Application of biomass extracted water-soluble binder for lithium-ion battery

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**NANYANG
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SINGAPORE

**APPLICATION OF BIOMASS EXTRACTED WATER-SOLUBLE
BINDER FOR LITHIUM-ION BATTERY**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

APPLICATION OF BIOMASS EXTRACTED WATER-SOLUBLE BINDER FOR LITHIUM-ION BATTERY

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2019

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Yan Qingyu

Abstract

Lithium-ion battery (LIB) is one of the most important energy storage devices used in various fields around the world, ranging from portable devices to electrical vehicles. However, most LIBs in the market use graphite as anode materials and their capacity (372 mAh/g) cannot meet the growing requirements of human development. Thus, silicon (with high theoretical capacity of 4000 mAh/g), has been widely investigated due to its great potential to be used as active materials for new generation batteries. Nevertheless, the huge volume expansion during cycling of Si is a big challenge urgently needs to be solved. In this regard, binders plays a crucial role in managing the problem. Anode of LIBs consists of three major parts, including active material, conductive material, and binder. Binder keeps anode integrated, ensuring continuous contact between the active material and conductive material. However, traditional binder polyvinylidene difluoride (PVDF) cannot meet the requirements for silicon-based anode. Thus, in this project, a new kind of organic binder is developed for silicon batteries. The binder here is one kind of pectin extracted from citrus peels, which is widely available and environmental friendly. Besides, unlike PVDF, the pectin binder is water-soluble, so it is easy and healthy to be used. Besides the alternation of binder, the modification of Si anode is also necessary. Considering the properties of nanosilicon and graphene, a composites consists of silicon and graphene is synthesized as anode material, and the batteries demonstrated promising performance. Firstly, 10 wt. %, 30 wt. % and 50 wt. % graphene is mixed into nanosilicon to obtain active material, afterwards fabricated into half-cell battery. The batteries achieved capacity retention rate of 34.8%, 25.3% and 52.6% after 100 cycles and under the current density of 1000 mA/g, respectively. The composites with 50 wt. % graphene outperforms other two composites. To further increase its capacity retention rate, the mass ratio of graphene is increased to 75 wt. %. Under this condition, the battery finally achieves less than 30% capacity loss after 200 cycles. The graphene doped into composites so far are obtained through thermal striping process, which causes the poor ability of graphene to disperse uniformly in water. The following inhomogeneous mixing decrease stability of electrode. Taking this factor into account, another lab-made graphene or RGO (reduced graphene oxide) is employed in anode to replace the commercial counterparty, and the final capacity

retention rate reaches more than 70% after 100 cycles under 600 mA/g, which is two times better than the graphene originally used. The comparison between PVDF and pectin is also carried out. After 50 cycles, the capacity difference between PVDF and pectin expands to 500 mAh/g while they have almost the same initial capacity. Other tests, including scanning electron microscopy and mechanical tests are also carried out. In addition, the modification of binder is conducted. The pectin with citric acid undergoing an esterification reaction under 120 °C for 2 hours ending up with forming a strong network that can help hold the electrode structure, and keep it intact. The resulting electrode shows a better stability than the former electrode with pure pectin binder. After 100 cycles, the specific capacity exceeds its initial capacity, which demonstrates the self-healing property of the new binder. Besides, the binder is also applied to sodium ion battery with red phosphorus/graphene composites as anode materials. The 16-hour ball milled composites with pectin shows impressive stability. However, the specific capacity is relatively lower due to the introducing of other elements during the intensive ball milling process. Finally, the specific ways that this project solves the initial problem are explained as below and some feasible ways to further improve the performance of LIBs are proposed.

Lay Summary

The development of battery is of essential importance for human's life. LIBs is most widely used among numerous kinds of batteries available in the market nowadays. The application range of lithium-ion battery varies from laptops, hand phones, to electric cars. However, further application is limited due to the low capacity it delivers. For example, electric cars are still confined to city areas. In addition, the electricity for mobile phones is still insufficient for daily usage. Thus, it is necessary to further increase the capacity of LIBs for practical applications.

Silicon has stood out from numerous materials due to its ultrahigh theoretical specific capacity which reaches 10 times more than graphite. Although silicon has been applied to anode materials for commercial batteries, it still suffers from instability during cycling, leading to capacity decreasing. The capacity fading is mainly due to the large volume expansion of silicon during reactions. The purpose of this project is to mitigate this problem by well-designed anode and binder.

Herein, several approaches are proposed. First, nanomaterials are used as anode material instead of bulk materials. Nanomaterials has larger specific surface area than bulk materials do, providing larger free space to accommodate the volume expansion of silicon and keeping the structure stable. Then, due to the stability of carbon, graphene is mixed with silicon to form a more stable composite as anode material.

Adopting a strong binder is another effective way to increase stability of silicon-based batteries. Binders are polymers that can help bind different parts of components in electrode together. A good binder can withstand large external forces caused by volume expansion. In this project, a safe, environmental friendly, and water-soluble biomass extracted binder is employed instead of traditional PVDF to improve the performance of batteries. This binder which is extracted from citrus peels can avoid recycling wastes and save significant costs for the industry. Moreover, some modification for the binder is made

in order to further increase the stability of batteries. The electrochemical performance of the binder is tested in sodium ion battery.

The new binder does help improve the stability of silicon-based lithium-ion batteries, especially under the condition where a high content ratio of graphene is mixed and the pectin binder is modified with citric acid. The modified binder helps the battery to achieve a capacity higher than its initial capacity after 100 cycles, which shows the potential for large scale applications. In addition, sodium ion battery with the binder also achieves excellent performance.

Although some mechanism behind the function of binder still need to be explored, this project does improve the performance of silicon-based lithium ion battery. The battery with pectin binder can achieve a capacity of at least 1.5 times more than the battery with traditional binder PVDF.

The pectin binder provides researchers with practical solutions to solve the unstable problem of silicon-based lithium-ion batteries, and it is a step forward for silicon-based LIBs to get practical application.

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Abbreviations

BSE Back Scattering Electron

CA Citric Acid

CE Coulombic Efficiency

FA Formic Acid

RGO Reduced Graphene Oxide

LIB Lithium-ion Battery

PAA Polyacrylic Acid

PEDOT Poly(3,4-ethylenedioxythiophene)

PR Polyrotaxane

PSS Poly-(styrene-4-sulfonate)

PVDF Polyvinylidene Difluoride

SEM Scanning electron microscopy

SEI Surface Electrolyte Interphase

SEI Secondary Electron Imaging

XRD X-Ray Diffraction

Chapter 1

Introduction

In this chapter, the importance of lithium-ion batteries (LIBs) and the reasons why silicon is chosen as anode part in batteries are demonstrated. Although silicon enjoys large theoretical capacity, the large volume expansion during cycling hinders its practical application in manufactures. Various nanostructures are introduced to accommodate the volume expansion during the reaction. Furthermore, the composites with nano silicon particles and graphene is adopted in this project. Then, some prerequisites of binders are demonstrated to emphasize the importance of binder. Due to the abundant resources of sodium, an attempt was made to apply pectin binder in sodium ion battery and find out more possible applications. Finally, pectin is modified by other chemicals with functional groups like hydroxyl and carboxyl group to further improve the stability of pectin binder.

1.1 Problem Statement

“This thesis exploring the fabrication of Lithium-ion batteries with biomass extracted binder that delivers quantitatively superior electrochemical performance in the domain sector.”

1.2 Objective and Scope

A large quantity of energy consumption nowadays relies on fossils fuels and other non-renewable resources, which causes severe environmental problems. The utilization of renewable energy is considered as one of the most practical approaches to solve this problem and keep a sustainable economic growth. [1-5] In this regard, a highly efficient energy storage device is needed.

Lithium-ion batteries (LIB) seems to be one of the best choices. [6] LIBs have been widely used, ranging from portable devices to electrical vehicles. However, most LIBs in the market use graphite as anode materials and their capacity (372 mAh/g) cannot meet the growing requirement of human. Thus, finding a new anode material to enlarge LIBs' capacity is crucial to develop relevant technologies. [7, 8]

There is a consensus that the alloying reaction mechanism can replace traditional intercalation mechanism because the alloying reaction is able to store much more Li when compared to intercalation mechanism. Many different elements have been researched that can be electrochemically alloyed with lithium, such as Sn, Pb, Al, Au and so on. Properties of these elements with Li alloy have been shown in Table 1.1. [10]

Table 1.1 Property of Li alloy elements [10]

Element	Gravimetric capacity (mAh/g)	Volumetric capacity (mAh/g)	Cost	Toxicity	Safety
Si	4200	2400	Low	No	High
C	372	890	Low	No	Low
Ge	1568	2300	High	High	High
Sn	990	2020	Low	No	High
P	2600	2250	Low	High	Low
Sb	660	1890	Low	High	Low
Pb	549	1790	Low	High	Low

Among these elements, silicon, whose theoretical capacity is nearly 4200 mAh/g, has been extensively researched recent years. [11, 12] Firstly, it is found that silicon has a very low lithiation and delithiation potential compared to other alloy-type anode.

Furthermore, Si is abundant in the earth and is environmental friendly when compared to other anode materials. [13] Another issue that makes silicon becomes possible to replace graphite is the lower cost. Features of economic, environmental friendly, safe, easy-access, and high capacity make silicon the next generation anode material.

However, while silicon-based batteries usually possess outstanding first cycle performance, it is hard for them to maintain its high capacity in subsequent cycles. It is because of its volume expansion, up to 300% during lithiation and delithiation process [14]. Volume expansion can lead to many serious damages to electrode, such as unstable surface electrolyte interphase (SEI) films, loss of electrical pathways, pulverization of the active material and so on. [15, 16] All these factors caused the failure of capacity maintenance. As shown in Fig 1.1.

Besides this, the electronic conductivity of Si is relatively low [17] as well as the lithium diffusion in this kind of materials is relatively slow [18-20] which can severely limit the

utilization of its full capacity and undermine the electrical performance of silicon electrode. [21-23]

Fig. 1.1. Schematic of capacity faded of silicon anode [14]

Before discussing how to improve the performance of silicon anode, it is essential to understand its reaction mechanism with lithium, and in return it can guide researchers to find approaches to solve relevant problems. Many works have been done by scientists and they found that reactions at high temperature, forming various intermetallic compounds and showing different voltage plateaus. [24] However, when it comes to room temperature and voltage at 0.1 V, only one two-phase region has been observed, and disappeared after first cycle, as shown in Fig 1.2. [24, 25]

Fig. 1.2. Voltage profile of silicon electrode for first and second cycle [24]

In order to unveil the mechanism underlies this phenomenon, many other works have been done, like X-ray diffraction (XRD) analysis. [13, 26] The mechanism is illustrated as below:

Discharge process:

Charge process:

When lithium ions react with Si that in amorphous state during second cycle, the two-phase region disappears, like shown in Fig 1.2, and sloping voltage can be observed in second cycle which means single phase region. After second cycle, only single-phase region remains and the reversible capacity of battery faded quickly.

The failure mechanism should also be demonstrated. It was widely investigated and two of main factors can be concluded as: [27, 28]

- (1) The large volume change during cycling will lead to the break of contact between Si and conductive additives, leading to poor transport of electrons, as shown in Fig 1.3. [29]

Fig. 1.3. Schematic of morphology change of Si during cycling [29]

- (2) As shown in Fig 1.4, Due to electrolyte decomposition, the SEI layer is formed on the surface of silicon during discharging process, and lithiation contributes to the expand of silicon. During delithiation, the silicon particles shrink and thus SEI layers break down, which makes a part of new surface exposed to the electrolyte, in later cycles, a thick SEI layer forms, which undermines the cycling performance of electrode. [30]
- (3)

Fig. 1.4. Schematic of thick SEI forming process [30]

During past tens of years, numerous efforts had been put into this field, and several issues were solved to some degree. The usage of nanotechnologies, including nanoparticles, nanowires and other nanoporous structures, can largely increase cycling life, enhance rate

performance as well as improve electrical conductivity of silicon based. [31-34] Nano structures can provide electrode with more space during volume expansion, which relieve the problem of particle pulverization.

