAh/g_{cathode} discharge capacity and 18.2% charge - to - discharge capacity ratio. Low discharge capacities observed in the first cycles (~83 mAh/g_{cathode} after stabilization) signifies that both carbon and silicon in the electrode was not properly activated. Expectedly, the electrode performed a low cyclic stability by preserving 74.5% of its discharge capacity with 100.7% average Coulombic efficiency. In terms of rate capability, the electrode provided average discharge capacities of 41 mAh/g_{cathode}, 10 mAh/g_{cathode} and 3 mAh/g_{cathode}, respectively. Having an average of ~77 mAh/g_{cathode} discharge capacity at 100 mAh/g_{cathode} at the end of the measurements further prove that the electrode cannot be activated at these current rates.

Electrochemical characterizations continued with galvanostatic measurement of SC5, see Figure 3.17. The first discharge capacity was observed to be 633 $mAh/g_{electrode}$, which yielded 43.3% charge - to - discharge capacity ratio with 274 mAh/g_{electrode} charge capacity. Like the previous samples, the efficiency obtained in the first cycle was very low; however, it was comparable to the first Coulombic efficiencies of SC1 and SC1'. So, it was commented that irreversibility of the first cycle was inherently coming from carbon nanofibers. In the following cycles, the capacity was stabilized at $\sim 220 \text{ mAh/g}_{electrode}$, which was comparatively lower than the capacity obtained in SC1'. It was inferred that the silicon activation problem was also present in SC5 although the effect was less catastrophic than it was for SC4. Defective carbon structure, which was revealed by Raman spectroscopy and SEM, and low conductivity of silicon were considered to be source of the overpotential, and the activation problem. Furthermore, in rate capability measurements, average discharge capacities of $169 \text{ mAh/g}_{electrode}$, 133 $mAh/g_{electrode}$, and 102 $mAh/g_{electrode}$ at current rates of 200 $mA/g_{cathode}$, 500 $mA/g_{cathode}$ and 1000 $mA/g_{cathode}$, respectively. Moreover, an average discharge



Figure 3.17: Galvanostatic charge/discharge curves of a) First 10 cycles at 100 mA/g_{cathode}, b) Last 10 cycles at 100 mA/g_{cathode}, c) Cyclic stability measurement at 20 mA/g_{cathode} between 40th and 90th cycles, and d) Rate capability measurement between 10th and 40th cycles, of SC5

capacity of 186 mAh/g_{electrode} was obtained in the following cyclic stability measurement with 97.2% capacity retention and 99.7% average Coulombic efficiency. Lastly, in the last 10 cycles, the electrode gave 217 mAh/g_{electrode} discharge capacity, which was very close to the initially stabilized capacity values. Although the obtained stability values were quite good, lack of silicon activation stood as a big disadvantage for the electrode.

It was predicted that eliminating the oxide shell around the particles in SC5 would enhance electron and Li⁺ ion transfer kinetics, as silicon oxide is known for its insulating properties for the both. Hence, HF treated SC5 was also electrochemically characterized. Figure A.4 represents CV curves of HF treated SC5. It was noted that the anodic peak at ~0.5 V shifted to ~0.4 V and its intensity was



Figure 3.18: Galvanostatic charge/discharge curves of a) First 10 cycles at 100 mA/g_{cathode}, b) Last 10 cycles at 100 mA/g_{cathode}, c) Cyclic stability measurement at 20 mA/g_{cathode} between 40th and 90th cycles, and d) Rate capability measurement between 10th and 40th cycles, of HF treated SC5

increased, which indicated overpotential was decreased and reversibility of the reaction was increased. In Figure 3.18, galvanostatic measurements of the electrode were shown. The first discharge capacity was increased to 710 mAh/g_{electrode} with 45.3% charge - to - discharge capacity ratio. It was observed that a clear plateau was formed at 100 mV, and it continued to appear in the following cycles. It was inferred that activation of silicon was partially achieved; however, the activation was not achieved completely in the first cycle, and it was carried on gradually. The capacity was stabilized at ~ 250 mAh/g_{electrode} at the end of 10 cycles, which was slightly higher than the value for SC5. In terms of rate capability, average discharge capacities were measured to be 201 mAh/g_{electrode}, 165 mAh/g_{electrode}, and 132 mAh/g_{electrode} at current rates of 200 mA/g_{cathode}, 500 mA/g_{cathode} and 1000 mA/g_{cathode}, respectively. Thus, 52.8% of the capacity was offered with 10 times higher current, which was comparatively higher than the value obtained for SC5, which was 46.4%. In terms of cyclic stability, the measurement started with 204 mAh/g_{cathode} at 200 mA/g_{cathode} current rate, 96.3% of it was conserved after 50 cycles with 99.8% average Coulombic efficiency. The measurements were finalized with 213 mAh/g_{cathode} at 100 mA/g_{cathode}. Although the HF treated electrode performed better than SC5 in terms of discharge capacity, rate capability, and cyclic stability, the results were very comparable to the results of SC1'. Furthermore, the performance of SC5 was even worse than the performance of SC1, even after HF treatment. Considering comparable discharge capacities obtained in HF treated SC5 to SC1', along with the ongoing activation, which was observed in the first 10 cycles, it was inferred that proper stimulation of silicon was not achieved. Since electric conductivity of SC1' was poorer than SC1 as previously discussed, and silicon nanoparticle addition was expected to reduce the conductivity even further, it was decided to apply lower current rates to the electrode.



Figure 3.19: Galvanostatic charge/discharge curves of HF treated SC5 at 400 mA/g_{silicon}

When 400 mA/g_{silicon} current rate was applied to HF treated SC5, first discharge capacity was increased to 890 mAh/g_{cathode} with 48.7% charge - to discharge capacity ratio. Plateau at 100 mV, which corresponds to crystalline silicon's transition to amorphous silicon, was not observed after the first cycle, which suggested that the activation of silicon was completed. On the other hand, discharge capacity was still far from the expected capacity values, after its stabilization at $\sim 280 \text{ mAh/g}_{cathode}$. So, it was concluded that the silicon nanoparticles, which were synthesized via laser ablation, were not electrochemically reacted with Li⁺ properly. Further research should be conducted to reveal origin of the problem.



Figure 3.20: SEM images (after cycling) of a) SC1, b) SC2, and c) SC5

As it was shown in Figure 3.20a and 3.20c, morphology of the fibers remain unchanged after 100 cycles for SC1 and SC5. Thicknesses and surface roughnesses of the fibers were similar to their pristine state, which indicates that no significant damage was occured on the fibers. SEI layer of carbon is already well - known for its stability. Furthermore, the fact that stability of morphology of SC5 was preserved, and presence of silicon was observed via EDAX, proves the particles were successfully embedded inside the carbon nanofibers, and direct interaction of silicon with the electrolyte was favorably prevented. In Figure 3.20b, however, it is clear that the commercial silicon nanoparticles were subjected to pulverization, and the their morphology was severely damaged, compared to their pristine state (see Figure 3.5b), which justified the drastic capacity loss upon cycling (see Figure 3.14).

When impedance spectra of the materials were investigated, expectedly, SC1 was observed to have the lowest electrode resistance because its semicircle in the nyquist plot had the lowest diameter. After silicon addition, there was a huge increase in the resistance due to low electrical conductivity of silicon. Although a slight change was observed between SC2 and SC5, it was not possible to make a proper comment before fitting resistance parameters. Furthermore, although HF



Figure 3.21: Nyquist plots of SC1 (black), SC2 (red), SC5 (blue), and HF treated SC5 (green) before cycling

treatment etched away the native oxide layer, an increase in electrode resistance was observed. Even though there was no detectable change in XPS and SEM data of the HF treated SC5, the impedance data indicated that some defects were introduced to the electrode.

