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Master's Thesis

Design of polymeric binder
for lithium-ion batteries with high energy density

Jimin Kim

Department of Chemistry

Graduate School of UNIST

2018

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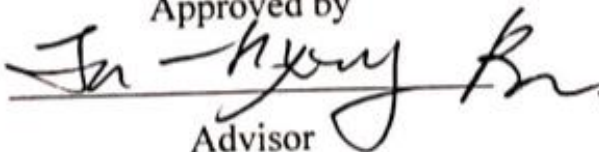
Graduate School of UNIST

Design of polymeric binder
for lithium-ion batteries with high energy density

A thesis
submitted to the Graduate School of UNIST
in partial fulfillment of the
requirements for the degree of
Master of Science

Jimin Kim

June / 12 / 2018

Approved by

Advisor

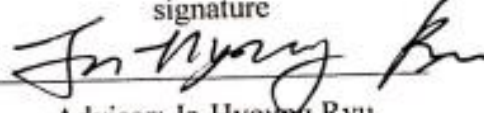
Ja-Hyoung Ryu

Design of polymeric binder for lithium-ion batteries with high energy density

Jimin Kim

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Abstract

Due to the environmental issue, electronic energy becomes more important and is more applied to various yield. As increasing demand for high energy density and high capacity, many researchers make an effort to increase the capacity and energy density of the battery.

One method is using the high theoretical capacity material. Si has received attention as the active material in anode due to its high theoretical charge capacity. However, the Si anode has a big challenge result from the large volume expansion (>300%) during the lithiation. This expansion causes isolated Si and rapidly fading the capacity of the electrode. To alleviate this ephemeral ability, we introduce boronic acid polymeric cross-linker for stable binding of Si. Boronic acids of crosslinker form stable chemical crosslink with vicinal hydroxyl groups of binder. And we utilize guar gum as main binder material which has high viscosity and abundant alcohol groups. It can form dynamic chemical crosslink with boronic acid. Cross-linked binder efficiently grasps expanded Si and prevents isolation of contracted Si. This crosslinking bond between boronic acid and guar gum will maintain electrode and eventually improve lifetime and capacity of Li-ion battery.

The other is making a composite of graphite and high theoretical capacity material. Graphite is a conventional active material which has little volume expansion but low capacity. And High theoretical capacity materials have high volume expansion. So these are big problems for practical use. One solving method is mixing a small amount of high capacity material to conventional material. Although the small amount of high capacity material also makes high volume expansion, we can increase capacity and control expansion of electrode. There is a need for a new binder to prevent volume expansion and interact with two active materials. We design hydrophobic styrene and hydrophilic alcohol and acrylate units contained random-co-polymer. Styrene group has interaction with graphite and hydrophilic units have interaction with Si and a current collector. This polymer has stable interaction with two active materials and maintains integrity during the charge-discharge cycle.

By changing anode material, demanded binder properties are also changed. Suitable properties of binder can maintain their integrity and give an improved lifetime to the battery.

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Chapter I. Introduction to binder in anode

1.1 introduction of binder

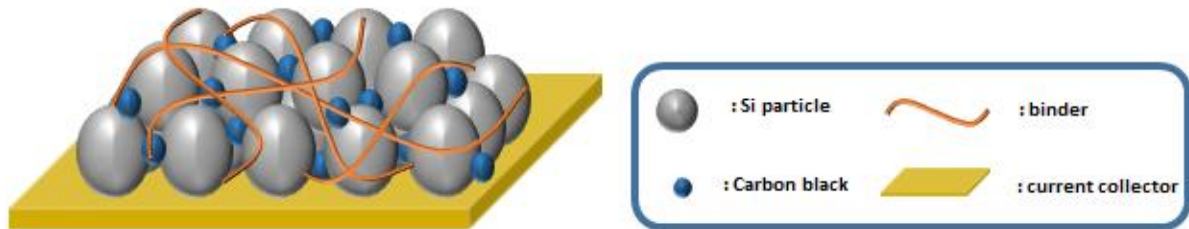


Figure 1.1 illustration of electrode structure

Environment pollution and global warming come to the fore as an important global issue. To reduce pollution result from fossil fuel, many alternative energies are developed and studied. Among them, lithium-ion battery is attracted power source due to high energy density and good cycle-ability. [1-3] Lithium ion battery applied to various portable devices and heavy machine like electric vehicles. Therefor various properties (flexible, high energy density and etc.) [4,5] demanded for application. For various application and making properties, understanding of electrode structure and component is important. Convention electrode consists of an active material, conductive material, binder and current collector. The active material is the main component in the electrode and reacting material for electrochemical reaction. The capacity of the battery is decided by this material. Conductive material enhances low conductivity of the active material. Binder is giving adhesion property between materials and the current collector. This three materials were mixed to a slurry and were casted in current collector. For making application many people made effort to change material. Among them, for high energy density battery, many methods were tried like changing active material or structure. But in high energy density battery means more electrochemical reaction and volume expansion during the cycle. This problem cause unstable cycle-ability and short lifetime of the electrode. To solve this problem binder has an important role to maintain the integrity of electrode.