Nanotechnologies including 0-dimensional (nanoparticles), 1-dimensional (nanowires and nanotubes) and 2-dimensional materials (films), because nano silicon particles is used in this research topic, so 0-dimensional nanotechnology will be briefly introduced in this chapter.

In addition, because nano silicon particles or other forms of composites cannot totally solve the problem, including loss of electrical pathways, the next step for scientific research will be focus on another part of anode materials, binder.

It is known that anode electrode comprised with active materials, like silicon or silicon-carbon composites, binder and conductive materials. The disconnection of active materials and conductive materials leads to the loss of electrical pathway, which is one of the most serious problems.

With the help of binder, this issue can be alleviated, besides, binder can restrain the particle pulverization with its mechanical properties. In the introduction chapter, nanoparticles technology and requirements of binder will be briefly introduced.

First, application of silicon nanoparticles based materials will be discussed. Silicon nanoparticles can be one of the most promising anode materials because of its easy access (second abundant element in earth), high theoretical capacity, compatibility with current LIBs industry process, mature synthesize methods, and the ability to prevent cracking during Li insertion.

Nevertheless, Due to the large degree of volume expansion, nanoparticles cannot solve this problem entirely, as described in Fig 1.5, silicon particles will be peeled off from current collector and the break of SEI layer will lead to uncontrolled growth of new SEI layer, both

factors will cause capacity falling. [35] So, in order to overcome this problem, other forms of silicon nanoparticles like porous silicon, core-shell silicon and silicon-graphene [35-37], silicon-nanotubes [38, 39] composited are introduced.

Fig. 1.5. Schematic of silicon particles failure mechanism [9]

Porous Si nanoparticles provides enough free space for expansion during cycling, which makes it a promising candidate for anode materials. Bao et al. [40] and Kim et al. [41] synthesized microporous silicon and 3-D porous bulk silicon respectively, especially Kim's invention made it possible for capacity to remain 99% of its first cycle capacity. However, when porous structure can significantly increase the cycling performance of LIBs, its volumetric capacity is largely compromised, which in turn, reduce the overall capacity of batteries.

Another novel structure of Si nanoparticles is core-shell structure which can be denoted as Si@C.[42-44] It was first developed by pyrolyzing silicon nanoparticles, which can kept nearly 1400 mAh/g after 20 cycles, and then Gao et al. used microporous carbon to coat the silicon nanoparticles with a simple encapsulation method, which produced an electrode whose capacity could be maintained at 1200 mAh/g.

Finally, silicon-graphene composite is introduced in this chapter as this is the form used in the project. Other composites like silicon with carbon tubes, porous carbon and other carbon composites will be omitted as these are not focus here. Graphene has many attracting features that can compensate the disadvantage of silicon, such as mechanical flexibility, chemical stability and outstanding conductivity. [35, 37]

According to the properties of graphene, it is possible to mix graphene with silicon nanoparticles to form a more stable anode material than simply silicon. As shown in Fig 1.6, Zhou et al. applied electrostatic force to encapsulate silicon nanoparticles uniformly in graphene by self-assembly method.

Fig. 1.6. Process of fabricating the SiNP@C nanocomposites [35]

In Fig 1.6, procedure 1 represents the self-assembly process of Si nanoparticles and poly (diallyl dimethylammonium) chloride (PDDA) changes silicon particles from negative charged to positive charged. Procedure 2 represents the process of negative charged GO (graphene oxide) with positive charged Si-PDDA nanoparticles combine through self-assembly. After two procedures, subsequent treatment including freeze-drying, thermal reduction and HF treatment. Composites produced by the method are observed owning a very stable cycling performance, whose capacity can remain 1205 mAh/g after 150 cycles. [35]

Besides the active part in anode electrode, binder is also of crucial importance in contributing to good performance of batteries. Before discussing specific types of binders, there are some prerequisites for all kinds of anode binders.

- (1) First, if the binder is not conductive, then other conductive materials like carbon black is needed in electrode, the binder should be capable of forming a uniform mixture together with active materials and conductive additive;
- (2) Second, binders are supposed to be electrochemically stable;

- (3) Third, it needs to provide suitable interaction with both active materials and conductive additives to form a stable electrical pathway to current collector, which is usually copper;
- (4) During the large volume change, binders ought to withstand the stress applied to anode, in other words, they should have good mechanical properties and it will be better if they can dissipate the stress;
- (5) As binders are immersed into electrolyte, binders should not react with electrolyte as well as keep a minimize swelling when in electrolyte;
- (6) Binders are required to help form a thin and stable SEI layer on the surface of silicon;
- (7) Maintain the adhesion both within anode materials and between overall compound and current collector. Besides these technical prerequisites, other conditions, like (8) economical; (9) compatible with current battery industry; (10) environmental friendly; (11) not difficult to produce in large quantities. All these factors should be taken into consideration, however, how to meet all these requirements in a single binder is also a big challenge.

Till now, researchers have developed many kinds of binders. It was reported by Chen et al. that use the PVDF-TFE-PP (PVDF: polyvinylidene fluoride; TFE: tetrafluoroethylene and pp: propylene) to replace the traditional binder PVDF can ameliorate the cycle performance of amorphous silicon alloy particles in 2003. [45] In 2010, Magasinski et al. examined the performance of silicon nanoparticles with different binders, including pure poly, carboxymethyl cellulose, and conventional PVDF. The result revealed that because of the highly elastic modulus and large quantities of carboxylic groups that PAA has that made PAA incorporated electrode had a better cycling performance than PVDF and CMC. [46]

Besides these, some other binders, like binders extracted from biomaterials, alginate [47], cyclodextrin [48] were also studied. Among these studies, some authors focus on incorporating elastic properties into electrode to improve the cycling performance [49-52]

while others might emphasize on optimize surface interaction between silicon and the binder. [53] There were also another way to improve the cycle performance of silicon anode, such as modify different function group on conductive binder. Liu et al. used carbonyl and methylbenzoic ester to modify the conductivity and mechanical strength of binder, like shown in Fig 1.7. [54] In Fig 1.7a, it can be understood that traditional binder which is not conductive, like PVDF, need other conductive additive in anode, however, the electrical pathway between active materials and conductive additives could be broken during volume expansion. But in a model which applied conductive binder, there was no need for other additives, so even this kind of electrode still undergo a large volume expansion, the electrical pathway would not be broken due to the fluidity of binder. So, in Fig 1.7c, PFFOMB, carbonyl and methylbenzoic ester have been used as key function groups to modify the conductivity and mechanical properties of binder.

Fig. 1.7. Schematic of improving the performance of binder with functional groups [54]

So far, many different types of binders have been simply introduced. Some other typical binders that are research hot spot nowadays will be demonstrated specifically in next literature review chapter.

In the project, this biomass extracted pectin is modified through esterification reaction with citric acid and alginate. The integrity of the electrode would be destroyed during cycling, so find a way to enhance the ability of the binder to hold the active materials and current collector together is another way to improve the performance of electrode. During the esterification reaction process, a polymer network will form which can improve the mechanical strength of electrode and make it stay integrated.

While it is well known that Lithium ion battery have achieved great success in many areas, including portable devices, electric cars as well as other fields. However, with the increasing demand of lithium resources and its limited storage volume in earth, the price of lithium ion battery will dramatically increase in foreseeable future. Thus, scientists turn their eyes to a new elements, sodium, which has similar intercalation mechanism in battery as lithium, and has much more abundant storage in earth, which makes it easier and cheaper to use it in future batteries [55].

Much efforts have been devoted to novel anode materials for sodium ion batteries (SIBs), including carbon-based materials [56], intermetallic metal (Sn, Ge) [57, 58] and metal oxide anode materials. [59, 60] However, the specific capacity of these anode materials is low and cycling performance is not satisfying. Recently, elemental phosphorus has been found to be another attractive anode material for sodium-ion battery as shown in Fig 1.8. P can react with sodium ions to form Na_3P compound, which has a high theoretical specific capacity of 2596 mAh/g, and it is the highest among known anode materials for sodium-ion battery.

Fig. 1.8. Schematics of different phosphorus [61]

Many research have been conducted related to solid phosphorus in sodium ion field. Jie Sun et al. synthesized black phosphorus nanoparticle–graphite composite battery anodes through mechanic-chemical reaction in a high energy mechanical milling process. At its initial cycle, this material deliver specific capacity of 2400 mAh/g, and retained 1849 mAh/g after 100 cycles under 0.2 C. [55]

Here, another chemically bonded phosphorus and graphene hybrid material will be mainly introduced. The work was done by Jiangxuan Song et al in Fig 1.9. In this paper, they reported a novel nanosheet hybrid as the anode material in sodium ion battery. This material is acquired through facile ball milling process, which will cause graphene stacks to exfoliate and then form chemical bond with the surface of phosphorus particles. [56]

Fig. 1.9. Schematics of synthesis of red phosphorus/graphene nanosheets [56]

The structure of P/G hybrid is examined by XRD and Raman spectroscopy in Fig 1.10. It is clearly that, after ball milling process, the P/G form an amorphous structure. Also, the intensity ratio of D band and G band increases after forming P/G hybrid, suggesting a decrease of average size. The exfoliated graphene is also been demonstrated through the shift of G band.

Fig. 1.10. a) XRD pattern and b) Raman spectra of red phosphorus, graphene stacks, and P/G hybrid [56]

The morphology of P/G hybrid was investigated by TEM and SEM. As shown in figures below in Fig 1.11. It can be concluded that the initial graphene stacks are several micrometers in size and red phosphorus is irregular shaped. After ball-milling, the particle size was much smaller and regular shaped.

Fig. 1.11. a) TEM image of graphene stacks; b) SEM image of red phosphorus and c) P/G hybrid; d) TEM image and corresponding mapping of carbon e) phosphorus f) P/G hybrid [56]

Then, the author conducted electrochemical testing of this P/G hybrid. The results are shown below in Fig 1.12.

Fig. 1.12. a) The cyclic voltammograms of P/G hybrid with scanning rate of 0.1 mV/s ; b) charge and discharge profile; c) cycle performance; d) rate performance [56]

The CV curve implies that the SEI layer formation of P/G anode is mainly at first cycle. From the anodic scan, three obvious peaks can be observed, which correspond to the de-intercalation of Na_3P to Na_2P , NaP , and NaP_7 . The charge/discharge profile in Fig 1.12(b) indicates at first discharge cycle, a platform exists around 0.25 V at the region2 in the figure. And following the charge curve, a plateau exists at 0.5 V at the region3. These plateau are consistent to the CV results and literatures. In Fig 1.12 (c), the P/G hybrid delivers an initial specific capacity at 2077 mAh/g , and 95% capacity retention after 60 cycles, which is 1706 mAh/g . Finally, the rate performance was also examined. The C-rates are from 0.05C to 2C . According to the results, it can be concluded that the P/G composites delivers a high reversible capacity even under a high current density.

In conclusion, the author developed a facile ball-milling approach to fabricate red phosphorus and graphene composites, this hybrid is cost saving when compared to lithium counterparty, and also delivers a good cycle stability.

1.3 Dissertation Overview

Chapter 1 provides rationales for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the application potential for silicon-based lithium-ion battery and its drawbacks as well as methods to overcome them.

Chapter 3 discusses the principles underlying the synthesis/characterization techniques employed and the methods of data analysis, including errors.