Chapter 4

Aluminum Based Anode Materials for Li - ion Batteries

In this chapter, aluminum as an anode material for lithium - ion batteries is introduced. Furthermore, effects of aging in aluminum - copper thin films deposited by sputtering method are presented and discussed as well as their fabrication method and characterizations.

4.1 Aluminum as an Anode Material for Lithium - Ion Batteries

Aluminum is the most abundant metal in the earth's crust, and is a well - studied element for its industrial uses. For years, it has been studied as an attractive electrode material for energy storage and conversion. Characteristically, it has a relatively small atomic weight of 26.98 g/mol, and it offers three valence electrons. It was first studied as a cathode material against zinc (mercury) anode by Hulot in 1850s, later on its alloys with various elements were proposed as anode materials in various battery systems [84, 85]. Moreover, Zaromb and Trevethan et al. demonstrated the aluminum - oxygen systems in the early 1960s [86, 87].

In the case of lithium - ion batteries, aluminum is an alloying based anode material, which offers high capacity and energy density, and decent power density. Thermodynamically, Al - Li binary phase diagram indicates that aluminum and lithium can form three different intermetallic compounds such as AlLi, Al_2Li_3 and Al_4Li_9 [88]. Keeping that in mind, if the Al_4Li_9 alloy is electrochemically formed during the battery operation, aluminum could hold 2.25 lithium atom per an atom, offering 2234 mAh/g gravimetric capacity [50]. Although the theoretical expectations from aluminum anode in lithium - ion batteries are tempting, only a few studies are reported in the literature. Unlike silicon, different nanomorphologies, other than thin films, are not thoroughly investigated for aluminum. According to the reported results for the thin film, formation of amorphous LiAl alloy occurs at ${\sim}0.3$ V vs Li/Li^+ electrode; however, further lithiation of the electrode could not be obtained electrochemically, which leads to utilization of only 993 mAh/g of aluminum's theoretical capacity [33, 50, 89]. Furthermore, a high overpotential (~ 0.2 V) was observed during charging. Coulombic efficiency for the first cycle was found to be inversely proportional to the film thickness, ranging from 44% at 0.1 μm to 58% at 1 μm [50]. The reason for low Coulombic efficiency values is very similar to what is observed in silicon. Aluminum is subjected to 96% volume change upon cycling, which triggers pulverization and contact loss with current collector, similar to the silicon anode [33].

4.2 Age Hardening in Aluminum - Copper Alloys

Age hardening is an effective heat treatment method to increase strength of various alloys of aluminum, magnesium, titanium etc. Basically, the idea is to distribute fine secondary phase particles inside the alloy matrix to hinder the movement of defects and dislocations. To achieve that, first step is the solutionizing, in which the main phase of the alloy is saturated with impurity atoms up to its saturation point at a specific high temperature. It is followed by quenching where the alloy is rapidly cooled down to room temperature. Fast cooling rate impedes movement of the atoms, hence a supersaturated metastable matrix is formed. If the mobility of the impurity atoms are sufficient, the atoms are segregated to suitable surfaces to form stable second phase particles, and the process is referred to as natural aging. In some cases the mobility of the impurity atoms are not enough for segregation, hence artificial aging is required to be triggered. The alloy is heated up to a temperature, which is lower than the equilibrium solvus temperature, and left there for some time for the second phase particles to form. If the heat is supplied for longer than required, hardness of the alloy starts to fade, which is called over - aging.

One of the well studied age hardening systems is the binary aluminum - copper system as it provides a long range of possibilities for age - hardenable alloys [90]. Aluminum matrix is able to dissolve more than 4% copper if the temperature is elevated to \sim 540 °C. Various compositions of aluminum - copper age hardenable alloys are commercially available. The system is mostly hired in aviation technology since the alloy offers high strength, low weight and is relatively cheaper. The precipitation sequence during aging is generally modeled as follows [91]:

$$GPI \to GPII(\theta'') \to \theta' \to \theta$$
 (4.1)

Having sufficient mobility, copper atoms form single layers on {100} planes of α aluminum. A widely accepted structural model describes GPII as two copper {200} planes seperated by three aluminum planes, corresponding to Al₃Cu stoichiometry [92, 93]. Metastable θ' phase is formed in the next step, having a body - centered tetragonal crystal structure and corresponding to Al₂Cu stoichiometry. Although being unstable, it is the main strengthening phase in the system [94, 95]. The process is finalized with the formation of incoherent, stable θ phase in a tetragonal C16 crystal structure and Al₂Cu stoichiometry [90]. It is reported that the coherent and metastable precipitates (i.e. GPI, GPII, and θ') are formed at aging temperatures below 200 °C while temperatures higher than 250 °C lead to θ phase formation in bulk age hardenable aluminum - copper systems [96].

4.3 Age Hardened Aluminum - Copper Thin Film Alloy

The precipitation kinetics in thin films are significantly different than their bulk counterparts. Prior to aging, high number of vacancies are present in a quenched bulk alloy. During aging, these vacancies act as nucleation sites for precipitates. In this films, however, excess vacancies cannot be retained as they are easily diffused to the free surface. As a result, equilibrium θ phase is preferentially nucleated on the film surfaces [97, 98]. Furthermore, the formation of GP zones are retarded in thin film alloys [96]. The XRD spectra of Al - 4 wt% Cu film, which is deposited by magnetron sputtering by Lin et al., show no peaks characterizing the precipitates [98]. Moreover, Frear et al. claimed that formation of the intermediate products are skipped and θ phase is directly precipitated during aging process in thin films [97]. Interestingly Mader et al. reported that they observed GP zones, θ' and θ particles via TEM in their single crystal Al - 3 wt% Cu films, which are deposited by R. F. sputtering [96]. It was also mentioned by Biswas and his colleagues that the observation of second phase particles were not possible via conventional XRD experiments at the aging temperatures of 165 °C and $190 \,^{\circ}\mathrm{C}$, but synchrotron radiation experiments can provide additional peaks in the spectrum [90].

In this study, our goal is to increase mechanical strength of aluminum electrode by applying age hardening to aluminum - copper binary alloy system. Raised strength of the electrode is supposed to prevent the pulverization and enhance its cyclic stability. To do that, an aluminum - copper binary system which contains 4 wt% copper was determined to be studied. 4 wt% copper is very close to the maximum solubility in α phase of aluminum in any temperature. We suggested that the amount of impurity or second phase particles is proportional to the electrode's yield strength under correct aging conditions. The solutionizing and aging parameters were taken from the literature [99], after the hardness values of aluminum - 4 wt% copper alloy at different temperatures were investigated.

4.4 Results & Discussion



Figure 4.1: SEM images of a) Uncoated SS, b) Aluminum coated on SS (as coated), c) Aluminum - copper coated on SS (as coated), d) Aluminum - copper coated on SS (after solutionizing and aging)

Thin film coatings of aluminum metal and aluminum - copper alloy were successfully achieved via sputtering method, as shown in Figure 4.1b and c. SEM image of uncoated SS was also presented for comparison in Figure 4.1a. The formation of small islands of aluminum, which were distributed on top of the thin film, is intrinsic to sputtering technique. Expectedly, there was no morphological difference between as coated aluminum and aluminum - copper samples as the copper layer was sandwiched between two aluminum layers during sputtering. In Figure 4.1d, however, morphology of the age hardened aluminum - copper alloy was changed dramatically. It was concluded that during the solutionizing procedure, the alloy had a tendency to agglomerate and form islands mostly in micrometer scale. Nevertheless, mesopores were introduced to the microstructure during the quenching process due to rapid limitation to mobility of the alloy atoms, see Figure 4.2.