Many research made effort to apply various nature polysaccharide as the binder in anode due to cheap cost and the abundant hydrophilic functional group which guarantees good adhesion with the current collector. CMC (carboxymethyl cellulose), one of the conventional binder in the lithium-ion battery, is also natural polymer. Natural polymer doesn't need to cost and time for polymer synthesis. And abundant hydroxyl and acrylic group in side chain give high interaction due to hydrogen bond and ion-dipole interaction with active material or current collector. Also it can be easily modified to various

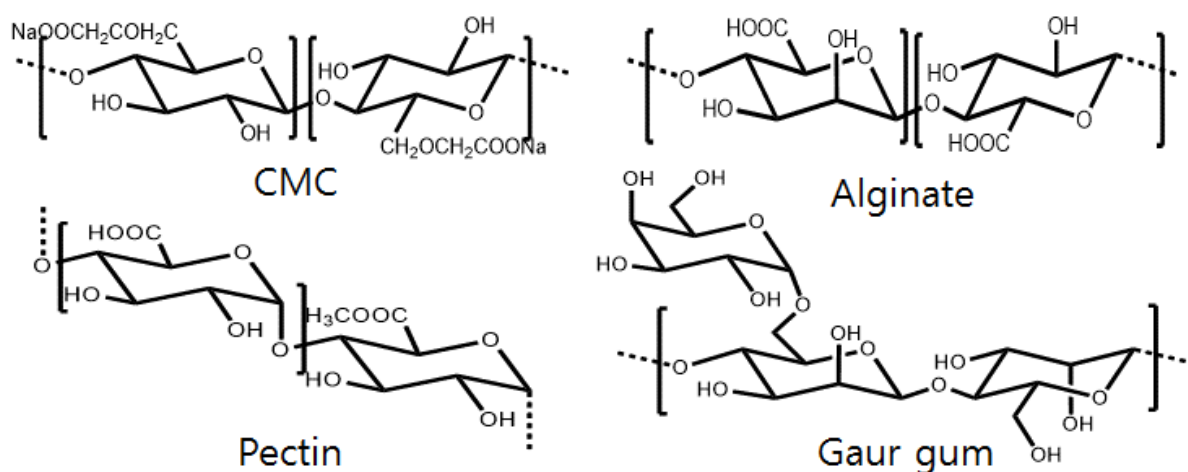


Figure 1.2 Chemical structure of CMC, alginate, pectin and guar gum.

functional group giving function in the binder. Alginate has self-healing ability when applied to the binder in silicon anode due to hydrogen bonding between OH groups of the side chain.^[6] Also the acrylic group of alginate can be physically crosslinked by adding metal ion.^[7] Natural polymer has various structure and structure giving different effect to the interaction between materials. Pectin has β-linkage in the structure which gives elastic property due to conformational transitions. This elasticity high stability to the electrode during big volume expansion.^[8] Guar gum is also good natural binder in silicon anode due to numerous hydroxyl group.^[9]

This natural polymer application to binder gives a clue for polymeric binder study by analysis electrochemical performance and mechanical properties. And to make the high energy density and stability of battery, many research and analysis should keep studying for the binder.

Chapter II. Network structure polymeric binder for silicon anode

2.1 Introduction

2.1.1 Polymeric binder for Silicon anode

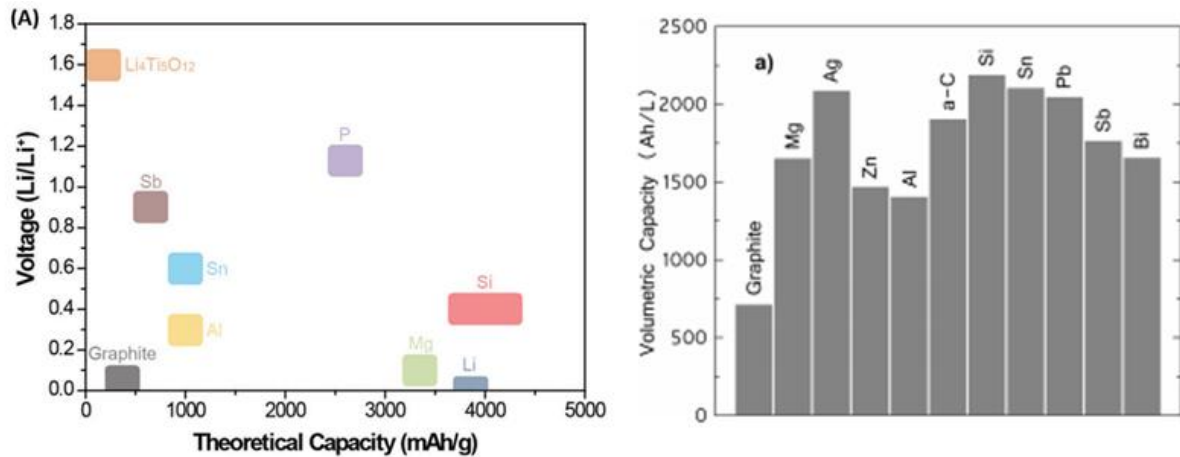


Figure 2.1 graph of theoretical capacity and voltage of active material ^[10,11]

High theoretical capacity material (Si, Ge, and Sn) ^[12-14] is one method for increasing energy density. Among them, silicon is a promising material for high energy density battery as anode active material in the lithium-ion battery. Figure 2.1 shows theoretical capacity and volumetric capacity of anode materials. Silicon has a high theoretical capacity (3572mAh/g at Li₁₅Si₄ state) ^[15-17] which is about ten times higher value than conventional anode material, graphite. But there is a big challenge for practical application of silicon as anode material due to volume expansion (over 300%) during the lithiation process. ^[18-21] Figure 2.2 shows that challenges of silicon anode during charge-discharge cycle process. During the electrochemical reaction between lithium ion and silicon particle, Solid Electrolyte Interphase (SEI) layer was formed in the surface of silicon due to the side reaction result from the big difference of ion transfer conductivity between silicon and lithium ion. This SEI helps to react between the active material and lithium ion as a pathway. But in silicon cases, silicon has big volume expansion and contraction during the charge-discharge cycle and it cause SEI broken during the cycle. Then SEI reformed continuously due to an exposed silicon surface. Eventually, after many cycles, thick SEI layer is formed in the surface of silicon and it causes high resistance and long distance of ion transfer. And