Chapter 4 elaborates the experimental results of projects.

Chapter X draws together the threads of the thesis and discusses the opportunities and strategies for future work.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Adopting a novel biomass extracted pectin binder that is water-soluble and environmentally friendly.
2. Find out a binder that can improve the overall performance of silicon nanoparticles/graphene based anode electrode, including rate and cycle performance.
3. Applying the pectin to both lithium-ion battery and sodium-ion battery, which leads to a great improvement in the stability of anodes.
4. Modifying the pectin through esterification with other chemicals, and the modified binder achieves better stability than original pectin.

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Chapter 2

Literature Review

In this chapter, basic requirements for binder selection are discussed. Then several types of binders, including binders extracted from natural organic resources, binders enjoying highly elasticity, and conductive binder, are reviewed. Besides, a systematical method to design binders is also introduced to reveal the underlying basic mechanisms. In addition, an interpenetrated gel polymer binder for silicon battery is discussed afterwards. The binder is obtained through modification reaction to make it mechanically stronger.

2.1 Introduction

Anode and cathode materials with high energy density are necessary to produce high performance batteries. Silicon has been highlighted for its outstanding capacity (over 3000 mAh/g) as promising anode materials to replace carbon anode (400 mAh/g).

Silicon undergoes severe pulverization during repeated charge-discharge cycles, which eventually undermine the performance of batteries. Anode electrode is comprised of active materials, conducting agent and binder. The effect of the binder is keeping the whole electrode integrated. Thus, one way to solve this problem or improve the cycling performance of silicon anode is choosing an appropriate binder used in electrode instead of traditional binder polyvinylidene difluoride (PVDF). Here are some potential principles to find a more suitable binder for silicon electrodes. [1, 2]

First, weak interaction between binders and electrolyte is important for stable performance of batteries. As shown in Fig 2.1. [1]

Fig. 2.1. Alginate origin and characterization [1]

If there is a strong interaction between binder and electrolyte, electrolyte or solvent may reach the surface of silicon anode and then decomposes, which in turn, will lead to rapid anode degradation through deposition of substances [1].

Second, an ideal binder is supposed to provide enough access for Li ions to reach the surface of silicon for reaction. While binder should cover most of surface area of silicon in order to prevent contact of silicon and solvent, there still need to be some area exposed, in order to be permeable for Li-ions.

Third, a stable solid-electrolyte interphase (SEI) layer is of crucial importance for long-term stable performance. If SEI layer is not stable or even growing too thick and become out of control, this may lead to electrical disconnection between Si particles.

Some mechanism has been put forward [2] recently. Some polymer network can be introduced into anode materials as binder and these polymers has the effect just like moving

pulleys, which can dissipate the stress that generated during volume expansion. Besides chemical and physical performance of binders, properties including easy-access and environmental friendly should also be considered during selection process. Conventional binder polyvinylidene difluoride (PVDF) needs to be dissolve into a polymer solvent to function as binders, In contrast, binders which are extracted from biomaterials is believed to have more promising future, as they are widely available and environment friendly.

Based on requirements for binder selection, researchers have developed many new binders. Here, several articles with long-term impact and inspiring features are selected to demonstrate recent progress in new binder development.

2.2 Organic extracted polymer binder

Igor Kovalenko et al. [1] reported that alginate yields a remarkably stable silicon battery anode [1]. They assembled anode electrode with alginate, silicon and metallic lithium counter to test the performance of this polymer binder. They used a relatively higher Si to C ratio (3:1) compared to testing which involved traditional binders. The electrochemical performance result is demonstrated as below:

Fig. 2.2. Electrochemical performance of alginate incorporated Nano silicon anode [1]

In Fig 2.2.A, charge-discharge cycling performance was tested with Li intercalation at 1200 mAh/g. From this testing, the electrode remains almost the same capacity even after 1200 cycles, which represents its excellent stable capacity. Also, in order to make the testing environment close to real-life application, the author test the electrode's performance under different current densities that were shown in Fig 2.2.C. When at low current density, 280 mAh/g, the cell remained same capacity after first cycling, the capacity of nano silicon in this paper is much higher than micro silicon as previous reported [3], and with the increase of current density, the capacity of cell fell, but even at a high current density at 4200 mAh/g, it can still keep a capacity nearly 2000 mAh/g, which is ~ 5 times higher than the theoretical capacity of graphite. Compared to other binders in Fig. 2.2.B, the outstanding performance of alginate-based battery is more obvious. The capacity of batteries with CMC binder and PVDF binder fall quickly only after less than 10 cycles and eventually only retain the same capacity as graphite, totally losing the superiority of silicon.

The Fig. 2.2.D show one broad Li cathodic insertion peak at ~ 0.21 V and two Li anodic extraction peaks at 0.33 V and 0.51 V. The first anodic peak is not always observed during this process; thus, this peak may represent the properties of silicon surface.

Besides the electrochemical performance, the author tests the stability of SEI layer as well. As mentioned above, a stable SEI layer is one of essential reasons to keep the performance of battery unchanged. The XPS result showed below in Fig 2.3:

Fig. 2.3. Stability of SEI layer in alginate incorporated silicon anode [1]

In the XPS testing, there is no major changes in the chemistry constitution of SEI layers that formed on silicon surface after 10 or 200 cycles. So, based the fact, a conclusion can be made concerning alginate polymer binder. It does have the features that are required by

a satisfactory binder, like outstanding stability, easy access, the ability to keep SEI layer stable, and finally leads to a good electrochemical performance of silicon batteries. Also, it inspired people to find out more biomaterials originate from various species.

2.3 Highly elastic binder

Jang Wook Choi et al [2] recently reported a highly elastic binder used in micro silicon particles anodes in lithium ion battery. This article introduced a pulley mechanism which can dissipate the stress that produced during volume expansion on anode. The group incorporated 5 weight percent polyrotaxane (PR) which is also been adopted for extreme elastic hydrogels [4, 5] into conventional polyacrylic acid binder (PAA) to form a new binder who owns extraordinary elastic that can help silicon to remain integrated. Micro particles silicon (SiMP) are more susceptible to pulverization compared to nano particles, thus, many three-dimensional polymer network binders reported till now are not able to solve this problem [6-9]. The group noticed the mode of action of moving pulley would work as a possible stress dissipation solution during volume expansion. The stress release mechanism is demonstrated as below:

It is known that a fixed pulley can change the direction of force while a moving pulley can reduce the force needed to half when lift an object. The total force the model can reduce is proportional to number of moving pulleys. From the right side of the Fig 2.4., it is noticed that polymer used in binders have the morphology as ring-thread, which is able to have the function exactly the same as pulleys.

Fig. 2.4. Model of pulley applied to binder [2]

Combined with the chemical components of PR-PAA, the mechanism can be more clearly understood.

Fig. 2.5. Proposed model of stress-dissipation [2]

PR is comprised of polyethylene glycol (PEG) which has function as thread and α -cyclodextrin (α -CD) which has function as rings, as well as traditional linear binder PAA. Also, from the Fig 2.5., the new binder can help disintegrated silicon particles to recover to nearly its pristine status [10-12] after several cycles. In contrast, only PAA binder doesn't have such functions, pulverized silicon in PAA binder contained batteries cannot recovery and lead to uncontrolled growth of SEI layer. The mechanism is concluded as: during lithiation, PR-PAA binder can lead to the movement of components closer to reduce mechanical stress and keep the pulverized silicon particles coalesced. First, we can examine the impact of this binder by carrying out mechanical test.

Fig. 2.6. Mechanical test result of PR-PAA [2]

In Fig. 2.6.A, there are three typical stretching behavior of polymer film: linear elastic (Hookean), non-linear softening (r shape), and nonlinear stiffening (J shape) which are usually found in biological system. Non-linear stiffening has high elastic characteristics while nonlinear softening is easy to undergo plastic deformation after a critical strain.

As illustrated in Fig. 2.6, the PAA film demonstrate an obvious r shape curve in its stress-strain plot, the PAA film will rupture only at a strain of 37%. However, PR-PAA film exhibited a performance far better than PAA film, it will not rupture until 390% strain. In the pictures under PR-PAA strain-stress plot, it can be seen that in r shape regime, from point 1 to point 2, PAA chains were rearranged along the direction of load, while in the J shape regime, from point 2 to point 3, the ring-sliding model endows sufficient resilience to film and keep the film unruptured.

From the result of mechanical test, high elastic of PR-PAA binder is proved, the electrochemical performance need to be tested after it.

The cycle, rate performance of PR-PAA binder have been examined by the author and the comparison with PAA binder.

Fig. 2.7. Electrochemistry performance of PR-PAA-SiMP [2]

At a Si loading of 1.07 mg cm^{-2} , the anode electrode based on PR-PAA (written as PR-PAA-SiMP) exhibited a higher reversible first cycling capacity at 2971 mAh/g with current density at 0.033C . In the meanwhile, the anode electrode based on PAA (written as PAA-SiMP) only retained 2579 mAh/g . In Fig. 2.7.B, PR-PAA-SiMP showed a far better cycling performance than PAA-SiMP. When measured at 0.2C , after 150 cycles, PR-PAA-SiMP retained 91% capacity compared to 48% capacity retain of PAA-SiMP only after 50 cycles. High columbic efficiency (CE) is of crucial importance for a good battery, so the author also measured the CE in this Fig. 2.7. As is denoted in Fig. 2.7.B, at 4th cycle to 22nd cycle, the CE of PR-PAA-SiMP increased form 99.1% to 99.82%. The average CE during cycles from 23 to 150 was 99.64%. In a separate test (Fig. 2.7.C), author extended cycle numbers to 400, and once the cell became stabilized after 10 cycles under 0.2C , the current density was increased from 0.2C to 0.4C , and kept to the end of test. At around 220th cycles, Li metal had to be changed, because the degradation of Li would affect the result of cell's

cycle performance. As can be obtain from testing result, nearly 85% of the capacity was retained for the remaining 370 cycles since 10 cycles.

The essential effect of PR-PAA binder can be unveiled by scanning electron microscopy (SEM) testing. As is shown below:

Fig. 2.8. SEM result of PR-PAA-SiMP and PAA-SiMP [2]

First, from cross-sectional view in Fig 2.8, the pristine state of both PR-PAA-SiMP and PAA-SiMP was almost same. They had similar thickness (9.8 mm) and particle size distributions. However, after 10 delithiation cycles, PR-PAA binder and PAA binder had totally different performance in SiMP. Together with Top-view pictures, consistent result was portrayed. The PAA-SiMP suffered from uncontrolled growth of SEI layer that can severely undermined electrochemistry performance of electrode.

In nutshell, the incorporation of PR changes the mechanical properties of binders and contributes to a largely improved performance of electrode. This can resolve the damage to silicon particles brought by volume expansion to some extent and offers an alternative strategy to extend cycle life of high capacity Li ion batteries.

2.4. Systematically designed binder

Tae-woo Kwon et al. [13] designed new binders systematically from molecular level for silicon anode. In order to identify the most important properties of binder for Si anode, including crosslinking, [14] self-healing, [15] stiff backbone, [16] and adhesive Interaction with Si [17, 18]. The author firstly divided binders into three proposed different groups, binders have no interaction between chains and particles, like PVDF; binders can react on silicon's surface and can also undergo covalent crosslinking; self-healing binders. They are all shown as below:

Fig. 2.9. Graphical schematic of three different types of binders [13]

It is worth mentioning that self-healing in Fig 2.9 refers to the capability that the interaction between binder-binder and binder-silicon can be recovered which may be destroyed in previous cycling due to volume expansion.