Figure 4.2: SEM image of aluminum - copper coated on SS (after solutionizing and aging) with a higher magnification

To observe the structural changes, EDS elemental mapping was performed on the age hardened alloy before and after the heat treatment procedures, see Figure 4.3 and 4.4. Before the age hardening process, aluminum and copper was homogenously distributed on the SS surface as expected. After the heat treatment steps, however, islands of the alloy were clearly observed in 4.4. Although the signal, which was collected from copper, was weak, it was clear that it was primarily concentrated on the islands.



Figure 4.3: EDS elemental mapping of aluminum - copper samples coated on SS before heat treatment



Figure 4.4: EDS elemental mapping of aluminum - copper samples coated on SS after heat treatment



Figure 4.5: EDS elemental ratios and EDS elemental mapping of aluminum thin film sample as deposited on SS


Figure 4.6: EDS elemental ratios and EDS elemental mapping of aluminum - copper sample coated on SS after heat treatment

EDS elemental ratios were given in Figure 4.5 and 4.6. As the stainless steel substrate contains chromium and nickel alloying elements, signals coming from these elements were also observed. In order to prove that these elements did not interfere with formation of the aluminum - copper islands, EDS elemental mappings of chromium and nickel are shown along with the EDS results. The mappings, which were presented in Figure 4.5, indicated that the substrate intrinsically accommodated these elements. In Figure 4.6, it was proven that both the elements were distributed in the matrix, rather than the islands. Furthermore, elemental weight ratio of copper to aluminum and copper corresponded to ~ 4.6 wt%, which proves that the aimed elemental ratio was obtained, considering the tolerance level of EDS.

XRD patterns of various samples were presented in Figure 4.7. SS substrate and aluminum thin film (as deposited) showed characteristic austenitic stainless steel and aluminum lines, respectively. There was no visible change in the XRD pattern of aluminum - copper thin film (as deposited) when it was compared to the pattern of aluminum because very thin layer of copper was sandwiched between aluminum layers and crystallographic structure was represented dominantly by them. The results, which were obtained from the age hardened aluminum copper, on the other hand, exhibited a significant deviation from aluminum's pattern. As it was mentioned in the introduction part, formation of second phase particles is not observable with conventional XRD methods [90, 98], so there was no peak corresponding to compounds of aluminum and copper in the patterns. Aluminum's characteristic peaks at 44.7° and 46.9° were shifted towards the characteristic peaks of the SS substrate, which were located at 43.6° and 44.5° in the age hardened aluminum - copper sample. To fully understand the modification in the crystallography of the age hardened aluminum - copper alloy, the mechanism should be investigated further, which is beyond the scope of this study.

Regional XPS scans for Al 2p, Cu 2p and Fe 2p of the same samples were performed and shown in Figure 4.8. According to the results, the SS substrate does not have aluminum and copper on its surface, intrinsically. Furthermore, results obtained in the Al 2p scan indicated that the thin layer of alumina (Al³⁺ observed at 74.6 eV) grew thicker at the surface after the heat treatment since



Figure 4.7: XRD patterns of SS substrate (black), aluminum thin film as deposited (red), aluminum - copper thin film sample as deposited (blue), aluminum - copper thin film sample after age hardening (green)

the peak corresponding to Al⁰ peak at 72.6 eV disappeared. Seeing no copper presence at the surface of as deposited aluminum - copper sample was a simple outcome of sandwiching it between two thick aluminum layers. After the age hardening steps, however, presence of copper at the surface was observed with a small intensity peak at 933 eV, which shows a correlation with the results obtained with EDS mapping on the same sample. The lack of high intensity was expected since only a small amount of copper was distributed through the aluminum matrix and there was a thick alumina layer on the surface. It was also noted that there was no iron presence on the surface of the age hardened sample. Hence, it was inferred that the iron atoms did not segregate through the surface from the substrate during the heat treatment steps. In addition, although aluminum - copper alloy was agglomerated on the surface to form islands, there



Figure 4.8: Regional XPS scans for Al 2p, Cu 2p and Fe 2p of SS substrate (black), aluminum thin film as deposited (red), aluminum - copper thin film sample as deposited (blue), aluminum - copper thin film sample after age hardening (green)

was still a thin layer of the alloy on the surface of the matrix.

To differentiate the effect of age hardening to electrochemical performance from the effect of heat treatment itself, aluminum sample was put through the same heat treatment steps without copper deposition. As shown in Figure 4.9, morphology of the aluminum became very similar to structure of the age hardened alloy. Aluminum thin film also showed a tendency to agglomerate to form islands on the matrix, see Figure 4.10.



Figure 4.9: SEM image of aluminum after the heat treatment



Figure 4.10: EDS elemental ratios and EDS elemental mapping of aluminum after the heat treatment



Figure 4.11: Regional XPS scans for a) Al 2p, b) Cu 2p, c) Fe 2p, and d) XRD spectra of aged hardened aluminum - copper (black) and aluminum after the heat treatment (red)

According to the regional XPS scans presented in Figures 4.11a, b and c, the surface was covered with alumina (due to Al^{3+} peak at 74.6 eV), however, presence of copper was not observed as expected. Crystallographic structure of the heat treated aluminum showed resemblance to the alloy (see Figure 4.11d), which indicates that the formation mechanisms were also analogous. The peak at 43.6° seemed to lose intensity in the heat treated aluminum, whose origin should be investigated further.



Figure 4.12: Cyclic voltammograms of a) Aluminum, b) Age hardened aluminum - copper alloy and c) The heat treated aluminum (1.cycle is black, 2.cycle is red and 3.cycle is blue)

Cyclic voltammetry was performed to investigate the electrochemical activity of the samples, see Figure 4.12. Aluminum thin film had a cathodic onset potential at ~ 0.2 V, which showed some correlation to the literature [50], and the reaction continued up to 0.01 V. The difference between the theoretical potential (~ 0.3 V) and the measured potential (~ 0.2 V) could be originated from overpotential, see Figure 4.12a. Aluminum's intrinsic low Li⁺ diffusivity forces Li⁺ions to spend more energy to intercalate. The oxidation peak observed at 0.58 V during the first cycle shifted towards higher potentials in the second and the third cycles, which expressed not only the intrinsic overpotential existed, but also it was increased over cycling. This was probably due to increasing electrode resistance, resulting from loss of contact within the electrode and with the current collector upon cycling. In Figure 4.12b, cathodic peak, which was observed at ~ 0.5 V in the first cycle, was attributed to SEI formation. Although a similar cathodic onset was observed at ~ 0.2 V in the first cycle of the alloy, the peak was replaced by a continuous slope in the further cycles. Furthermore, shift in the oxidation peak at ~ 0.5 V was less pronounced upon cycling in the alloy, which signaled a better cyclic stability. Finally, although the voltammogram of the heat treated aluminum showed resemblance to the alloy's, peak intensities seemed to be reduced and there was ~ 30 mV shift in the oxidation peak. Meanly, in addition to having a higher overpotential, the reaction took place less efficiently in the heat treated aluminum.

Results obtained from galvanostatic measurements of the samples further proved the findings of cyclic voltammograms. Aluminum offered a discharge capacity of 926 mAh/g, which was very close to its theoretical capacity, see Figure 4.13. On the other hand, it delivered a charge capacity of 538 mAh/g, yielding only 58.1% charge - to - discharge capacity ratio. The Coulombic efficiency was increased in the upcoming cycles and noted as 93% at the end of first 10 cycles at a discharge capacity of 227 mAh/g. It was noted that a discharge plateau was located at 0.25 V while the corresponding charge plateau was observed at 0.45 V, which showed correlation with cyclic voltammogram of the aluminum. Furthermore, roughly 200 mV of overpotential was recorded at 100 mA/g current rate.