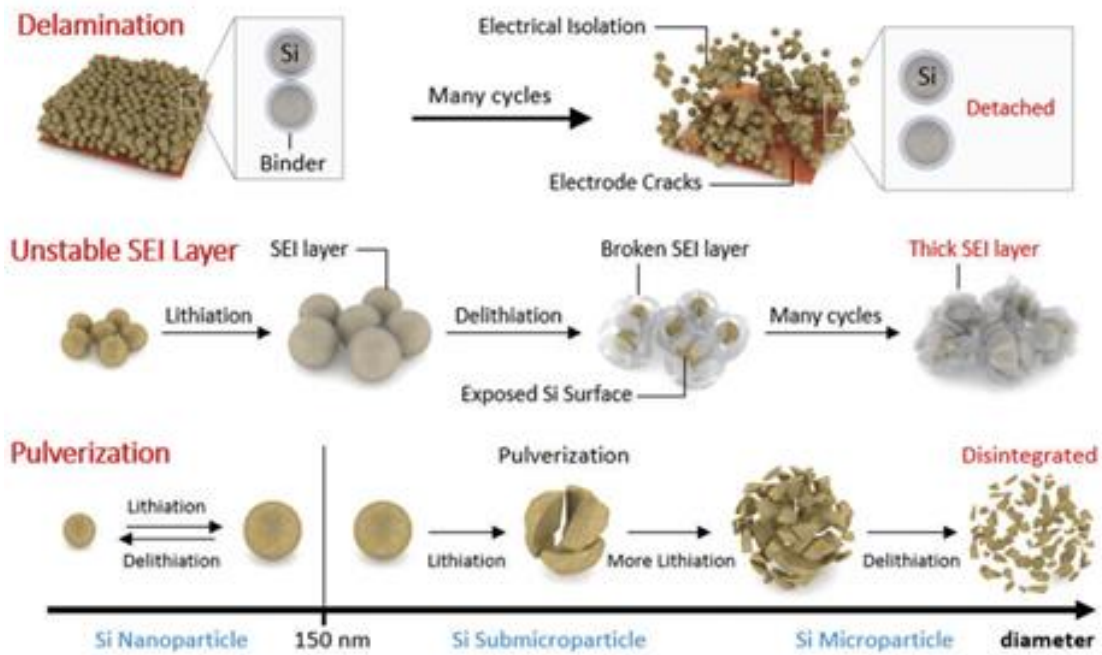


Figure 2.2 Illustration of silicon material challenge during the cycle ^[10]

due to big volume expansion and low adhesion silicon lose electrochemical contact between silicon and the current collector. Also, the electrode loses working active material and have cracks. Eventually capacity is rapidly fading due to delamination of silicon electrode.

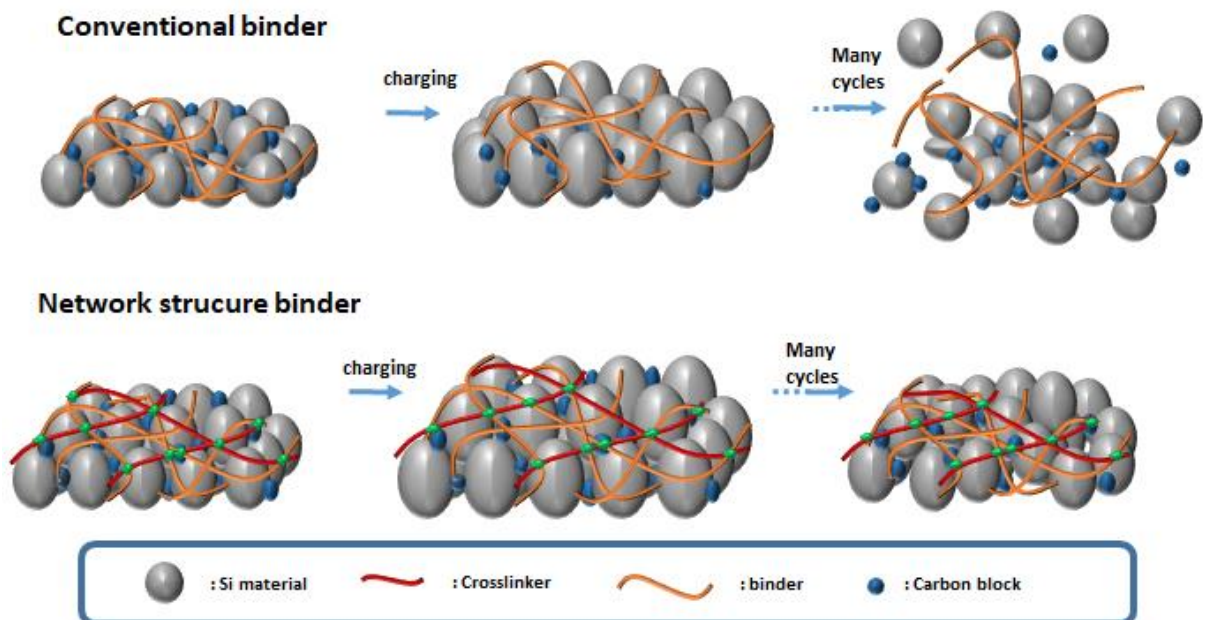


Figure 2.3 Schematic image of electrode integrity change during charge-discharge cycle

To overcome this challenge of silicon, the polymeric binder is important for improving the stability of integrity during the charge-discharge cycle. Conventional binder, polyvinylidene difluoride (PVDF),^[22] has a linear structure and weak van der Waals interaction with active material. Therefore it is slid and can't grasp silicon particle during the cycle. Eventually, electrode loss working active material and capacity is rapidly fading. To grasp silicon particle during charge-discharge cycle and maintain integrity, many researchers studied net-like crosslinked structure which can enhance the stability of electrode integrity and have good cycle life to silicon electrode.^[23-25]