Fig. 2.10. Modularity of synthetic approach [13]

The author used different polymer as different modules to ‘built’ new binder with various characteristics, like shown in Fig. 2.10. In Fig 2.10.a, there are 4 different modules, K, represents 5-methyl-5-(4-vinylbenzyl) Meldrum acid, which has the function as crosslinking and covalent attachment to Si; S, represents Styrene, which has the function as stiffness; M, have the function as flexibility because of its low Young’s modulus; C,

which can help binders to have self-healing property. By simply adjust ratio of these four monomeric, critical parameters of binder that mentioned above can be investigated. In addition, the process of how to synthesize these monomeric is illustrated in Fig 2.10., however detailed procedures will not be included.

In order to find influence of these new binders on batteries, several electrochemical testing have been carried out among conventional binder PVDF and different combination of K, M, S and C. Result is shown as below:

Fig. 2.11. Electrochemical analysis the Si electrodes with different binders [13]

First, in Fig 2.11.a, PVDF has the worst performance due to weak Van der Waals interaction with silicon, and it has the same result as previous report. [14, 16, 19, 20] By comparing K₁₅S_{42.5}M_{42.5} and K₁₅M₈₅, a slightly improvement can be found, which suggested that with same K ratio, the stiffness brought in by S monomeric can provides some improvement to cycling performance of batteries.

Second, performance of K₁₀₀ is better than any of binders comprised of K, M and S, which represents crosslinking/covalent attachment is more essential than the stiffness or flexibility of binders to improve the cycling performance. In order to test this result in more detail, the author prepared more series combination of K and M in Fig 2.11.b. The KM copolymers with higher K ratio exhibits better performance, which confirmed previous result.

Third, the self-healing binder (C100) demonstrated the best cycling performance among all these binders. It retained nearly 50% capacity after 500 cycles, which was far better than others. Also, in Fig 2.11.d, C100 has the highest CE when compared to other binders.

Fig. 2.12. SEM images of Si electrode for first two cycles [13]

The self-healing effect can be seen from SEM pictures from Fig 2.12. After first cycle, it is obvious that there were many cracks on silicon surface, but after one cycle, some of cracks were disappeared while others shrink.

2.5 Conductive binder

Finally, a commercially available conductive polymer that is used as both binder and conductive additive will be introduced. Thomas M. Higgins et al. used PEDOT: PSS as primary binder and together with a small quantity of formic acid functions as secondary dopant.

While there was already some work related to conductive binders, they often require complicated in-house synthesis [22, 23], additional binders [24], nonaqueous solvents [22] and cannot fit in the slurry coating process of industry [25]. PEDOT: PSS however, can be commercially available at low cost and is soluble in water which makes it possible to use conventional techniques to process. With a small amount of secondary dopant, it can possess excellent electrical conductivity. Besides, it is also mechanical robust, electrochemical stable. [26-28]

Fig. 2.13. Scheme for the experimental PEDOT: PSS SiNPs electrode [21]

From Fig 2.13.a and b, the difference between traditional binder and conductive binder is clear. Traditional binder like PAA needs other conductive additives like carbon black (CBs), it will segregate at silicon's surface, then during volume expansion, and the electrical pathway would be largely lost. In contrast, due to the fluidity of binder, it can uniformly mixed with silicon particle and not suffer from this problem. Fig 2.13.E and 2.13.F are high magnification images while rest are low magnification. H and I are energy dispersive X-ray (EDX) spectroscopic mapping and J, K are electron back scattering (EsB). These images indicated the uniformity of PEDOT: PSS/SiNPs and Inhomogeneity of PAA/SiNPs. The inset of Fig G is the chemical formula of PEDOT: PSS.

Fig. 2.14. Performance with different ratio of FA [21]

In order to determine the best ratio of secondary dopant, the author conducted several experiments with 20% weight ratio of PEDOT: PSS. In Fig 2.14.A, the conductivity of binder increases with FA ratio from 0% to 10%, and remain unchanged. Fig 2.14.B, C, D are first cycling performance, cycling performance and rate performance, respectively. It is clear that binder treated with 10% formic acid has the best performance.

In next step, the author tested the performance of various ratios of PEDOT: PSS (5% to 30%) with 10% FA. In Fig 2.15.A and 2.15.B, more conductive binder improves the performance of the available silicon.

Fig. 2.15. Electrochemical performance with various ratio of PEDOT: PSS [21]

Nevertheless, it is apparent that capacity does not vary with binder loading. The inset of C is the capacity retention rate graph when compares 100th cycle and second cycle.

There are other good solutions related to develop new kind of binders, such as Jie Liu developed robust biopolymer network binder [29] for Li-S battery; Yuxin Tang developed Water-Soluble Sericin Protein to enable stable SEI layers. [30]

2.6 interpenetrated gel polymer binder

In this work, an interpenetrated gel polymer binder for silicon battery is adopted. The anode is prepared through thermo-induced in-situ crosslinking of poly(acrylic acid) (PAA) and polyvinyl alcohol (PVA) precursors. The deformable polymer binder can well stand the large volume expansion during reaction process. In the thermal process, the carboxyl functional group of PAA and hydroxyl functional group of PVA undergoes esterification reaction. In the meanwhile, the carboxylic acid group of PAA would also react with the hydroxyl groups of SiO_2 which is on the surface of the Si particles to form covalent ester bonds between the Si particles and polymer network, which can make the structure more stable. [31] This process is illustrated in the below Fig 2.16.

Fig. 2.16. Chemical structure of PAA and PVA and interaction between them [31]

Then, the electrochemical performance tests among the new PVA-PAA binder, NaCMC, and PVDF were conducted.

Fig. 2.17. Cycling performance and Coulombic efficiency comparison among three binders [31]

The result in Fig 2.17 well proofed that the formation of integrate structure among PVA, PAA, and active materials help to withstand the large structure change during lithiation. A specific capacity of 3616 mAh/g was achieved at the initial cycle of PVA-PAA anode, and after 100 cycles, the capacity retention rate achieves 63.1%, much better than PVDF.

The best cycling performance is also confirmed by SEM imagines.

Fig. 2.18. Morphology of electrodes before and after 100 cycles with different binders [31]

It can be found in Fig 2.18 that at the initial state, these electrodes have uniform distribution, silicon nanoparticles with carbon black are also mixed uniformly. Obvious morphology changes can be observed after 100 cycles. The white arrows in the figure points at the cracks on the surface area, electrode with PVDF has most cracks while PVA-PAA electrode has no obvious cracks, which is correspond to their electrochemical performance.

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Chapter 3

Experimental Methodology

In this chapter, reasons for choosing pectin extracted from citrus as experimental binder material, the rationale behind the fabrication process and the characterization methods are demonstrated. Pectin is extracted from organic fruits which is environmentally friendly and widely distributed. Besides, pectin is water-soluble so that no polymer solvent during the production process can be achieved unlike traditional polymer binder PVDF. Then, the sources of different materials in the fabrication process and types of half-cells as well as how they were assembled are introduced. Afterwards, the reasons for choosing different characterization facilities and their underlying principles are thoroughly demonstrated, including SEM, battery testing system and mechanical testing system.

3.1 Rational for selection

Firstly, pectin extracted from citrus is chosen as the experimental binder in this project, because it is extracted from organic fruits, thus, it is environmentally friendly and distributes widely. Besides, pectin is water-soluble, and does not need any other polymer solvent during the production process when compared to traditional polymer binder PVDF, so pectin is less harmful to both environment and workers.

Then, the chemical structure of pectin also proves it is feasible in acting the function of binder in electrode. The basic domain structure consists of citrus pectin is illustrated below.

Fig. 3.1. Basic domains of pectin [Vincken et al. (2003)]

From the above figure 3.1, it can be known that the most commonly found structural elements are: (i) homogalacturonan, (ii) xylogalacturonan, (iii) rhamnogalacturonan I backbone, (iv) rhamnogalacturonan II, (v) arabinan, (vi) arabinogalactan I, and (vii) arabinogalactan II. [Vincken et al. (2003)]

While the actual structure of pectin is still under discussion, there are two widely accepted models that can help to understand the macromolecular structure of pectin.

Fig. 3.2. Smooth and hairy regions model [Schols and Voragen 1996]

The first model in Fig 3.2 is called smooth and hairy region model. In this model, the pectin backbone consists of alternating homogalacturonan (HG) (smooth regions), xylogalacturonan and rhamnogalacturonan-I (RG-I).

Fig 3.3. RG-I backbone model of pectin [Vincken et al. 2003]

The second model in Fig 3.3 is called RG-I backbone model. In this model, the RG-I backbone is decorated, with arabinan, arabinogalactan I and II side chains, as well as homogalacturonan (HG) and xylogalacturonan (XGA) domains.

From the basic components and macromolecular structures, it can be concluded that pectin possesses many hydroxyl and carboxyl functional groups, which gives the possibility to modify the binder through esterification reaction with other chemicals who also has

hydroxyl or carboxyl groups, and after the reaction, the mixture binder can form a strong network which can enhance the mechanical property of the whole electrode and is helpful to withstand the volume change during cycling. Besides, the chain structure of pectin also plays an important role while reaction happens.

During the synthesis process, half-cells are being assembled using the standard procedure except that pectin binder are used to replace traditional PVDF binder. Then during characterization process, scanning electronic microscopy (SEM) and battery testing system (NEWARE) are two major characterization techniques. SEM is capable of characterize the surface morphology of materials while battery testing system is used to perform electrochemical tests, including rate, cycling and CV tests. In conclusion, methods adopted in this project aim to tell whether the performance of pectin binder is satisfying and outperformance other binders, like PVDF.

3.2 Experimental materials

1. Silicon Nano powder, <100 nm particle size (TEM), $\geq 98\%$ trace metal basis purchased from Sigma Aldrich.
2. Graphene powder, 15-20 layers, <6 nm thickness, 10-20 μm slice size, >35 m^2/g specific surface area, 5-6wt% oxygen, <0.5% ash, >40000 S/m electrical conductivity purchased from Carbonene.
3. 1M LiPF_6 in EC: DMC 1:1 purchased from Dong Guan Shan Shan Battery Material.
4. Type 2032 CR32 battery components, copper foil and Lithium battery separator.
5. 20wt% (water) sodium alginate, 20wt% (water) pectin from citrus peel, 20wt% (water) pectin from apple pomace.
6. Graphite oxide powders, <0.5-5 μm >, purchased from XFNANO INC.

3.3 Experiment procedures

3.3.1 Preparation of binder

The original binder solution obtained from another group is of 20 wt. %. Taking 100 mg original binder and dissolve it in 1 ml distilled water, then use ultrasonic to disperse the solution. After that, a binder solution of 20 mg/ml is obtained.

3.3.2 Preparation of working electrode

First, a mixture of 70 wt. % active materials, 20 wt. % conductive material which is super P or carbon black, and 10 wt. % binder is prepared. The active materials are consists of Nano silicon particles and graphene, different ratios of graphene and silicon are used in different experiments. The numbers after the letters in following contexts stands for the weight ratio of carbon black. For example, Si10 means there is 10 wt. % of carbon black in active material while Si50 means there is 50 wt. % of carbon in active material.

After the preparation of mixture, it is poured into a small mortal and manual mixing for 30-40 minutes to make the composites distribute homogenously.

Then, the mixture is transferred onto the surface of current collector which is copper foil in the project with 1 cm diameter. Finally, the prepared electrode is dried in vacuum oven under 60 degree for 10 hours. Till now, the preparation of electrode is finished.

The final electrode is shown in the below picture 3.4.

Fig. 3.4. Prepared electrode on copper foil

3.3.3 Fabrication

In this procedure, half-cell will be fabricated in glove box, because as mentioned, nanoparticles are easily to be oxidized under air atmosphere. Electrode, metal lithium, battery shell, electrolyte, separator, gasket, spring will be used to fabricate the half-shell. LiPF_6 is used as electrolyte and metal lithium is used as anode in half-cell.