Capacity retention in the first 10 cycles at 100 mA/g was calculated to be only 24.5%. In the following cyclic stability measurement, discharge capacity of aluminum thin film decreased to 59 mAh/g at 16th cycle at 200 mA/g current



Figure 4.13: Galvanostatic charge/discharge curves of aluminum thin film in a) the first 10 cycles at 100 mA/g current rate (1.cycle is black, 10.cycle is red), b) Cyclic stability measurement at 200 mA/g current rate and c) Rate capability data at different current rates

rate and remained stable afterwards. The average Coulombic efficiency for the aluminum sample was calculated to be 97.9% whereas its capacity retention in 50 cycles was only 26.6%.

After 50 cycles, current rate was reduced back to 100 mA/g for rate capability measurements. In first few cycles, ~ 150 mAh/g discharge capacity was obtained but then the capacity was rapidly diminished to ~ 50 mAh/g. At a high current density of 1000 mA/g, the material could only deliver 24.5 mAh/g average discharge capacity. Thus, the practical limit of usage for the aluminum was determined to be 10 cycles at 100 mA/g and 16 cycles at 200 mA/g current rate.

It was inferred from the results that the pulverization effect strongly dominates cyclic performance of the aluminum sample.



Figure 4.14: Galvanostatic charge/discharge curves of age hardened aluminum - copper alloy in a) the first 10 cycles at 100 mA/g current rate (1.cycle is black, 10.cycle is red), b) Cyclic stability measurement at 200 mA/g current rate and c) Rate capability data at different current rates

In age hardened aluminum - copper alloy, first discharge capacity was recorded to be 987 mAh/g and it delivered 41.2% charge - to - discharge capacity ratio with 407 mAh/g charge capacity, see Figure 4.14. Unlike the aluminum sample, the alloy presented a continuous slope rather than a plateau, which was in correlation with CV findings. Low efficiency obtained in the first cycle was associated with SEI formation. The heat treatment steps, specifically solutionizing and quenching, introduced mesopores to the structure and increased the electrode electrolyte interaction surface, as shown in Figure 4.2. Increased active surface area gave rise to SEI formation in the sample. Indeed, in the second cycle, a discharge capacity of 516 mAh/g was achieved with a Coulombic efficiency of 79.3%. At the end of 10 cycles at 100 mA/g current rate, a reversible capacity of 401 mAh/g was measured. Hence, 40.6% of the initial capacity was obtained after 10 cycles, whereas in the aluminum sample was only 24.5%.

Cyclic stability measurement at 200 mA/g current rate offered even more promise with first discharge capacity of 367 mAh/g and final discharge capacity of 241 mAh/g, yielding 65.7% capacity retention. Compared to the 26.6% retention obtained from the aluminum sample, the alloy offered more than twofold cyclic stability. On the other hand, overall Coulombic efficiency in 50 cycles was recorded to be 96.2%. It indicated that some of the capacity was still lost to side reactions or electrode pulverization, but the situation was not as severe as it is in the aluminum case.

When the current was set at 100 mA/g after the stability measurement, an average discharge capacity of 305 mAh/g was achieved. With increasing current rates of 200 mA/g, 500 mA/g and 1000 mA/g, the average capacities were recorded to be 227 mAh/g, 155 mAh/g and 101 mAh/g, respectively. It was observed that the alloy did not practically fail and run efficiently as an average capacity of 266 mAh/g was obtained when the current was fixed back to 100 mA/g. Hence, 27.2% of the initial capacity was preserved after 110 cycles of operation at various current rates. However, if the first cycle of the sample, where a large SEI formation happened, was omitted, the overall retention was calculated to be 65.9%, which was superior to the aluminum sample. It was noted that although the age hardening steps, which were followed, increased the cyclic stability dramatically, there is still room for improvement in terms of the stability.

Electrochemical characterization data of the heat treated aluminum were given in Figure 4.15. Interestingly, the performance of this sample was even poorer than the aluminum thin film. Potential profile of the sample resembled to the aluminum - copper sample, and SEI formation was observable in the first cycle. It proved that the continuous potential slope and SEI indeed formed because of the heat treatment steps. First discharge capacity was measured to be 245



Figure 4.15: Galvanostatic charge/discharge curves of the heat treated aluminum in a) the first 10 cycles at 100 mA/g current rate (1.cycle is black, 10.cycle is red), b) Cyclic stability measurement at 200 mA/g current rate and c) Rate capability data at different current rates

mAh/g with 34.5% charge - to - discharge capacity ratio, and its capacity was dropped to 67.5 mAh/g after 10 cycles. Although its capacity retention seemed to be stable in the following 50 cycles, the electrode had practically no use. It seemed that without copper as a second phase particle former, aluminum tended to lose its electrochemical activity with these age hardening steps. This poor performance could be originated because aluminum could be more vulnerable to pulverization without the second phase particles. The exact reason should be investigated further.

To further check the stability of the electrodes, SEM and XPS were performed



Figure 4.16: SEM image after cycling of a) Aluminum thin film, b) Age hardened aluminum - copper alloy and c) Age hardened aluminum - copper alloy at a higher magnification

after cycling. As shown in Figure 4.16a, the aluminum sample experienced a harsh pulverization where aluminum plates lost contact, some of them lifted off, which resulted in loss of electrical contact of the active material to the current collector. On the other hand, microstructure of the alloy showed no effect of pulverization, and electrical contact of the islands remained intact with the current collector, see Figure 4.16b. Furthermore, Figure 4.16c gives a closer look to the mesopores. Hence, it was inferred that the mesopores were structurally stable during the battery operation.



Figure 4.17: Regional XPS scans for a) Al 2p, b) Cu 2p, c) C 1s, and d) Li 1s of age hardened aluminum - copper alloy before (black) and after (red) cycling

In Figure 4.17, regional XPS scans for the pristine and the cycled samples were given. Al 2p scan indicated that there was no chemical change in alumina on the surface of the electrode. In Figure 4.17b, however, it seemed that there was no signal coming from copper from the surface. This was probably because SEI layer, which was formed on and covered the surface, hindered X-ray interaction with copper. Furthermore, after cycling, a new peak appeared at ~290 eV (see Figure 4.17c), which arose from carbon in O=C-O groups present in the SEI layer. Furthermore, a lithium peak was formed at 55.3 eV after cycling (see Figure 4.17d), which indicated Li_2CO_3 formation. Hence, formation of SEI layer and stability of the structure upon cycling were confirmed with XPS analysis.

Chapter 5

Summary and Future Outlook

LIBs are currently the most widely used electrochemical energy storage system, which rules over a big market. Since it is not possible to use lithium as an anode material in LIBs due to safety reasons, new electrode materials with high capacities and high energy densities are required to advance technology in highly sophisticated areas such as electric vehicles. Thus, in this thesis study, we tried to synthesize two different high capacity anode materials for LIBs. Problems, which prevent commercial use of the materials, were addressed for each material, and various strategies were employed to overcome the complications.