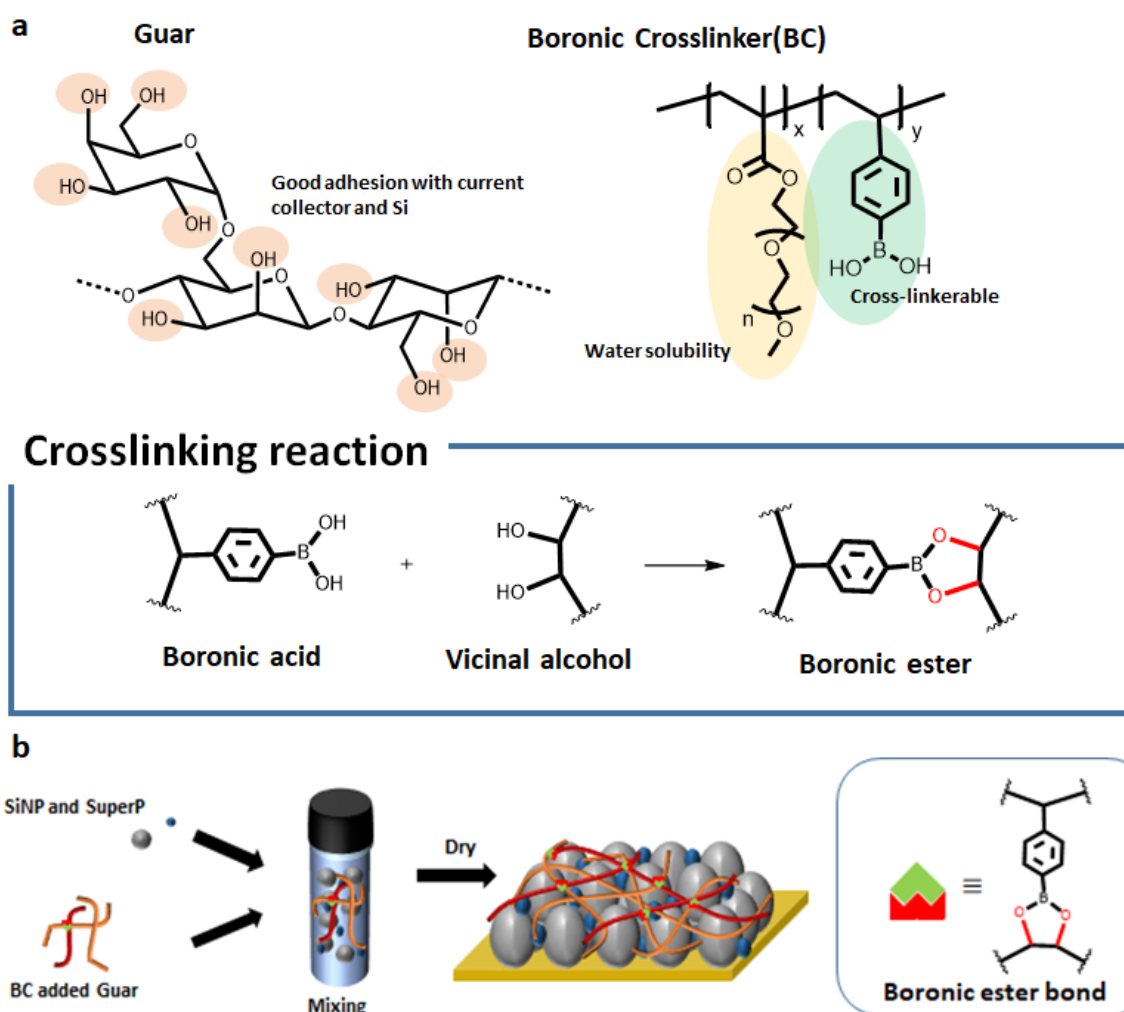


Figure 2.4 a) Chemical structure and crosslinking reaction of guar and boronic crosslinker, b) Schematic illustration of electrode preparation process

We also design crosslinked natural binder using boronic crosslinker for forming bonds between vicinal alcohols and boronic acid group (Figure 2.4 a). Guar gum is natural polymer from the endosperm of the guar or gavar bean and has abundant hydroxyl groups in the back bond and side chain. This

hydroxyl group has good adhesion with the current collector and Si and enhance the stability of electrode integrity. ^[26] We design boronic acid contained crosslinker for making networking polymer binder. Boronic crosslinker has poly (ethylene glycol) and phenylboronic acid unit. Boronic acid can spontaneously form two boronic ester bonding with a vicinal hydroxyl group. For giving water solubility properties to boronic crosslinker we used PEG monomer in the synthesis of boronic crosslinker. Many polysaccharides have high solubility in water and we want to crosslink with polysaccharides so we gave water solubility property to crosslinker. And PEG group has high lithium ion transfer conductivity due to coordination bond of lone pair electron in the oxide. ^[27-30] Boronic crosslinker and guar can form crosslink bond by just mixing two solution without any treatment. Figure 2.4 a shows schematic illustration of boronic acid added guar binder electrode preparation process and crosslinking between guar and boronic crosslinker. Before dry process of electrode, some crosslinking was already formed but in dry process water was evaporated and solution concentration was increased. That time crosslinking density was increased and network of binder formed. By controlling concentration of guar and crosslinker solution we can make proper viscosity binder solution for making slurry casting.

2.2 Experimental

2.2.1 Materials

4-Vinylphenylboronic acid purchase from Matrix Scientific. Guar, poly (ethylene glycol) methyl ether methacrylate ($M_n \approx 300$, PEG) and Aluminum oxide from Sigma-Aldrich is used. 2, 2-Azobis (isobutyronitrile) was obtained from JUNSEI. Potassium hydroxide was got from SAMGHUM, Korea. THF was obtained from HoneyWell, Korea. Silicon powder (50nm size) was purchased from Alfa Aesar, Korea.