During the first step, prepare the same size counter electrode and membrane used for separator. Then transfer type 2032 cells' components and electrode into argon-filled glove box.

Place the working electrode on the cell cup. Add eight drops of the electrolyte and place one separator before placing the lithium counter electrode on it. Place a stainless steel spacer and a spring on the lithium disc.

Close the cell using the cell cap and crimp using the MTI KJ Group MSK-110 hydraulic crimping machine to 50 kg/cm² (~700 psi).

After assembling the cells, handle the finished cells using plastic tweezers (to avoid short-circuiting)

Clean the excess electrolyte leaking from the sides of the cell using a paper napkin.

After fabrication, the half-cell which is shown below in Fig 3.5 can be used in battery testing system of other machines to examine its electrochemical as well as other kinds of performances.

Fig. 3.5. Prepared lithium ion half-cell

3.4 Characterization

3.4.1 Scanning electron microscopy (FESEM 6340F)

Scanning electron microscopy is one of electron microscopes that produce image of sample's surface with a beam of electrons. The electron react with atoms in the sample when they collides. Various electrons like secondary electrons, back scattering electrons emitted during this process, producing different signals containing the information concerning the sample, including topography and composition. Like shown in Fig.3.6, it is the reaction between electron beams with the sample. It is also known as interaction diagram of SEM.

Fig. 3.6. Interaction between electron beams with sample [1]

Usually, secondary electrons and back scattering electrons will be collected to analyze the surface morphology and sample composition, respectively. Other signals are not used in this project so that they will not be introduced.

In secondary electron imaging, which is also known as SEI, the secondary electron signals are collected by detector. Since secondary electron are emitted from very close to sample surface, typically 5-10 nm region. The resolution of surface image can be very high, revealing details of surface less than 1nm in size. [2, 3]

Back scattering electrons (BSE) are emitted from relative deeper location of sample compared to secondary electrons, so the resolution of BSE image is lower than SEI. However, BSE images also carry some compositional information about the sample that is not in the SEI images, which help researchers to understand the distribution of different elements in the sample. Besides, BSE alone with characteristic X-rays spectra is a typical analytical method for scientists, as the intensity of BSE images are highly related to atomic number. The mechanism of emission of electrons is demonstrated below in Fig 3.7.

Fig. 3.7. Mechanism of emission of electrons [1]

The energy exchange between the electron beam and the sample results in inelastic scattering such as secondary electrons, and the most common collected secondary electrons (SE) is the electrons ejected from the k-shell of the specimen atoms, then the transition of outside shell electron to inside shell can release characteristic X-ray. Back scattering electrons (BSE) are electrons originate from high energy electron beams (PE). Because high atomic number atoms reflect electrons more strongly than lower one, which appears to be brighter in the image, the contrast can be taken to analyze the distribution of composition in the sample.

However, there are several limitations for SEM. First, SEM testing is a kind of ex-situ method, the process during lithiation and delithiation cannot be discovered by researchers. In contrast, in-situ methods can help people better understand the mechanism under

phenomena. Then, when compared to transmission electron microscope (TEM), the magnification is lower, so that the deeper morphology or changes are hard to discover.

In SEM result, on the one hand, SEI layer formation can be analyzed by top-view pictures while on the other hand, how large the volume expansion with binder can also be revealed by cross-sectional view of electrode. Besides these two factors, the porosity, the integrity of silicon particles can help researchers to understand the change happening during cycling and emphasize on the different function of various binders.

3.4.2 X-ray diffraction

X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. Due to the comparable wavelength between x-rays and the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules among various materials. The energetic x-rays can penetrate deep into the materials and provide information about the bulk structure.

X-rays primarily interact with electrons in atoms. When x-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they originally travel. If the wavelength of these scattered x-rays did not change, the process is called elastic scattering, which only momentum has been transferred in the scattering process. These are the x-rays that been measured in diffraction experiments.

Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material. The whole process is illustrated in Fig 3.8.

Fig. 3.8. Interaction between incoming beams with atoms

The peaks in x-ray diffraction pattern are directly related to the atomic distances, which is also known as Bragg's Law.

$$2d\sin\theta = n\lambda$$

In this equation, λ is the wavelength of the x-ray, θ is the scattering angle, and n is the integer representing the order of the diffraction peak.

Through XRD analysis, structures of materials can be deduced, which also helps researchers to confirm the existence of specific materials.

3.4.3 Fourier transform infrared spectroscopy (FTIR)

FTIR in Fig 3.9 is a characterization method that provides an infrared spectrum of absorption or emission. When IR radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted). The detector will capture this signal and the result will form a spectrum representing the vibration mode of molecules.

Since every molecule or chemical structure have different vibration mode, it can produce different signals and provides a way to distinguish them.

Fig. 3.9 Illustration of FTIR [4]

Infrared spectrum is molecular vibrational spectrum. When exposed to infrared radiation, sample molecules selectively absorb radiation of specific wavelengths which causes the change of dipole moment of sample molecules. Consequently, the vibrational energy levels of sample molecules transfer from ground state to excited state. The frequency of the absorption peak is determined by the vibrational energy gap. The number of absorption peaks is related to the number of vibrational freedom of the molecule. The intensity of absorption peaks is related to the change of dipole moment and the possibility of the transition of energy levels. Therefore, by analyzing the infrared spectrum, one can readily obtain abundant structure information of a molecule. [5-7]

Since the FTIR can help analysts to identify unknown materials and specific chemical structure. It is adopted in the experiments to identify the structure change or to tell whether the origin functional groups are still preserved.

3.4.4 Battery testing system (NEWARE)

Cells are subjected to repeated charge - discharge cycles in the battery testing system machine, for its rate and cycle performance in this project.

Rate performance: Cells will undergo repeated charge – discharge under different rate C . $1C$ means the cell needs to finish its discharge or charge process in 1h. The capacity of each cycle will be recorded.

Cycle performance: Usually, cells will undergo repeated charge – discharge under the same rate C . The capacity of each cycle will be recorded.

From cycle performance test, researchers can tell how much capacity of the battery can retain after a fixed number of cycles and under a specific current density. While from rate performance test, the capacity retention can also be discovered after several cycles under various current density, especially the performance under high current density.

Cyclic voltammetry testing (Solartron analytical):

In cyclic voltammetry (CV) testing, the potential of electrode changes periodically and linearly versus time. The experiment's scan rate (V/s) can be described as the voltage change over time. The machine used is showed in Fig 3.10.

Fig. 3.10. Image of battery testing system

3.4.5 Mechanical testing (Instron 5567 Electromechanical Tester)

It's able to perform static and cyclic testing, and from another aspect, it can perform tension, compression, shear, and flexure as well as bend tests. This machine is suitable for testing a wide variety of materials (e.g. metals, ceramics, plastics, composites, textiles, etc.). In this project, the aim of this test is to examine the mechanical properties of electrode with

traditional binder PVDF or experimental binder pectin. Tensile test will be performed and compared. In the result of this test, researchers can tell which one has better mechanical performance. Due to the large volume expansion of silicon, electrode should have the ability to withstand large tensile stress under large strain. The used machine is showed in below Fig 3.11.

Fig. 3.11. Image of mechanical testing system

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Chapter 4

Result and Discussion

In this chapter, different mass ratios between silicon and graphene are chosen as active materials. After the suitable ratio is figured out, the electrochemical performances are tested and compared. The comparison between pectin and traditional binder PVDF is conducted to certify the better suitability of pectin binder, including mechanical and electrochemical performance. To further improve the cycling performance of silicon based anode, 75 wt. % of graphene is mixed with silicon. An alternative way to modify the anode material is applying lab synthesized reduced graphene oxide to replace commercially available graphene. The electrochemical performance tests with such anode are carried out. In addition, esterification reaction between pectin and other chemicals who possess abundant hydroxyl and carboxyl functional groups turns out to be an efficient solution to increase its stability. Finally, in order to explore more application possibility of the binder, it is applied to sodium ion battery.

4.1 Introduction

Firstly, 10 wt. %, 30 wt. % and 50 wt. % graphene is mixed into silicon to obtain active material and fabricated into half-cell battery. The numbers after the letters in following contexts stands for the weight ratio of graphene. For example, Si10 means there is 10 wt. % of graphene in active material while Si50 means there is 50 wt. % of carbon in active material. After 100 cycles and under 1000 mAh/g, they achieved capacity retention rate of 34.8%, 25.3% and 52.6%, the silicon with 50 wt. % graphene outperforms other two composites. Then, the comparison between PVDF and pectin is demonstrated. After 50 cycles, the capacity difference between PVDF and pectin expands to 500 mAh/g while they have almost the same initial capacity. Other tests, including scanning electron microscopy and mechanical testing are also carried out. In order to further increase its capacity retention rate, the contents ratio of graphene is increased to 75 wt. %. Under such condition, the battery finally achieves less than 30% capacity loss after 200 cycles. The graphene that has been doped into composites so far are commercially available and obtained through thermal stripping process, which leads to the poor ability of graphene to disperse uniformly in water, which then cause inhomogeneous mixing of active materials. Inhomogeneous mixing can cause the poor stability of electrode. Take this factor into account, another lab-made graphene or RGO (reduced graphene oxide) is used in anode. When using RGO in anode, its final capacity retention rate achieves more than 70% after 100 cycles under 600 mA/g, which is two times larger than commercially available graphene. In addition, pectin is modified through esterification reaction with citric acid (CA). The results show better stability of new binder than other binders in the experiment, however, due to the heat treatment during the synthesis process, some silicon becomes oxidized by oxygen, the content of silicon decreased while the total mass increased, and this may attribute to the reason why specific capacity of batteries declined. Finally, the binder is applied to sodium ion battery to explore more application possibility and the results show a promising future for pectin.

4.2 Comparison among Si10, Si30, and Si50

In the first step, due to the poor performance of nano silicon particles, nano silicon particles with graphene (commercial) are mixed as active composite material employed in anode. Various ratios of silicon and graphene composite are obtained by ball milling method. 50 wt. %, 70 wt. % and 90 wt. % of silicon in composites are labelled as Si50, Si30, and Si10, respectively. In this step, an appropriate weight ratio of graphene should be decided in order to achieve a better electrochemical performance of electrode.

The electrochemical performance test was carried out to evaluate the performance of pectin binder in Si10, Si30, and Si50 anodes. Each electrode is composed of Si/graphene composites, binder, and super P with a weight ratio of 7:2:1.

Firstly, the charge and discharge cycling performance of Si10, Si30, and Si50 were tested separately, the capacity is normalized to the whole mass of active materials.

Fig 4.1. Cycling performance along with Coulombic efficiency of (a) Si10, (b) Si30, and (c) Si50

When measured at 1000 mA/g, the initial capacity of Si10 is 1564.7 mAh/g, and during the second cycle, the capacity reached 1258 mAh/g, but preserved only 437.9 mAh/g after 100 cycles, which means the capacity retention rate of 100th/2nd is 34.8%. Also, capacity information concerning Si30 and Si50 can be obtained in the Fig 4.1. The initial capacity of Si30 is 1645.2 mAh/g, and after the first cycle, its capacity drops down to 1269.9 mAh/g, after 100 cycles, the left capacity is 321.7 mAh/g, indicating the capacity retention of Si30 is 25.3%, when using the same calculation method as Si10.

It can be seen from Fig 4.1 that the curve of Si50 is flatter than Si10 and Si30, so it is reasonable to assume Si50 is more stable. This assumption is proved by following calculation based on experimental results. The initial capacity of Si50 is 1252.1 mAh/g, during the second cycle, its capacity changed to 882.1 mAh/g, and after 100 cycles, its remaining capacity still has 464.2 mAh/g. The capacity retention rate of Si50 is 52.6%.