Although silicon offers very high capacity and energy density, it suffers from miscellaneous type of problems. Its operating potential is below lithium plating potential, which arises safety issues. Most importantly, pulverization prevents formation of a stable SEI, and proper utilization of its high capacity after a few cycles. Electrospinning is one of the effective ways to synthesize free standing, carbon coated silicon electrodes. We tried to completely embed Si nanoparticles, whose size was smaller than 20 nm. The particles were synthesized via laser ablation method, then embedded inside carbon nanofibers, which were obtained by carbonizing PAN fibers. For optimization, we employed different PAN ratios in the precursor solution for electrospinning, and Si solutions with different concentrations. For comparison, we also electrospun all CNF, and commercial Si

nanoparticles (50 nm) & CNF composite electrodes. For characterization of the electrodes, we exploited various tools including XPS, Raman spectroscopy, TGA, SEM, TEM, CV, galvanostatic measurements and impedance spectroscopy. According to the electrochemical characterizations, the electrode with commercial nanoparticles offered a high first discharge capacity of 1618 $\mathrm{mAh}/\mathrm{g}_{cathode}$ with 70.2% charge - to - discharge capacity ratio; however, the capacity retention was as poor as 5.1%, yielding only 46 mAh/g_{cathode} discharge capacity after 50 cycles at 200 mA/ $g_{cathode}$ current rate. In the electrode, which was the best performing one among the electrodes consisted of the synthesized Si nanoparticles, capacity retention was as high as 97.2% with 99.7% average Coulombic efficiency in 50 cycles. On the other hand, the capacity values obtained $(186 \text{ mAh}/\text{g}_{cathode} \text{ av-}$ erage in cyclic stability measurement) were lower than the capacities of pristine CNF electrodes. Low capacities and lacking of characteristic transition plateau of crystalline Si to amorphous Si brought suspicions upon electrochemical Si activation. Hence, by etching native oxide layer via HF, 204 mAh/ $g_{cathode}$ average discharge capacity with 96.3% capacity retention and 99.8% average Coulombic efficiency was obtained. To further activate the Si, we applied a current rate of 400 mA/ $g_{silicon}$ was applied to the sample. The first capacity was increased up to $890 \text{ mAh/g}_{cathode}$ with 48.7% charge - to - discharge capacity ratio, which was still comparable to the performance of pristine CNFs. We concluded that although cyclic stabilities of our electrodes were satisfactory, proper activation of the Si nanoparticles was not achieved in our samples.

Aluminum offers a high capacity and energy density; however, it faces the same complications as silicon. Interestingly, very few studies in the literature addresses some routes for its application in LIBs. Age hardening is an extensively used strengthening mechanism for aluminum alloys, especially for aluminum - copper binary system. By employing age hardening to our Al - 4 wt%Cu thin film electrodes, which were sputtered on SS substrates, we aimed to suppress volumetric changes in Al during battery operation. We also applied the same heat treatment steps to pristine Al thin film electrode for comparison. For characterization of the electrodes, we made use of different sophisticated tools such

as grazing incidence XRD, XPS, SEM, CV and galvanostatic measurements. According to our observations, Al showed a tendency to form islands on SS after quenching. Although Cu presence on the surface was confirmed with XPS, we were not able to identify any phase of Al - Cu alloys as it was reported in the literature that conventional XRD methods fail to identify those alloys in thin film samples. After the heat treatment steps of age hardening procedure, both Al and Al - Cu electrodes switched to continuous potential slope. Al thin sample showed a high first discharge capacity of 926 mAh/g at 100 mA/g current rate, along with 58.1% charge - to - discharge capacity ratio and high overpotential. After 10 cycles at the same current, the capacity was reduced to 227 mAh/g. In the following cyclic stability measurement at 200 mA/g, the capacity retention was only 26.6% in 50 cycles, yielding 59 mAh/g discharge capacity. On the other hand, when the same test parameters were applied to the the age hardened alloy, it provided 987 mAh/g discharge capacity in the first cycle with 41.2% charge to - discharge capacity ratio. The lower efficiency was related to SEI formation on the increased surface area. After 10 cycles, the electrode offered 401 mAh/g discharge capacity. Furthermore, the cyclic stability measurement resulted in 241 mAh/g discharge capacity and 65.7% capacity retention, which were quite higher than the performance of the Al thin film sample. Heat treated Al sample provided even worse electrochemical performance than pristine Al thin film sample. Hence, we concluded that age hardening in Al - 4 wt% Cu system increases stability of Al anode in LIBs, and further studies could be performed to raise the performance even more.

Bibliography

- [1] G.-A. Nazri and G. Pistoia, *Lithium batteries: science and technology*. Springer Science & Business Media, 2008.
- [2] P. G. Bruce, B. Scrosati, and J.-M. Tarascon, "Nanomaterials for rechargeable lithium batteries," Angewandte Chemie International Edition, vol. 47, no. 16, pp. 2930–2946, 2008.
- [3] F. K. Butt, M. Tahir, C. Cao, F. Idrees, R. Ahmed, W. S. Khan, Z. Ali, N. Mahmood, M. Tanveer, A. Mahmood, et al., "Synthesis of novel znv2o4 hierarchical nanospheres and their applications as electrochemical supercapacitor and hydrogen storage material," ACS applied materials & interfaces, vol. 6, no. 16, pp. 13635–13641, 2014.
- [4] L. Ji, Z. Lin, M. Alcoutlabi, and X. Zhang, "Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries," *Energy & Environmental Science*, vol. 4, no. 8, pp. 2682–2699, 2011.
- [5] M. Armand and J.-M. Tarascon, "Building better batteries," *Nature*, vol. 451, no. 7179, pp. 652–657, 2008.
- [6] H. H. Susapto, O. U. Kudu, R. Garifullin, E. Yılmaz, and M. O. Guler, "One-dimensional peptide nanostructure templated growth of iron phosphate nanostructures for lithium-ion battery cathodes," ACS Applied Materials & Interfaces, vol. 8, no. 27, pp. 17421–17427, 2016.
- [7] S. Lau and L. A. Archer, "Nucleation and growth of lithium peroxide in the li–o2 battery," *Nano letters*, vol. 15, no. 9, pp. 5995–6002, 2015.

- [8] P. Sennu, M. Christy, V. Aravindan, Y.-G. Lee, K. S. Nahm, and Y.-S. Lee, "Two-dimensional mesoporous cobalt sulfide nanosheets as a superior anode for a li-ion battery and a bifunctional electrocatalyst for the li–o2 system," *Chemistry of Materials*, vol. 27, no. 16, pp. 5726–5735, 2015.
- [9] Z. Jian, V. Raju, Z. Li, Z. Xing, Y.-S. Hu, and X. Ji, "A high-power symmetric na-ion pseudocapacitor," *Advanced Functional Materials*, vol. 25, no. 36, pp. 5778–5785, 2015.
- [10] M. Yang, Y. Zhong, J. Ren, X. Zhou, J. Wei, and Z. Zhou, "Electrochemical capacitors: Fabrication of high-power li-ion hybrid supercapacitors by enhancing the exterior surface charge storage (adv. energy mater. 17/2015)," *Advanced Energy Materials*, vol. 5, no. 17, 2015.
- [11] Q.-C. Liu, J.-J. Xu, S. Yuan, Z.-W. Chang, D. Xu, Y.-B. Yin, L. Li, H.-X. Zhong, Y.-S. Jiang, J.-M. Yan, *et al.*, "Artificial protection film on lithium metal anode toward long-cycle-life lithium–oxygen batteries," *Advanced Materials*, vol. 27, no. 35, pp. 5241–5247, 2015.
- [12] M. T. McDowell, S. W. Lee, W. D. Nix, and Y. Cui, "25th anniversary article: Understanding the lithiation of silicon and other alloying anodes for lithium-ion batteries," *Advanced Materials*, vol. 25, no. 36, pp. 4966–4985, 2013.
- [13] U. S. A. B. Consortium *et al.*, "Electric vehicle battery test procedures manual," USABC, Jan, 1996.
- [14] J. Xiao, X. Wang, X.-Q. Yang, S. Xun, G. Liu, P. K. Koech, J. Liu, and J. P. Lemmon, "Electrochemically induced high capacity displacement reaction of peo/mos2/graphene nanocomposites with lithium," *Advanced Functional Materials*, vol. 21, no. 15, pp. 2840–2846, 2011.
- [15] H. Zhang, G. Cao, and Y. Yang, "Carbon nanotube arrays and their composites for electrochemical capacitors and lithium-ion batteries," *Energy & Environmental Science*, vol. 2, no. 9, pp. 932–943, 2009.