2.2.2 Boronic crosslinker synthesis

Monomer filtered with Aluminum Oxide for removing inhibitor. PEG (1.36g, 4.53mmol) was dissolved to THF in well dried 25ml round bottom flask. 4-vinylphenylboronic acid (1g, 6.8mmol) and 0.2g AIBN was added to a mixture. Then connected long needle with Ar gas and short needle of outlet for 30min to remove oxygen. And heat mixture at 70°C for 1day with stirring. After the polymer is solved THF and purified by precipitation in ether two times. This polymer was characterized by 400 MHz $^1\text{H-NMR}$ spectroscopy, gel permeation chromatography (GPC, Agilent Technologies, Santa Clara, CA) and FT-IR.

2.2.3 Hydrogel characterization

To examine mechanical properties of different crosslinker added hydrogel, hydrogels were measured using rheometer (Haake MARS III – ORM Rackage, Thermoelectron). Hydrogel made 1wt%.

2.2.4 Electrochemical measurement and morphology

Polymer film for testing electrochemical stability was prepared by drying 1w% polymer solution after casting in Cu foil. Cyclic voltammetry of polymer film measured in from 0.01V to 3V voltage range.

In the electrochemical characterization, the carbon coated silicon anodes were fabricated by traditional slurry coating technique, wherein the composition ratio of the anodes was carbon-coated silicon active material (80 wt. %, Alfa Aesar, 50nm size), Super-P as an electro conductive agent (10 wt. %) and boronic cross linked polymer as an anode binder. The half cells which composed lithium metal as counter electrode and carbon coated silicon anode as working electrode were fabricated by using a 2032 R-type coin cell (= carbon coated silicon anode/Liquid electrolyte/Li metal). Used electrolyte consisted of 10w% fluoroethylene carbonate and LiPF₆ (1.3M) in ethylene carbonate and

diethyl carbonate (3: 7 volume ratio). Half-cells were tested in the voltage range of 0.005 to 1.5 V at 0.05 C for formation cycle and 0.01 to 1.2 V at 0.1 C for cycle performance. The cells were tested with WBCS-3000 battery cycler (Wonatech Co.) at 25°C. After cycles electrode surfaced was observed using scanning electron microscopy (Hitach High-Technologyies, S-4800)

2.3. Result and Discussion

2.3.1 Boronic crosslinker synthesis

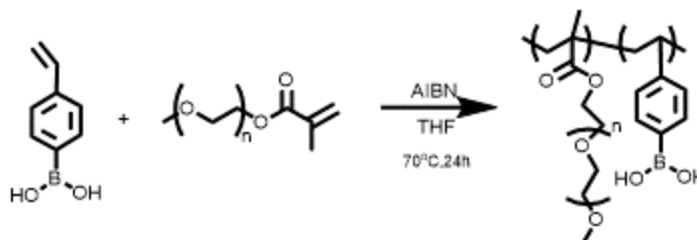


Figure 2.5 Boronic crosslinker synthesis scheme

Boronic crosslinker was synthesized by free radical polymerization of vinyl phenyl boronic acid and PEG ($M_n=950$ and 300g/mol) in THF. Figure 2.7 shows difference ratio of monomer peaks and can be calculated by monomer ratio. First PEG monomer ($M_n=950\text{g/mol}$) was used for synthesizing polymer for giving high water solubility but later it was changed to shorter $M_n=300\text{g/mol}$ monomer because small one has also enough high water solubility and it less hinder crosslinking than the longer one. After polymerization, molecular weights of Boronic crosslinker were measured by GPC (Figure 2.8). By changing smaller PEG monomer, a molecular weight of the polymer is slightly decreased from 33k to 10k Da . Synthesized copolymer was also confirmed by FT-IR spectra. Stretching B-O peak and O-H peak of boronic acid monomer appeared at 1340cm^{-1} and $3200\text{-}3700\text{ cm}^{-1}$ wavenumber and stretching C-O peak of PEG monomer appeared at 1090cm^{-1} wavenumber. This peaks means peg monomer and boronic acid monomer were contained in polymer. These results are evidence for successfully synthesized boronic crosslinker.