When normalized the capacity to the mass of silicon, a figure of comparison can be obtained. As shown below in Fig 4.2. Another test had been carried out to compare the cycling performance of Si10, Si30, and Si50, the current density is further increased to 2000 mA/g after 100 cycles. Each of these three electrodes showed an obvious decline of capacity after increasing of current density, however, Si50 still possessed the best stability of these three anodes. Si10 and Si30 has capacity less than 250 mAh/g when they became stabilized after 100 cycles, in the meanwhile, Si50 had a stable capacity near 500 mAh/g, which is two times than Si10 and Si30.

Fig 4.2. Comparison of cycling performance of Si10, Si30, and Si50

The result can be explained by high initial specific capacity of silicon and high stability of graphene. Since silicon has a theoretical capacity of 4000 mAh/g while graphene only possesses 400 mAh/g, when the electrode consists of more silicon, it will show high initial capacity when the result is normalized to the mass of whole electrode. However, as reaction happening, the silicon will undergo volume change repeatedly, and finally the structure of

electrode will be destroyed. Graphene, in contrast, due to its larger layer distance, suffers little from volume change during reaction and can help to maintain the morphology of electrode, which contributes to the stability of electrode.

Thus, choose a proper ratio of silicon and graphene is to balance capacity and stability, and the results turns out the Si50 demonstrates the best performance among them.

When applying the electrode to real life, it has to face various working conditions, so it is necessary to test its performance under different current density, especially under a large rate of current density. Due to the poor capacity retention of Si30, it has been excluded from rate testing, so rate testing has been carried out between Si10 and Si50, the result has been shown in Fig 4.3.

Fig 4.3. Rate performance of Si10 and Si50

The C-rate test was carried out in the range of current density from 100 mA/g to 5000 mA/g, then back to 100 mA/g, in order to test its reversibility after working under large current rate. Under each current density, 5 cycles were tested. From the result, some conclusion can be drawn. During the second cycle, Si10 has a discharge capacity of 1459.1 mAh/g

while Si50 has a discharge capacity of 1723.3 mAh/g. And in the whole range of testing, the Si50 shows better performance than Si10, both in specific capacity and capacity retention rate. When the current density back to 100 mA/g, the Si50 has the specific capacity about 1550 mAh/g while Si10 only possesses 1220 mAh/g, which indicated the capacity retention rate after 35 cycles are 90.0%, 83.6% of Si50 and Si10, respectively.

Due to the insufficient reaction time under large current density, the lithium ions are not fully lithiated/delithiated, which leads to the reduction of capacity. Also, under large current density, materials react much more quickly, which cause the problem of volume change more severely. Under this condition, the function of graphene becomes more prominent.

Finally, a separate test for Si50 was carried out for the first 10 cycles shown in Fig 4.4. This test was carried out under an extremely low current density, which is 100 mA/g. The result shows after the initial cycle, the capacity falls to 2000 mAh/g, indicating more than 1500 mAh/g irreversible capacity loss. After initial cycle, the capacity keeps almost unchanged in the following 10 cycles, demonstrates the high stability under low current density. This result also reveals the fact that when the charge/discharge process happens under low current density, due to the slow reaction rate, the damage to the connection between active material with conductive additives or current collector can be minimized, which in turn, would cause less capacity loss and contributes to the better stability.

Fig 4.4. First 10 cycle's cycling performance of Si50 under 0.033C (100 mA/g)

In nutshell, after both cycle and rate performance testing, it is clear that Si50 demonstrates the best performance among them, the superiority of Si50 is owed to the stability of graphene. So far, the ratio of 50 wt. % graphene in anode has shown the most outstanding performance, so in the later section, Si50 will be adopted to carry out other experiments. In order to illustrate the better properties of binder itself compared to other traditional binders, in the next part, the comparison performance between pectin and PVDF will be carried out.

4.3 Comparison between pectin and PVDF

In order to demonstrate the better performance of pectin than traditional polymer binder PVDF, series of testing were carried out, including electrochemical cycling test, mechanical performance test, SEM images, etc.

Before introducing the mechanical test results, some basic idea concerning mechanical testing will be explained.

Fig 4.5. Stress-strain behaviours of three representative modes [1]

In general, the stretching behaviours of polymer films can be categorized into three types, like shown in the Fig 4.5 [1]: Nonlinear stiffening behaviour demonstrates high elasticity especially under high region of strain, having this feature helps to preserve the main body or framework of polymer film in response to extreme external conditions, and this kind of stretching behaviour is usually found among biological materials.

Based on this knowledge, the mechanical performance testing was carried out by Instron 5567 Electromechanical. The result is shown in Fig 4.6. The result demonstrates that both PVDF and Pectin binder show an r-shape stretching behaviour. Although they will both undergo plastic deformation under large stress, the pectin binder shows a stronger resistance. The PVDF binder breaks apart only under 7.97 Kpa, while pectin binder can withstand 56.55 Kpa, 7 times more than PVDF.

Thus, it can deduced that when electrode undergoes large volume expansion during reactions, using pectin binder can withstand more stress applied to the electrode, which in

turn, can withhold more volume expansion of active materials as compared to PVDF electrode.

Fig 4.6. Mechanical property of PVDF and Pectin binders

The strong mechanical property of pectin can be partly explained by its chemical structure models as mentioned in chapter 3. The long chain structure or back bone structure of the polymer has the similar function as a thread, when numerous threads are put into the active materials, they can link particles together and keep the whole structure of electrode integrate.

After examining the mechanical property of PVDF and pectin binder, the half-cell was assembled using PVDF and pectin, respectively, then tested their cycling performance and stability. Results are shown below in Fig 4.7.

Fig 4.7. Cycling per performance of PVDF and pectin included electrodes under 0.2C (600 mA/g)

In this part, the electrode with PVDF binder and pectin binder are stated using their abbreviate PVDF and pectin, respectively. It can be observed from the result that at the initial cycle, both PVDF and pectin have almost the same specific capacity, around 3200 mAh/g. However, only after 10 cycles, the difference between PVDF and pectin is more than 150 mAh/g. After 50 cycles, this difference even enlarges to more than 500 mAh/g, and according to the trend, the capacity of PVDF decays more rapidly even after 50 cycles. From a separately testing, before 100th cycle, the specific capacity of PVDF decays to less than 400 mAh/g, which is very close to the theoretical capacity of graphite. When increase the current density to 0.4C (1200 mA/g) after 200 cycles as shown in Fig 4.8, the specific capacity of PVDF is less than 100 mAh/g, even worse than graphite and will become worthless in real application.

Fig 4.8. Cycling performance of PVDF electrode under 0.2C (600 mA/g) and 0.4C

So far, both mechanical and electrochemical performance have been examined for PVDF and pectin, both results show that pectin is much more stable than PVDF and is more capable of maintaining its specific capacity. In order to reveal the structure change before and after cycling of PVDF and pectin, the comparison of morphology is needed and the experiments were carried out by SEM.

The electrode used in SEM test was first reacted for 10 cycles, then used to compare with its initial morphology it's shown in Fig 4.9. The morphology was observed from top-view. Left side figures A and C are the morphology of PVDF, right side figures B and D are the morphology of pectin.

Fig 4.9. Top-view morphology of (a) initial PVDF, (b) initial pectin, (c) reacted PVDF, (d) reacted pectin

From SEM images A and B, there was no obvious distinction between PVDF electrode and pectin electrode, their morphologies are similar, so judgements can be made that after reaction the change of morphology is due to the different properties of binder. After 10 cycles, the differences between PVDF and pectin become apparently. There are many clear cracks on PVDF electrode while no obvious cracks on pectin electrode.

The crack itself may not lead to capacity loss, however, it would cause peel off of active materials from current collector and this would result in capacity loss and damage the performance of electrodes. Another conclusion can be obtained from SEM result is that both PVDF and pectin underwent uncontrolled SEI layer growth on the surface of silicon, and finally undermined the performance of both electrode.

Results from SEM and mechanical testing both prove the better ability of pectin to maintain the structure integrity, and finally contributes to the better performance.

In the meanwhile, PVDF electrode demonstrated in the same range of reaction voltage, which indicates the same reaction mechanism behind them. It is illustrated in Fig 4.10. The first 0.33 V anodic peak is not always observed, for example, in this paper [2], only one Li extraction peak at ~ 0.5 V appears.

Pectin does not change the reaction process or react with active materials, which is a crucial property of a good binder.

Fig 4.10. Differential capacity curves of the Nano-Si electrode

4.4 Comparison between Si75 and Si50

Although 50 wt. % commercial graphene was doped into Nano silicon to improve its cycling stability, the battery still losses its' nearly 60% capacity after 100 cycles, so it is necessary to further increase its stability. A feasible method is to further increase the content of graphene in active materials. The sample in this part was prepared with the ratio of Si: C = 3:1. Cycling and rate performance have been tested and compared to confirm whether stability is improved.

The electrochemical cycling performance of the composite electrodes was evaluated under voltage from 1.5 to 0.01V.

Fig 4.11. Cycling performance of Si75 (600mA/g)

As shown in Fig 4.11, at its initial cycle, it has a specific capacity of 1734 mAh/g, the Si75 exhibits capacity of near 1200 mAh/g after 200 deep cycles based on the weight of only silicon. Based on this result, the capacity loss can be calculated, which is less than 30%. When the cycling numbers are narrowed down to 100 cycles, as it did previously for Si50, the capacity loss of Si75 is only 16%, much better than Si50, which indicates the capacity retention is 84% after 100 cycles. In order to further compare the performance between Si50 and Si75, the results are integrated into one figure, as shown in Figure 4.12.

Fig 4.12. Cycling performance comparison between Si50 and Si75

Although the initial capacity of Si50 is larger than Si75, it quickly declines, and becomes less than Si75 after only 25 cycles. From the result, Si75 owns much better stability than Si50, the retention rate of Si75 after 100 cycles is near two times than Si50. 200 cycles later, the retention rate of Si75 is 2.5 times larger than Si50. Besides the performance before 200 cycles, the tendency or trend of Si75 and Si50 is also different. It can be obtained that the capacity of Si75 tends to maintain current level and only undergo small capacity loss.

As shown in Fig 4.13, the capacity of a Si75 composite electrode varies from 2685 mAh/g to 1450 mAh/g at a charge and discharge rate from 100 mA/g to 5000 mA/g. By contrast, the capacity of Si50 varies from 2600 mAh/g to 500 mAh/g, under the same current density range as Si75 does. Based on the result, one conclusion can be obtained that Si75 demonstrates better stability than Si50 especially under large current densities. The larger current density, the larger difference between Si50 and Si75.

Fig 4.13. Rate performance of Si50 and Si75

As mentioned above, the weight ratio between graphene and silicon is a balance of stability and capacity. The content ratio of graphene is too high for application in Si75, so another alternative method should be adopted in order to decrease the ratio of graphene.

4.5 Comparison between RGO and commercially graphene

The graphene that have been doped into composites so far are commercially available and obtained through thermal stripping process, which leads to the poor ability of graphene to disperse uniformly in water, which will cause inhomogeneous mixing of active materials. Inhomogeneous mixing itself then can cause the poor stability of electrode. Taking this factor into account, another lab-made graphene or RGO (reduced graphene oxide) have been employed in anode.

The RGO is synthesized through reduction of commercial GO (graphene oxide) through chemical reduction or thermal reduction. Due to the abundant water soluble functional group in RGO, it can increase its ability to disperse uniformly in water. In the following part, the content of graphene will again be reduced to 50 wt. %. In order to compare the performance of RGO and graphene bought commercially, the electrodes with these two kinds of graphene are assembled and electrochemical performance tests are carried out. Abbreviates of silicon with 50 wt. % RGO and silicon with 50 wt. % graphene will be used as Si50/RGO, Si50/commercial, respectively.