- [16] M. R. Palacin, "Recent advances in rechargeable battery materials: a chemists perspective," *Chemical Society Reviews*, vol. 38, no. 9, pp. 2565– 2575, 2009.
- [17] J. B. Goodenough, "Design considerations," Solid State Ionics, vol. 69, no. 3, pp. 184–198, 1994.
- [18] J. B. Goodenough and Y. Kim, "Challenges for rechargeable li batteries," *Chemistry of Materials*, vol. 22, no. 3, pp. 587–603, 2009.
- [19] K. Edström, T. Gustafsson, and J. O. Thomas, "The cathode–electrolyte interface in the li-ion battery," *Electrochimica Acta*, vol. 50, no. 2, pp. 397– 403, 2004.
- [20] L. Shen, X. Zhang, E. Uchaker, C. Yuan, and G. Cao, "Li4ti5o12 nanoparticles embedded in a mesoporous carbon matrix as a superior anode material for high rate lithium ion batteries," *Advanced Energy Materials*, vol. 2, no. 6, pp. 691–698, 2012.
- [21] L. Zhao, Y.-S. Hu, H. Li, Z. Wang, and L. Chen, "Porous li4ti5o12 coated with n-doped carbon from ionic liquids for li-ion batteries," *Advanced Materials*, vol. 23, no. 11, pp. 1385–1388, 2011.
- [22] F. M. Balcı, Ö. U. Kudu, E. Yılmaz, and Ö. Dag, "Synthesis of mesoporous lithium titanate thin films and monoliths as an anode material for highrate lithium-ion batteries," *Chemistry-A European Journal*, vol. 22, no. 52, pp. 18873–18880, 2016.
- [23] J. K. Lee, C. Oh, N. Kim, J.-Y. Hwang, and Y.-K. Sun, "Rational design of silicon-based composites for high-energy storage devices," *Journal of Materials Chemistry A*, vol. 4, no. 15, pp. 5366–5384, 2016.
- [24] J. Cho, Y. J. Kim, T.-J. Kim, and B. Park, "Enhanced structural stability of o-limno2 by sol-gel coating of al2o3," *Chemistry of Materials*, vol. 13, no. 1, pp. 18–20, 2001.

- [25] X. Ji, K. T. Lee, and L. F. Nazar, "A highly ordered nanostructured carbon– sulphur cathode for lithium–sulphur batteries," *Nature materials*, vol. 8, no. 6, pp. 500–506, 2009.
- [26] N. Recham, J.-N. Chotard, L. Dupont, C. Delacourt, W. Walker, M. Armand, and J.-M. Tarascon, "A 3.6 v lithium-based fluorosulphate insertion positive electrode for lithium-ion batteries," *Nature materials*, vol. 9, no. 1, pp. 68–74, 2010.
- [27] A. S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. Van Schalkwijk, "Nanostructured materials for advanced energy conversion and storage devices," *Nature materials*, vol. 4, no. 5, pp. 366–377, 2005.
- [28] Z. Shi, A. Attia, W. Ye, Q. Wang, Y. Li, and Y. Yang, "Synthesis, characterization and electrochemical performance of mesoporous fepo 4 as cathode material for rechargeable lithium batteries," *Electrochimica Acta*, vol. 53, no. 6, pp. 2665–2673, 2008.
- [29] Y.-S. Kim, Y.-G. Cho, D. Odkhuu, N. Park, and H.-K. Song, "A physical organogel electrolyte: characterized by in situ thermo-irreversible gelation and single-ion-predominent conduction," *Scientific reports*, vol. 3, 2013.
- [30] J. Mindemark, B. Sun, E. Törmä, and D. Brandell, "High-performance solid polymer electrolytes for lithium batteries operational at ambient temperature," *Journal of Power Sources*, vol. 298, pp. 166–170, 2015.
- [31] D. Zhou, Y.-B. He, Q. Cai, X. Qin, B. Li, H. Du, Q.-H. Yang, and F. Kang, "Investigation of cyano resin-based gel polymer electrolyte: in situ gelation mechanism and electrode-electrolyte interfacial fabrication in lithiumion battery," J. Mater. Chem. A, vol. 2, pp. 20059–20066, 2014.
- [32] C. Wang, H. Wu, Z. Chen, M. T. McDowell, Y. Cui, and Z. Bao, "Selfhealing chemistry enables the stable operation of silicon microparticle anodes for high-energy lithium-ion batteries," *Nature chemistry*, vol. 5, no. 12, pp. 1042–1048, 2013.
- [33] H. Wu and Y. Cui, "Designing nanostructured si anodes for high energy lithium ion batteries," *Nano Today*, vol. 7, no. 5, pp. 414–429, 2012.

- [34] P. Simon, Y. Gogotsi, and B. Dunn, "Where do batteries end and supercapacitors begin?," *Science*, vol. 343, no. 6176, pp. 1210–1211, 2014.
- [35] N. Mahmood, J. Zhu, S. Rehman, Q. Li, and Y. Hou, "Control over largevolume changes of lithium battery anodes via active-inactive metal alloy embedded in porous carbon," *Nano Energy*, vol. 15, pp. 755–765, 2015.
- [36] J. N. Weker, N. Liu, S. Misra, J. Andrews, Y. Cui, and M. Toney, "In situ nanotomography and operando transmission x-ray microscopy of micronsized ge particles," *Energy & Environmental Science*, vol. 7, no. 8, pp. 2771– 2777, 2014.
- [37] X. Zhang, M.-L. Zhang, H. Liub, and L.-M. Liu, "Materials chemistry a," 2014.
- [38] S. Xu, C. M. Hessel, H. Ren, R. Yu, Q. Jin, M. Yang, H. Zhao, and D. Wang, "α-fe 2 o 3 multi-shelled hollow microspheres for lithium ion battery anodes with superior capacity and charge retention," *Energy & Environmental Science*, vol. 7, no. 2, pp. 632–637, 2014.
- [39] W. Wang, Y. Guo, L. Liu, S. Wang, X. Yang, and H. Guo, "Gold coating for a high performance li 4 ti 5 o 12 nanorod aggregates anode in lithium-ion batteries," *Journal of Power Sources*, vol. 245, pp. 624–629, 2014.
- [40] N. Liu, Z. Lu, J. Zhao, M. T. McDowell, H.-W. Lee, W. Zhao, and Y. Cui, "A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes," *Nature nanotechnology*, vol. 9, no. 3, pp. 187–192, 2014.
- [41] N. Zhang, Q. Zhao, X. Han, J. Yang, and J. Chen, "Pitaya-like sn@ c nanocomposites as high-rate and long-life anode for lithium-ion batteries," *Nanoscale*, vol. 6, no. 5, pp. 2827–2832, 2014.
- [42] N. Nitta and G. Yushin, "High-capacity anode materials for lithium-ion batteries: Choice of elements and structures for active particles," *Particle & Particle Systems Characterization*, vol. 31, no. 3, pp. 317–336, 2014.
- [43] J. Luo, J. Liu, Z. Zeng, C. F. Ng, L. Ma, H. Zhang, J. Lin, Z. Shen, and H. J. Fan, "Three-dimensional graphene foam supported fe3o4 lithium battery

anodes with long cycle life and high rate capability," *Nano letters*, vol. 13, no. 12, pp. 6136–6143, 2013.