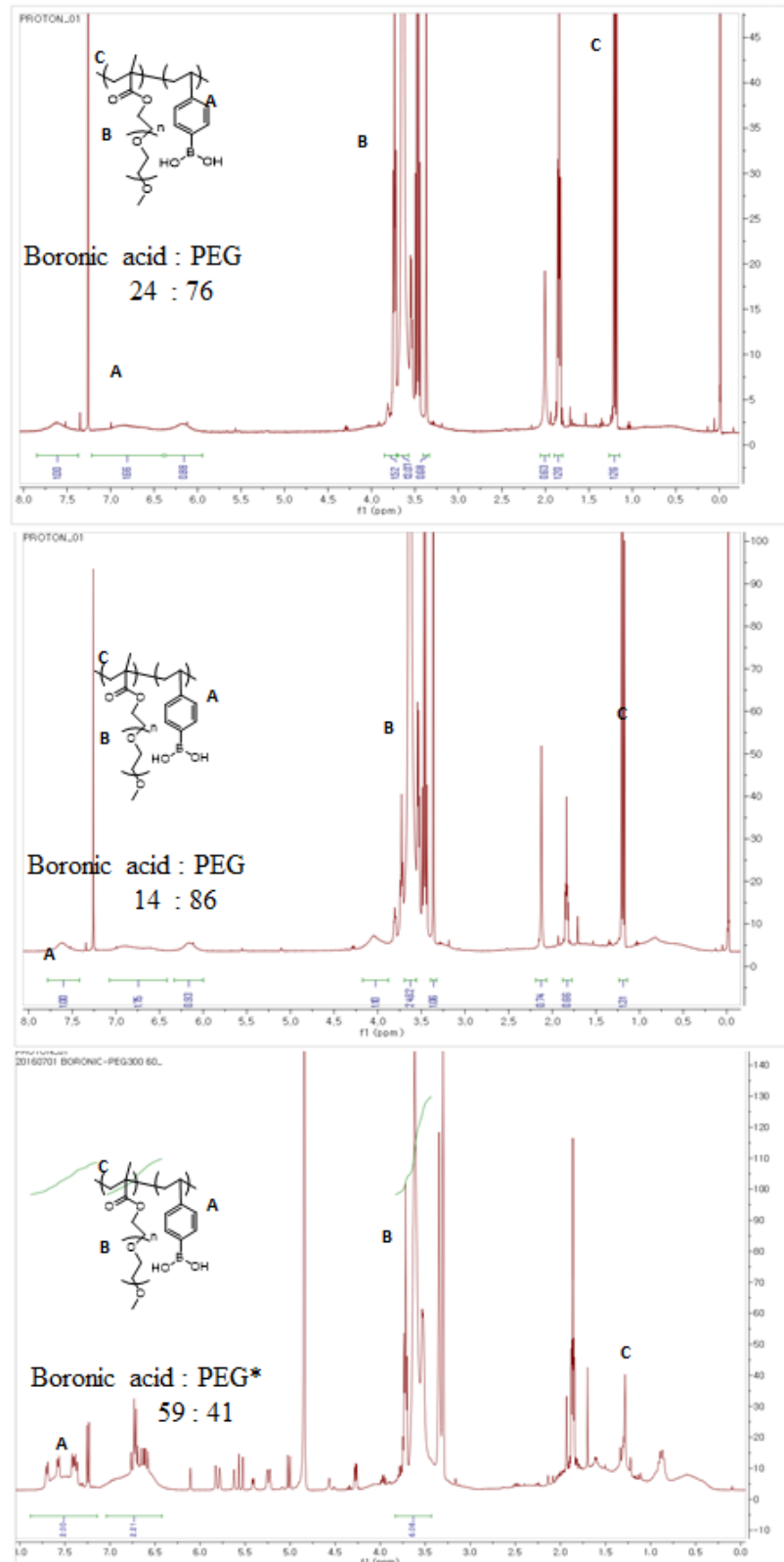


Figure 2.6 $^1\text{H-NMR}$ spectra of different monomer ratio boronic crosslinker (*Boronic acid: PEG = 59:41 crosslinker used $M_n=300$ PES differently with other two which used $M_n=950$ PEG)