Fig 4.14. Cycling performance of Si50/RGO

At first 25 cycles, as shown in Fig 4.14, the specific capacity of anode almost keeps unchanged, in the following cycles, the curve decrease at a low rate. Even after 100 cycles, the capacity still maintains at around 1300 mAh/g.

To further compare the property of RGO and commercially available graphene, the result of these two materials have been contrasted. The result is demonstrated in Fig 4.15.

At the initial cycle, both of them own the nearly same capacity and then the difference enlarged as the cycle number increases. The initial capacity of Si50/RGO is 1917.2 mAh/g

while the capacity of Si50/commercial is 1905.9 mAh/g. After 100 cycles, the capacity of Si50/GRO still maintained at 1350.3 mAh/g, however, the capacity of Si50/commercial only possessed 747.6 mAh/g. When calculating the capacity retention of these two electrodes, the difference is also tremendous. After 100 cycles, the capacity retention of Si50/RGO is about 70.5%, which also means less than 30% capacity losses. By contrast, the capacity retention of Si50/commercial is only 39.2%, which demonstrated a capacity losses larger than 60%. Thus, the superiority of Si50/RGO is obvious.

Fig 4.15. Cycling performance comparison between Si50/RGO and Si50/commercial

The mechanism behind this improvement by adopting RGO is mainly due to the uniformity distribution of graphene and silicon. This result indicates the importance of uniformity, it can help accommodate the volume expansion and disperses the stress and strain across the whole area of electrode uniformly but not confined in small area and leads to the breakdown of electrode. It can maximally exert the stability of graphene and high capacity of silicon. The uniformity of electrode comes from the hydrophilicity of as-prepared RGO. RGO in the experiment is synthesized through chemical reduction of GO, which enriches the formation of hydrophilic group on RGO, these function group can help RGO to disperse uniformly in water. Graphene obtained through thermal split does not possess these hydrophilic groups, thus, as long as they are put into water with silicon, they are easily to

clustering at local areas rather than disperse uniformly, during the reaction, areas where only have silicon will break down and undermine the performance of electrode.

4.6 Modifying pectin with citric acid

The pectin binder used in the project is extracted from citrus peels, which explains its biodegradability during reaction. Thus, in order to maintain its functionality, one possible solution is tested.

The electrode with modified binder is obtained using the same process except for the heat treatment procedures. The modified binder is obtained through following process. First, mixing of pectin and citric acid with weight ratio of 1:1. Then stirring for 2 hours. After that, transfer the slurry onto the copper foil, the electrode is put into vacuum oven to react for 2 hours under 120 degree Celsius. During the heat treatment, the functional group on CA and pectin will undergo esterification reaction and form a strong network which can hold the silicon and other active materials firmly, keeping the structure intact.

After the fabrication process, same electrochemical tests are carried out using the same method before. The result is shown below in Fig 4.16.

Fig. 4.16. Cycling performance with modified binder

At first, the specific capacity gradually increases with cycle numbers increases, at around 50th cycles, the specific capacity reaches highest and after that, gradually decreases and becomes stable compares to first 50 cycles. At second cycle, it has a specific capacity of 971.6 mAh/g, and after 50 cycles, it reaches 1402.0 mAh/g. Finally after 100 cycles, the specific capacity declines to 1154.9 mAh/g, still, it's higher than the second cycle. Although the graph shows a tendency for capacity to keep decreasing after 100 cycles, the capacity retention rate of this new electrode at first 100 cycles proves the better performance of the modified binder as compares to the origin one.

Besides the cycling performance, rate performance is also carried out. The results in shown below.

Fig. 4.17. Rate performance with modified binder

From the rate test result in Fig 4.17, it can be concluded that when compared to improved cycling performance, rate performance seems only improved very little. The current density range of rate testing is same as other materials, varies from 100 mA/g, 200 mA/g, 500 mA/g, 1000 mA/g, 2000 mA/g, 3000 mA/g, 4000 mA/g to 5000 mA/g, and then back to 100 mA/g. Under the largest current density 5000 mA/g, the capacity drops dramatically to around 300 mAh/g, the capacity retention is only 20 %, which is similar to Si50 in previous experiment.

Due to the high temperature used in the heat treatment process, and the limited vacuum degree the machine can achieve, much nano silicon particles might be oxidized, which cause the total mass of electrode to increase and mass of active material to decrease, thus, leads to the relatively low capacity.

Then, the mechanical tests of binder itself was conducted to prove whether the network structure formed during esterification reaction has strengthened.

Fig. 4.18 Mechanical testing of pectin-CA and pectin

From the testing results in Fig 4.18, it can be concluded that under the same tensile strain, the CA modified pectin can withstand larger tensile stress, which prove its enhanced mechanical property. The test was only carried out under small deformation.

FTIR test was carried out as well to help analysts understand the structure change after modification.

Fig. 4.19 FTIR results of pectin and CA-pectin

From the FTIR result in Fig 4.19, in the region of 2000-1000 cm⁻¹, two intense bands between 1800 and 1500 cm⁻¹ are observed both in pectin and CA modified pectin. These bands may attribute to the vibration mode of COO groups. The strong and sharp absorbance peak at 1227 cm⁻¹ may attribute to the vibration mode of C=O, which is formed during esterification reaction. Another new peak formed at 1402 cm⁻¹ is the vibration mode of COO-, which also prove the binding formation between CA and pectin.

The mechanism in this experiment can be demonstrated as follows: pectin and CA are mixed with silicon and react under high temperature, during this process, the reaction between CA and pectin forms strong polymer network and fixes silicon particles in the network, so in the following charge/discharge reactions, the morphology and structure of electrode can maintain integrated. Besides, the formed chemicals would not degrade during following reactions, unlike pure pectin. However, also due to the high temperature, silicon particles are easily oxidized and causes the specific capacity to decline. The mechanical and FTIR testing can prove the reaction taken place between CA and pectin.

4.7 Applying pectin to sodium ion battery

Due to the limited natural resources of lithium and its' unevenly distribution, the cost of lithium may increase dramatically near incoming future. Thus, exploiting a novel and low-cost element to replace lithium is necessary. Sodium, whose intercalation mechanism is very similar to lithium and is natural abundant, has attracted increasingly attentions. Sodium-ion batteries (SIBs) become a promising low cost substitute of LIBs. In the meanwhile, phosphorus, a low-cost and abundant material with high theoretical specific capacity of 2596 mAh/g is considered to be employed as anode material, and its low discharge potential range (0.4 V to 1.2 V) indicates its relatively safe application. [3] Hence, red phosphorus and its composite will be adopted in SIBs.

Here, the experiment will use pectin to replace traditional organic binder PVDF to fabricate cells and test the performance of SIBs. First, pure red amorphous phosphorus is employed as anode material, then red phosphorus (red P) and carbon black (CB) hybrid material will be prepared with different ball-milling time to improve its electrochemical performance. The comparison between pectin and PVDF will also be illustrated in this section.

Firstly, electrochemical performance test was carried out with Na metal as counter/reference electrode. The electrode is composed of red P, binder, and super P in a weight ratio of 7:2:1. The capacity are normalized to mass of red P.

Fig. 4.20. Cycling performance of red P in SIBs

As the result shown in Fig 4.20, it owns poor electrochemical performance. At initial cycle, it shows a specific capacity of 1900 mAh/g, then it quickly drops to 800 mAh/g after 1 cycle, and becomes stable after 25 cycles at nearly 100 mAh/g. This result can be explained by the small layer distance of phosphorus, and the larger volume of Na ions than Li ions, both two physical properties contributes to the poor stability of phosphorus anode. Due to its poor performance, some modification is needed. Hence, red P with CB composites have been obtained by easy and facile ball-milling process. The weight ratio is red P: CB = 7: 3. The ball-milling time was set at 1 hour and 16 hours, respectively, in order to examine the influence of the length of time.

1) Red P and carbon black composites --- 1 hour ball-milling

First, the structure of red P/CB composites was examined by XRD. From the result showed in Fig 4.21, it can be referred that the main structure of the material is still dominated by red P, since the XRD pattern is correspondent to red P, which has three obvious peaks.

Fig. 4.21. XRD result of red P/CB composites after 1 hour ball-milling

Then, electrochemical performance of red P/CB was carried out. The cycle performance was tested under 0.05C. Also, the comparison between pure red phosphorus and the composited will be demonstrated.

Fig. 4.22. Performance of red P and CB composites after 1 hour ball-milling a) First cycle charge/discharge b) cycling

At its initial cycle in Fig 4.22, the specific capacity is around 2276 mAh/g, then at second cycle, its recoverable specific capacity drops to 1885 mAh/g, after that, the capacity

continues decreasing until 20th cycles, and it became stable at 305 mAh/g. When compared to pure red phosphorus, the composites shows better performance. After 20 cycles, the capacity retention rate for pure red P and the composites are 12.5 % and 16.2 %, respectively. The slightly improvement of stability of electrode can be attributed to the existence of carbon. Although the initial capacity of both anodes is high and close to their theoretical capacity, its capacity drops dramatically only after few cycles, thus, it is necessary to further improve the capacity retention rate of red phosphorus anode. Here, longer ball-milling time is considered because longer time can effectively grind large bulk materials into microscale or nanoscale particles, which in turn can accommodate the volume expansion during intercalation. Also, longer time may be benefit for the uniform mix.

2) Red P and carbon black composites --- 16 hour ball milling

Similarly, the structure of red P/CB composites was examined by XRD. From the result in Fig 4.23, it can be referred that the structure of composites has changed. Major peaks moved from origin red phosphorus to other places. According to XRD results, While P and C are still exists in the powder, some Fe, O elements are mixed into the composites, and this may attribute to the long ball-milling time that cause these atoms moved from the container to the composites, which changed the chemical structure of the composites.

Fig. 4.23. XRD result of red P/CB composites after 16 hour ball-milling

Then, electrochemical performance of red P/CB was carried out. From the first cycle charge/discharge curve in Fig 4.24, the reaction process was clearly changed. At its initial discharge cycle, when compared to 1 hour milling sample, which has a platform around 0.2 – 0.3 V, the 16 hour sample has no obvious platform while it discharge with the decreasing voltage. At its initial charge cycle, it has no obvious charge platform as well while 1 hour milling sample has a platform around 0.5 V. This result was caused by the unwanted doping of other elements, and leads to the decreasing content of element phosphorus.

Fig. 4.24. Performance of red P and CB composites after 16 hour ball-milling a) First cycle charge/discharge b) cycling c) Rate

The cycling performance is illustrated in Fig 4.24b. At its initial cycle, the specific capacity is 345 mAh/g, it is quite low as compared to the theoretical capacity of red phosphorus, the reason why the charge platform became less obvious and its initial capacity drop so dramatically attributes to the reaction during long-time ball-milling. The red phosphorus change to another material consists of P, O, and Fe. Surprisingly, this material has a

superior stability after long cycles. The results show that after 50 cycles, its capacity retention rate is near 90 %, and even after 200 cycles, its capacity retention is higher than 85 %. As to its rate performance, the testing is under 100 mA/g, 200 mA/g, 500 mA/g, 1000 mA/g, 2000 mA/g, 3000 mA/g, 4000 Ah/g, 5000 mA/g, and then back to 100 mA/g. This material also shows good reversibility even after high reaction current density.

2) Comparison between pectin and PVDF in 16 hour sample

From the results shown below in Fig 4.25, the pectin binder demonstrates relatively better performance than PVDF in sodium-ion battery.

It can be concluded that pectin shows both good cycling and rate performance and owns higher specific capacity and higher capacity retention rate when compared to PVDF, the reason here is the same as in lithium ion battery, the pectin has stronger mechanical properties than PVDF.