- [44] D. H. Youn, M. L. Meyerson, K. C. Klavetter, K. A. Friedman, S. S. Coffman, J.-W. Lee, A. Heller, and C. B. Mullins, "Mixing super p-li with n-doped mesoporous templated carbon improves the high rate performance of a potential lithium ion battery anode," *Journal of The Electrochemical Society*, vol. 163, no. 6, pp. A953–A957, 2016.
- [45] B. Zhang, C. M. Ghimbeu, C. Laberty, C. Vix-Guterl, and J.-M. Tarascon, "Correlation between microstructure and na storage behavior in hard carbon," *Advanced Energy Materials*, vol. 6, no. 1, 2016.
- [46] Y. Tang, Y. Zhang, W. Li, B. Ma, and X. Chen, "Rational material design for ultrafast rechargeable lithium-ion batteries," *Chemical Society Reviews*, vol. 44, no. 17, pp. 5926–5940, 2015.
- [47] M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novak, "Insertion electrode materials for rechargeable lithium batteries," *Advanced materials*, vol. 10, no. 10, pp. 725–763, 1998.
- [48] Y. Yin, Y. Hu, P. Wu, H. Zhang, and C. Cai, "A graphene–amorphous fepo 4 hollow nanosphere hybrid as a cathode material for lithium ion batteries," *Chemical Communications*, vol. 48, no. 15, pp. 2137–2139, 2012.
- [49] H. Wu, G. Chan, J. W. Choi, Y. Yao, M. T. McDowell, S. W. Lee, A. Jackson, Y. Yang, L. Hu, and Y. Cui, "Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control," *Nature nanotechnology*, vol. 7, no. 5, pp. 310–315, 2012.
- [50] Y. Hamon, T. Brousse, F. Jousse, P. Topart, P. Buvat, and D. Schleich, "Aluminum negative electrode in lithium ion batteries," *Journal of Power Sources*, vol. 97, pp. 185–187, 2001.
- [51] W.-M. Zhang, J.-S. Hu, Y.-G. Guo, S.-F. Zheng, L.-S. Zhong, W.-G. Song, and L.-J. Wan, "Tin-nanoparticles encapsulated in elastic hollow carbon spheres for high-performance anode material in lithium-ion batteries," Advanced Materials, vol. 20, no. 6, pp. 1160–1165, 2008.

- [52] J. Cabana, L. Monconduit, D. Larcher, and M. R. Palacin, "Beyond intercalation-based li-ion batteries: The state of the art and challenges of electrode materials reacting through conversion reactions," *Advanced Materials*, vol. 22, no. 35, 2010.
- [53] N. Mahmood, T. Tang, and Y. Hou, "Nanostructured anode materials for lithium ion batteries: Progress, challenge and perspective," *Advanced Energy Materials*, vol. 6, no. 17, 2016.
- [54] P.-L. Taberna, S. Mitra, P. Poizot, P. Simon, and J.-M. Tarascon, "High rate capabilities fe3o4-based cu nano-architectured electrodes for lithiumion battery applications," *Nature materials*, vol. 5, no. 7, pp. 567–573, 2006.
- [55] R. Khatib, A.-L. Dalverny, M. Saubanere, M. Gaberscek, and M.-L. Doublet, "Origin of the voltage hysteresis in the cop conversion material for li-ion batteries," *The Journal of Physical Chemistry C*, vol. 117, no. 2, pp. 837– 849, 2013.
- [56] K. T. Nam, D.-W. Kim, P. J. Yoo, C.-Y. Chiang, N. Meethong, P. T. Hammond, Y.-M. Chiang, and A. M. Belcher, "Virus-enabled synthesis and assembly of nanowires for lithium ion battery electrodes," *science*, vol. 312, no. 5775, pp. 885–888, 2006.
- [57] Y. S. Kim, K. W. Kim, D. Cho, N. S. Hansen, J. Lee, and Y. L. Joo, "Silicon-rich carbon hybrid nanofibers from water-based spinning: The synergy between silicon and carbon for li-ion battery anode application," *Chem-ElectroChem*, vol. 1, no. 1, pp. 220–226, 2014.
- [58] J. R. Szczech and S. Jin, "Nanostructured silicon for high capacity lithium battery anodes," *Energy & Environmental Science*, vol. 4, no. 1, pp. 56–72, 2011.
- [59] R. A. Huggins, "Lithium alloy negative electrodes," Journal of Power Sources, vol. 81, pp. 13–19, 1999.
- [60] P. Limthongkul, Y.-I. Jang, N. J. Dudney, and Y.-M. Chiang, "Electrochemically-driven solid-state amorphization in lithium-metal anodes," *Journal of Power Sources*, vol. 119, pp. 604–609, 2003.

- [61] M. Obrovac and L. Christensen, "Structural changes in silicon anodes during lithium insertion/extraction," *Electrochemical and Solid-State Letters*, vol. 7, no. 5, pp. A93–A96, 2004.
- [62] W. Luo, Y.-X. Wang, L. Wang, W. Jiang, S.-L. Chou, S. X. Dou, H. K. Liu, and J. Yang, "Silicon/mesoporous carbon/crystalline tio2 nanoparticles for highly stable lithium storage," ACS nano, 2016.
- [63] X. Wu, Z. Wang, L. Chen, and X. Huang, "Ag-enhanced sei formation on si particles for lithium batteries," *Electrochemistry communications*, vol. 5, no. 11, pp. 935–939, 2003.
- [64] R. Ruffo, S. S. Hong, C. K. Chan, R. A. Huggins, and Y. Cui, "Impedance analysis of silicon nanowire lithium ion battery anodes," *The Journal of Physical Chemistry C*, vol. 113, no. 26, pp. 11390–11398, 2009.
- [65] P. Verma, P. Maire, and P. Novák, "A review of the features and analyses of the solid electrolyte interphase in li-ion batteries," *Electrochimica Acta*, vol. 55, no. 22, pp. 6332–6341, 2010.
- [66] C. K. Chan, R. Ruffo, S. S. Hong, and Y. Cui, "Surface chemistry and morphology of the solid electrolyte interphase on silicon nanowire lithium-ion battery anodes," *Journal of Power Sources*, vol. 189, no. 2, pp. 1132–1140, 2009.
- [67] W.-J. Yu, C. Liu, P.-X. Hou, L. Zhang, X.-Y. Shan, F. Li, and H.-M. Cheng, "Lithiation of silicon nanoparticles confined in carbon nanotubes," *ACS nano*, vol. 9, no. 5, pp. 5063–5071, 2015.
- [68] K. E. Aifantis and S. A. Hackney, "Nanoscale engineering for the mechanical integrity of li-ion electrode materials," *Nanostructured Materials in Electrochemistry*, pp. 319–347, 2008.
- [69] M. T. McDowell, S. W. Lee, J. T. Harris, B. A. Korgel, C. Wang, W. D. Nix, and Y. Cui, "In situ tem of two-phase lithiation of amorphous silicon nanospheres," *Nano letters*, vol. 13, no. 2, pp. 758–764, 2013.