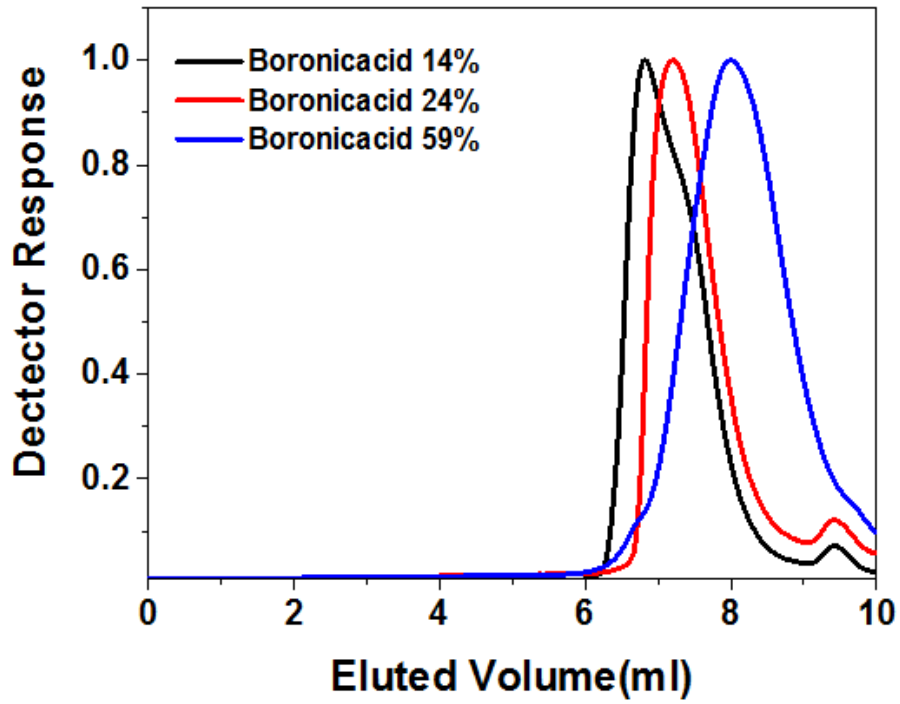


Figure 2.7 GPC peak data of different monomer ratio boronic crosslinker

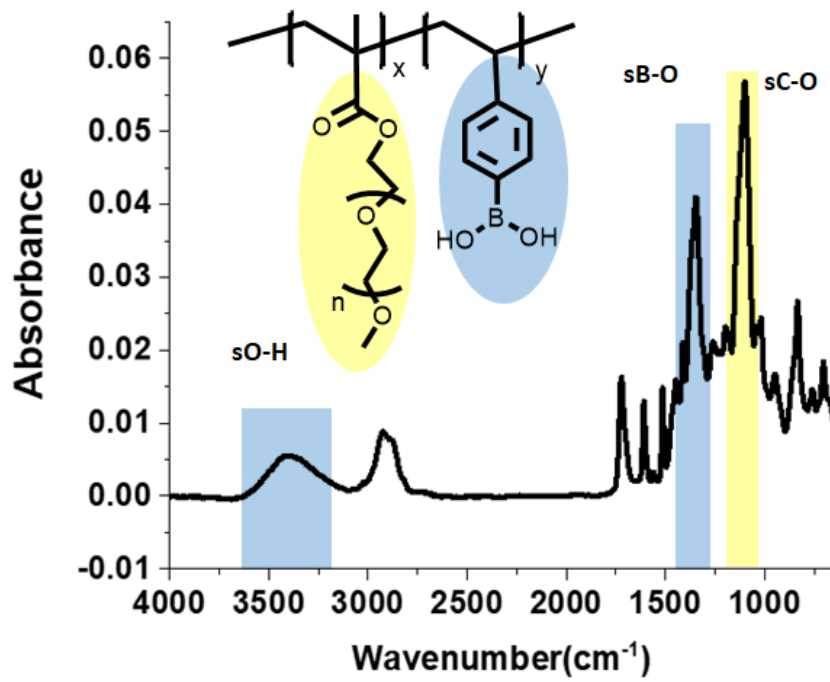


Figure 2.8 FT-IR spectra of boronic crosslinker

2.3.2 Crosslinked guar hydrogel characterization

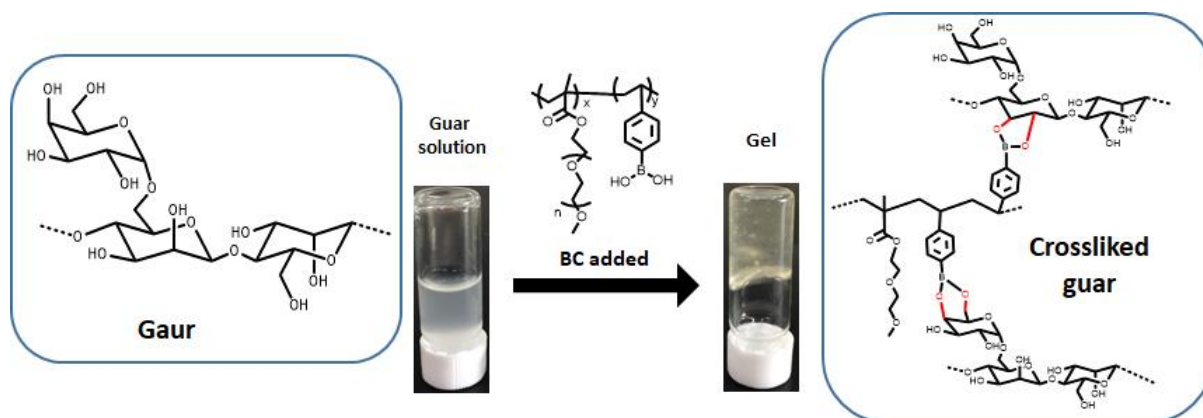
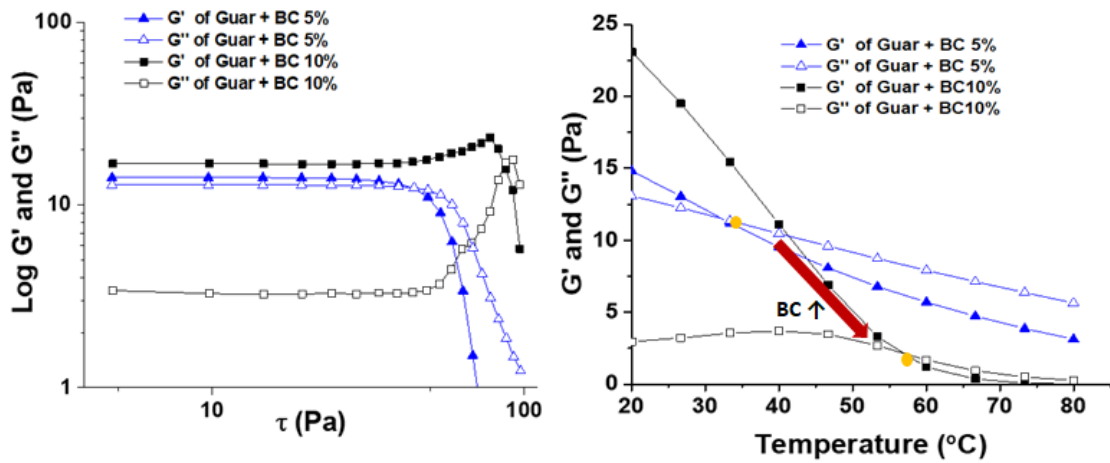


Figure 2.9 Gelation test of guar and boronic crosslinker

Before the testing of the electrochemical performance, we experimented gelation test of guar and boronic crosslinker to check crosslink-ability of boronic crosslinker. By mixing crosslinker with guar gum, polymer crosslinker makes crosslink bonding with guar and forms a gel. Figure 2.10 shows that guar solution is changed to gel after adding boronic crosslinker in solution. Without treatment, covalent bonds between crosslinker and guar are formed. In solution guar dissolve in water and it has low viscosity that can flow to tilted direction. After adding boronic crosslinker, the crosslinker makes crosslinking bonds with guar and solubility of guar is decreased by reducing hydroxyl group and crosslinked structure. This reaction is a spontaneously reversible covalent bond between the hydroxyl group and boronic acid group at room temperature. These bonds make cross-linked network structure between guar polymers and change guar solution to the gel state and high viscosity solution.