Fig. 4.25. Performance of red P and CB composites between pectin and PVDF a) cycling b) Rate

Besides, the thermal split graphene is also used, the results is illustrated in Fig 4.26.

Fig.4.26. Cycling performance of red P and CB/graphene composites

Clearly, carbon black is more suitable and has better cycling performance in the composites. In conclusion, red phosphorus with carbon black composites has better electrochemical performance than pure red phosphorus, and pectin plays an important role in holding the structure integrate. Long-time ball milling will result in forming new structure instead of keeping the structure of red phosphorus, and the produced chemicals shows good cycling stability, but poor specific capacity. In future work, it is necessary to figure out the mechanism behind this change.

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Chapter 5

Discussion and Future Work

In this chapter, all works mentioned above in the project are discussed in short. The rationale behind the choice of active material and binder are demonstrated respectively. In addition, methods for modifying binder and the relating mechanism are introduced. The new binder helps to improve the electrochemical performance of both lithium ion and sodium ion battery when compares to traditional binders PVDF. Moreover, some proposals for future work is introduced, including justifications for approaches, resources required, challenges and solutions. In addition, the opportunities and strategies for future work are put up. Following this proposed schedule, a feasible plan for future research is established.

5.1 General discussion

5.1.1 Weight ratio of active materials

In the first section of this project, the proper weight ratio between nano silicon particles and graphene was decided. The rationale behind the final choice is: with the increasing content of graphene or carbon black, the stability of the whole electrode is increased. However, the absolute capacity of the electrode will decline. While the aim of the research is to find a way to improve the cycling stability of silicon-based lithium-ion battery, the main advantage of silicon should not be compromised.

The weight ratio between silicon and graphene is chosen as 9:1, 7:3, 5:5, and 1:3 at initial. After considering the capacity retention rate of each electrode, which are 35 %, 25 %, 53%, 84 %. The capacity retention of Si50 increase more than twice when compares to Si30. Although the retention rate of Si75 is higher than Si50, the content of graphene is higher than acceptable. Thus, Si50 is selected as the active material in the following experiments. Given the retention rate of Si50 is not high enough after 100 cycles, a method to further improve the stability of battery is needed.

The graphene that has been doped into composites so far are commercially available and obtained through thermal striping process, which leads to the poor ability for dispersing uniformly in water, and this character will cause inhomogeneous mixing of active materials. Inhomogeneous mixing can cause the poor stability of electrode. Take this factor into account, another lab-made graphene or RGO (reduced graphene oxide) is employed in anode.

The capacity retention rate of RGO contained electrode with 50 wt. % of silicon after 100 cycles reached higher than 70 %, which is a further improvement of the stability

In conclusion, the mix of graphene into silicon battery is necessary to improve the stability while the weight ratio needs to be controlled in order to have a high specific capacity which

is the main advantage of silicon-based lithium-ion battery. Besides, different forms of carbon should also be carefully considered to better suits the cells in the experiments.

5.1.2 The choice of binder and its counterparties

Firstly, pectin extracted from citrus is chosen as the experimental binder in this project, because it is extracted from organic fruits so it is environmentally friendly and distributes widely. Besides, pectin is water-soluble, and does not need other polymer solvent during the production process, thus, the pectin binder is less harmful to both environment and workers

Then, pectin also meets the prerequisites of binder which are listed as:

- (1) A weak interaction between binders and electrolyte should be included for stable performance of batteries.
- (2) An ideal binder is supposed to provide enough access for Li ions to silicon surface for reaction
- (3) A stable solid-electrolyte interphase (SEI) layer is or crucial to long-term stable performance for silicon-based batteries, so an ideal binder should assist this goal to achieve.
- (4) Other requirements, like the binder should have a strong mechanical strength to hold the structure together even undergoing dramatically deformation.

PVDF is chosen as the comparable in the experiment because it is the most widely used binder in carbon based LIBs in the industry. It is cheap and has good stability during the reaction, however, it is poisonous and shows unsatisfactory performance in silicon based batteries.

Besides PVDF, other biomass extracted binders are also tested and compared to pectin, including apple pomace and alginate. Both of them shows relatively good performance. Biomass extracted materials are cheap, widely available, and using these abandoned materials also protects the environment. They are safe and clean, has no harm to bodies,

which makes it more preferable than other traditional polymer binders. In future work, more types can be tried and tested to find more possibilities and apply these biomass materials can bring society with a huge economic and environmental benefits.

5.1.3 Modification of pectin

The pectin is extracted from citrus peels, which explains its biodegradability during the reaction. Thus, in order to keep its functionality, one possible modification method was introduced.

In this project, pectin is modified through esterification reaction with citric acid. The integrity of the electrode would be destroyed during cycling, so find a way to increase the ability of the binder to hold the active materials integrated is another way to improve the performance of electrode. During the esterification reaction process, a strong polymer network will form and improve the mechanical strength of electrode and keep it stay integrated

From the testing results, the specific capacity gradually increased at initial, at around 50th cycles, the specific capacity reaches highest, then gradually decreased. At the second cycle, it has a specific capacity of 971.6 mAh/g, and after 50 cycles, it reaches 1402.0 mAh/g, which is more than its initial capacity. Finally, after 100 cycles, the specific capacity declines to 1154.9 mAh/g, still, it's higher than the second cycle. Although the results show a tendency to keep decreasing after 100 cycles, the capacity retention rate of this new electrode at first 100 cycles still proves the better performance of the modified.

From the rate testing result, the performance seems only improved very little. Besides, due to the high temperature used in the heat treatment process, and the limited vacuum degree the machine can achieve, a large quantity of nano silicon particles might be oxidized, which cause the total mass of electrode to increase and the mass of active material to decrease.

In future work, firstly, the high vacuum degree needs to be achieved in order to prevent silicon from oxidized. Other alternative ways are supposed to be found to improve the efficiency and reliability of binders.

5.1.4 Applying pectin to sodium ion battery

Lithium ion batteries have achieved great success in many areas, including portable devices, electric cars as well as other fields. However, with the increasing demand for lithium resources and its limited storage volume in the earth, the price of lithium ion battery will dramatically increase in foreseeable future. Thus, scientists turn their eyes to a new element, sodium, which has similar intercalation mechanism as lithium, and has much more abundant storage in the earth, which makes it easier and cheaper to use it in batteries.

In this project, the experiment will use pectin to replace traditional organic binder PVDF to fabricate cells and test the performance of SIBs. Firstly, pure red amorphous phosphorus is used as anode material, then red phosphorus (red P) and carbon black (CB) hybrid material are prepared with different ball-milling time to improve its electrochemical performance. The comparison between pectin and PVDF is also be illustrated.

As the performance of 1-hour ball milling material is not satisfying, the reaction time was extended to 16 hours to ensure the complete reaction between red phosphorus and carbon black. The results show that after 50 cycles, its' capacity retention rate is near 90 %, and even after 200 cycles, its capacity retention rate is higher than 85 %.

However, according to the XRD results, another material consists of P, O, and Fe is formed. For its rate performance, the testing is under 100 mA/g, 200 mA/g, 500 mA/g, 1000 mA/g, 2000 mA/g, 3000 mA/g, 4000 Ah/g, 5000 mA/g, and then back to 100 mA/g. This material shows good reversibility.

It is not surprising that pectin outperforms PVDF in sodium ion battery. In conclusion, red phosphorus with carbon black composites has better electrochemical performance than

pure red phosphorus, and pectin plays an important role in holding the structure integrated. Long-time ball milling will result in forming new structure instead of keeping the structure of red phosphorus, and the produced structure shows good cycling stability, but poor specific capacity. In future work, it is necessary to figure out the mechanism behind this change.

5.1.5 Justification for Approach/Breadth of Research

In future work, the breadth of research will be broadened to sodium-ion and other kinds of batteries, and further investigate underlying mechanism and methods to improve the stability. It is reasonable because Lithium-ion and Sodium-ion batteries have very similar reaction mechanism and fabrication process. If the application of the binder in sodium-ion batteries is proved useful, then widening the application range of pectin can be considered, and thus build a complete eco-system for pectin employed in batteries. Furthermore, promoting the application of pectin in manufactures, which can bring a more green and economical ecosystem for battery industry.

Second, the declining capacity may be attributed to the decomposition of binder, so it is necessary to confirm whether the binder is stable in the reaction process and how to improve its stability to keep the active materials in anode integrated by other methods.

In conclusion, improve the stability of binder can make battery more stable during cycling and keep high capacity retention rate after cycles; Testing the performance of pectin in sodium-ion battery is a step to widen the application range of pectin.

5.1.6 Resources Required/Available

Database resources: A polymer molecules database is needed to find the structures of pectin and some polymers related to it, and how to modify the functional group of pectin to let it have different chemical properties should also be included. First, many databases are available in NTU library and it is useful to look through.

Experimental resources: Materials related to synthesize and fabricate anode and batteries are needed and these materials are available in lab.

Characterization resources: Many characterization machines are needed to characterize the performance of material or batteries, including SEM, XRD, and battery testing system, etc.

5.2 Reconnaissance work not included in main chapters

Works can be divided into two parts:

- (1) Modification of binder by changing its functional groups to make it more stable during reaction time. Till now, esterification of pectin has been tried with citric acid. Another feasible way is employing a mixture of different bio-extracted binders. For instance, pectin and alginate was examined in the project. Because they are both biomass extracted, no extra polymer reagents are added into the binder, thus it's the same as clean and healthy as pure pectin. Second, they both have abundant functional groups like hydroxyl and carboxyl, therefore, they can undergo esterification reaction during heat treatment to form a strong interlink network to hold different parts of anode together. The obtained result shows relatively close performance as compared to modified citric acid. Further, besides esterification reaction between polymers, analysts can turn to some inorganic reagents, such as Ca^{2+} . According to the paper of Li Zhang, et. al [3], they reported using Ca ion to form a 3-D cross-linked polymeric network to help silicon to withstand the large volume expansion during cycling.
- (2) The pectin binder used in silicon based lithium ion battery achieved better performance than PVDF, and there are many other green binders can be applied to lithium ion battery. In this project, apple pomace and alginate were used as binder as well. The cycling performance of apple pomace and alginate is slightly worse than pectin, however, they shows similar performance with pectin under rate testing.

5.3 Outstanding questions

Firstly, it is hard to find methods to modify pectin used in batteries. Lacking of references is one serious confinement for progress. One of the possible solutions is to find out under what situation will pectin become unstable and how to avoid it in battery. For example, pectin is more stable under weak acid environment, so strong alkali should be avoided. Then, finding a possible approach to modify the functional group on pectin to make it more stable while keeping its functions.

Moreover, decreasing the content of carbon used in lithium ion battery is another issue. For application, it's necessary to improve the specific capacity while maintaining the stability after long cycles. The ratio of carbon used in silicon based lithium ion battery has been decreased to 50 wt. %. In future work, in order to further decrease the content of carbon, developing a more stable structure of silicon, such as hollow structure needs to be considered.

Another issue is related to the application of pectin to sodium ion battery. Sodium ions are bigger than lithium ions, so it is harder for them to intercalated into layered materials, and thus make the structure even more unstable. In this case, applying pectin binder to sodium ion batteries may be insufficient, so it is also necessary to adopt some composites or structures in sodium ion battery.

In conclusion, this project has improved the stability of silicon based lithium ion battery by adopting the new biomass extracted pectin binder, but the performance need to be further enhanced in future work through ways mentioned previously. In addition, other applicable fields need to be explored, including the sodium ion battery, the mechanism behind the function of pectin needs to be investigated as well. Works have been done in the project solve some real problems and improve the performance of current batteries, while still remain some insufficient points to be improved in future work.

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