- [70] W. Luo, D. Shen, R. Zhang, B. Zhang, Y. Wang, S. X. Dou, H. K. Liu, and J. Yang, "Germanium nanograin decoration on carbon shell: Boosting lithium-storage properties of silicon nanoparticles," *Advanced Functional Materials*, 2016.
- [71] W. Luo, Y. Wang, S. Chou, Y. Xu, W. Li, B. Kong, S. X. Dou, H. K. Liu, and J. Yang, "Critical thickness of phenolic resin-based carbon interfacial layer for improving long cycling stability of silicon nanoparticle anodes," *Nano Energy*, vol. 27, pp. 255–264, 2016.
- [72] S. Ohara, J. Suzuki, K. Sekine, and T. Takamura, "A thin film silicon anode for li-ion batteries having a very large specific capacity and long cycle life," *Journal of Power Sources*, vol. 136, no. 2, pp. 303–306, 2004.
- [73] J. Maranchi, A. Hepp, A. Evans, N. Nuhfer, and P. Kumta, "Interfacial properties of the a-si/ cu: active-inactive thin-film anode system for lithium-ion batteries," *Journal of the Electrochemical Society*, vol. 153, no. 6, pp. A1246– A1253, 2006.
- [74] D. Li and Y. Xia, "Electrospinning of nanofibers: reinventing the wheel?," Advanced materials, vol. 16, no. 14, pp. 1151–1170, 2004.
- [75] A. Greiner and J. H. Wendorff, "Electrospinning: a fascinating method for the preparation of ultrathin fibers," Angewandte Chemie International Edition, vol. 46, no. 30, pp. 5670–5703, 2007.
- [76] Q. Xiao, Q. Zhang, Y. Fan, X. Wang, and R. A. Susantyoko, "Soft silicon anodes for lithium ion batteries," *Energy & Environmental Science*, vol. 7, no. 7, pp. 2261–2268, 2014.
- [77] Y. Li, G. Xu, Y. Yao, L. Xue, M. Yanilmaz, H. Lee, and X. Zhang, "Coaxial electrospun si/c-c core-shell composite nanofibers as binder-free anodes for lithium-ion batteries," *Solid State Ionics*, vol. 258, pp. 67–73, 2014.
- [78] G. Zhang, H. B. Wu, H. E. Hoster, and X. W. D. Lou, "Strongly coupled carbon nanofiber-metal oxide coaxial nanocables with enhanced lithium storage properties," *Energy & Environmental Science*, vol. 7, no. 1, pp. 302–305, 2014.

- [79] Z.-L. Xu, B. Zhang, and J.-K. Kim, "Electrospun carbon nanofiber anodes containing monodispersed si nanoparticles and graphene oxide with exceptional high rate capacities," *Nano Energy*, vol. 6, pp. 27–35, 2014.
- [80] X. Li, G. Lei, Z. Li, Y. Zhang, and Q. Xiao, "Carbon-encapsulated si nanoparticle composite nanofibers with porous structure as lithium-ion battery anodes," *Solid State Ionics*, vol. 261, pp. 111–116, 2014.
- [81] Y. Liu, K. Huang, Y. Fan, Q. Zhang, F. Sun, T. Gao, Z. Wang, and J. Zhong, "Binder-free si nanoparticles@ carbon nanofiber fabric as energy storage material," *Electrochimica Acta*, vol. 102, pp. 246–251, 2013.
- [82] S. Piscanec, M. Cantoro, A. Ferrari, J. Zapien, Y. Lifshitz, S. Lee, S. Hofmann, and J. Robertson, "Raman spectroscopy of silicon nanowires," *Physical Review B*, vol. 68, no. 24, p. 241312, 2003.
- [83] S. Zhang, M. S. Ding, K. Xu, J. Allen, and T. R. Jow, "Understanding solid electrolyte interface film formation on graphite electrodes," *Electrochemical* and Solid-State Letters, vol. 4, no. 12, pp. A206–A208, 2001.
- [84] Q. Li and N. J. Bjerrum, "Aluminum as anode for energy storage and conversion: a review," *Journal of Power Sources*, vol. 110, no. 1, pp. 1–10, 2002.
- [85] M. Winter and J. O. Besenhard, "Electrochemical lithiation of tin and tinbased intermetallics and composites," *Electrochimica Acta*, vol. 45, no. 1, pp. 31–50, 1999.
- [86] S. Zaromb, "The use and behavior of aluminum anodes in alkaline primary batteries," *Journal of The Electrochemical Society*, vol. 109, no. 12, pp. 1125– 1130, 1962.
- [87] L. Bockstie, D. Trevethan, and S. Zaromb, "Control of al corrosion in caustic solutions," *Journal of the Electrochemical Society*, vol. 110, no. 4, pp. 267– 271, 1963.
- [88] A. McAlister, "The al- li (aluminum- lithium) system," Journal of Phase Equilibria, vol. 3, no. 2, pp. 177–183, 1982.

- [89] R. Hu, L. Zhang, X. Liu, M. Zeng, and M. Zhu, "Investigation of immiscible alloy system of al-sn thin films as anodes for lithium ion batteries," *Electrochemistry Communications*, vol. 10, no. 7, pp. 1109–1112, 2008.
- [90] A. Biswas, D. J. Siegel, C. Wolverton, and D. N. Seidman, "Precipitates in al-cu alloys revisited: Atom-probe tomographic experiments and firstprinciples calculations of compositional evolution and interfacial segregation," Acta Materialia, vol. 59, no. 15, pp. 6187–6204, 2011.
- [91] F. W. Gayle, M. Goodway, et al., "Precipitation hardening in the first aerospace aluminum alloy: the wright flyer crankcase," SCIENCE-NEW YORK THEN WASHINGTON-, pp. 1015–1015, 1994.
- [92] T. Konno, K. Hiraga, and M. Kawasaki, "Guinier-preston (gp) zone revisited: atomic level observation by haadf-tem technique," *Scripta materialia*, vol. 44, no. 8, pp. 2303–2307, 2001.
- [93] C. Wolverton, "First-principles prediction of equilibrium precipitate shapes in al-cu alloys," *Philosophical magazine letters*, vol. 79, no. 9, pp. 683–690, 1999.
- [94] C. Wolverton and V. Ozoliņš, "Entropically favored ordering: the metallurgy of al 2 cu revisited," *Physical review letters*, vol. 86, no. 24, p. 5518, 2001.
- [95] J. Silcock and T. Heal, "The θ'structure in aluminium-copper alloys," Acta Crystallographica, vol. 9, no. 8, pp. 680–680, 1956.
- [96] S. Mader and S. Herd, "Formation of second phase particles in aluminumcopper alloy films," *Thin Solid Films*, vol. 10, no. 3, pp. 377–389, 1972.
- [97] D. Frear, J. Sanchez, A. Romig, and J. Morris, "The evolution of microstructure in al-2 pct cu thin films: Precipitation, dissolution, and reprecipitation," *Metallurgical Transactions A*, vol. 21, no. 9, pp. 2449–2458, 1990.
- [98] T. Lin, K. Ahn, J. Harper, P. Madakson, and P. Fryer, "Relationship between substrate bias and microstructure in magnetron-sputtered al-2 cu films," *Thin solid films*, vol. 154, no. 1, pp. 81–89, 1987.

[99] A. Mandal, R. Maiti, M. Chakraborty, and B. Murty, "Effect of tib 2 particles on aging response of al-4cu alloy," *Materials Science and Engineering: A*, vol. 386, no. 1, pp. 296–300, 2004.

Appendix A

Data



Figure A.1: a) High Resolution TEM image of, b) EDX results of the silicon nanoparticles synthesized via laser ablation



Figure A.2: Regional XPS scans of SC5 before (black), and after (red) HF treatment for a) Si 2p, b) C 1s, and c) F 1s



Figure A.3: a) SEM image of, b) EDS results of SC5 after HF treatment



Figure A.4: CV curve of HF treated SC5



Figure A.5: Galvanostatic charge/discharge curves of a) First 10 cycles at 100 mA/g_{cathode}, b) Last 10 cycles at 100 mA/g_{cathode}, c) Cyclic stability measurement at 20 mA/g_{cathode} between 40th and 90th cycles, and d) Rate capability measurement between 10th and 40th cycles, of SC1'