Different crosslinker ratio sample (1 wt%)



Different Concentration sample (Guar+BC 10%)

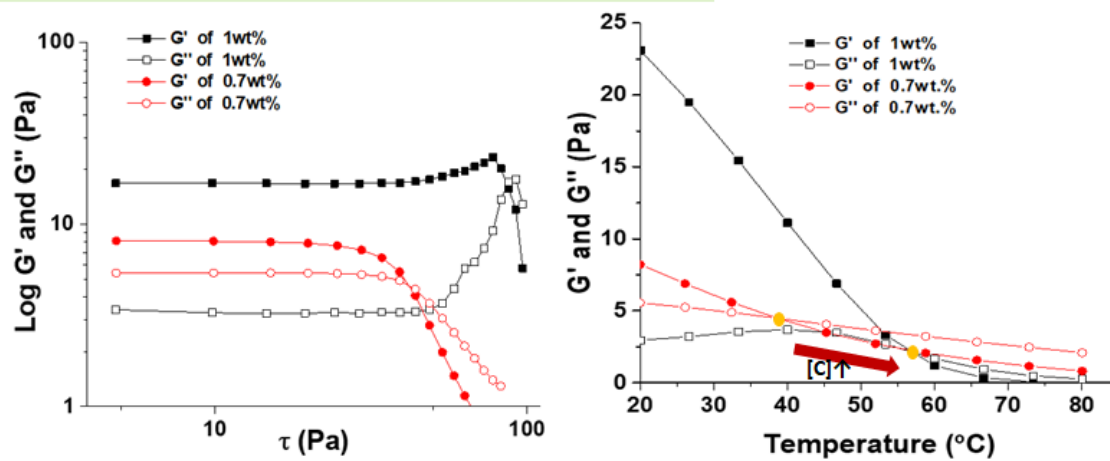


Figure 2.10 Rheology measurement of crosslinked guar gel in different condition (● = crossover point)

To determine mechanical properties of crosslinker added guar gel, rheological behaviors were measured by the rheometer with different crosslinker ratio and concentration. By increasing crosslinker ratio from 5% to 10%, G' (storage modulus) increase and G'' (loss modulus) decrease at 2-100 Pa in Figure 2.10. G' is solid like property, which is shape maintenance tendency when applied stress, and G'' is liquid like property, flow tendency. This results mean that 10% crosslinker ratio sample has higher solid like property and low liquid like property than 5% crosslinker ratio one. Increased G' value of 10% boronic crosslinker added guar gel means that harder gel formed than 5% crosslinker added one. In other words, more crosslinker ratio has more crosslinked gel. The crossover points of G' and G'' (loss moduli) are also increased by more crosslinker added. In this point crosslinked guar gel change into solution state by losing the crosslinked bond between boronic acid and alcohol. This results also confirm

the properties tendency which more crosslinker makes more crosslinked and harder gel. The crossover points which solution-like property (G'') is higher than solid-like property (G') means that gel was changed to the solution. 10% boronic crosslinker added sample has a higher crosslinked point than 5% crosslinker added one because higher crosslinker added sample has more crosslinked points and needs more energy for breaking bond between boronic acid and alcohol group. Also increasing concentration has higher G' and the crossover point, and lower G'' value. By reducing space between crosslinker and gaur, higher concentration has more crosslinked points which give harder properties. We can control mechanical properties of hydrogel to making slurry casting by changing crosslinker ratio and concentration.

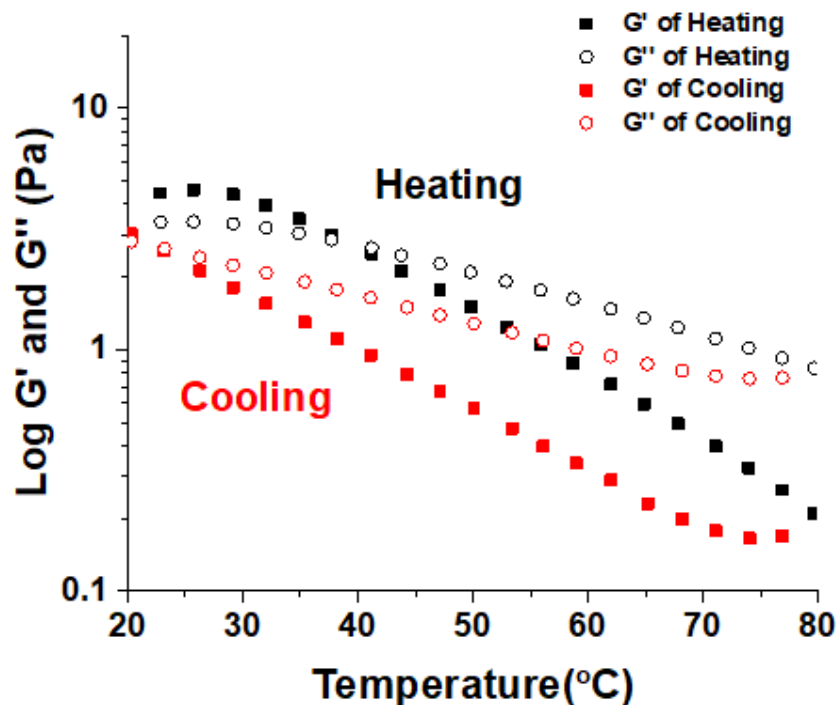


Figure 2.11 Rheology measurement of crosslinked guar gel in heating and cooling condition

To determine reversible mechanical properties of crosslinked guar gel, we measured modulus change during heating and cooling process (Figure 2.11). The crossover points of G' and G'' were different during the heating and cooling process but after heating and cooling process, modulus values were same. This mean that hydrogel recover mechanical properties and crosslinking and mismatching of crossover points mean temperature changing is faster than recover time. However condition of measurement is different with real condition of binder. we guess in electrode crosslinked guar has fast recover due to more thin condition which more fast temperature transfer for making bond of guar and crosslinker.

2.3.3 Electrochemical performance of network structure binder

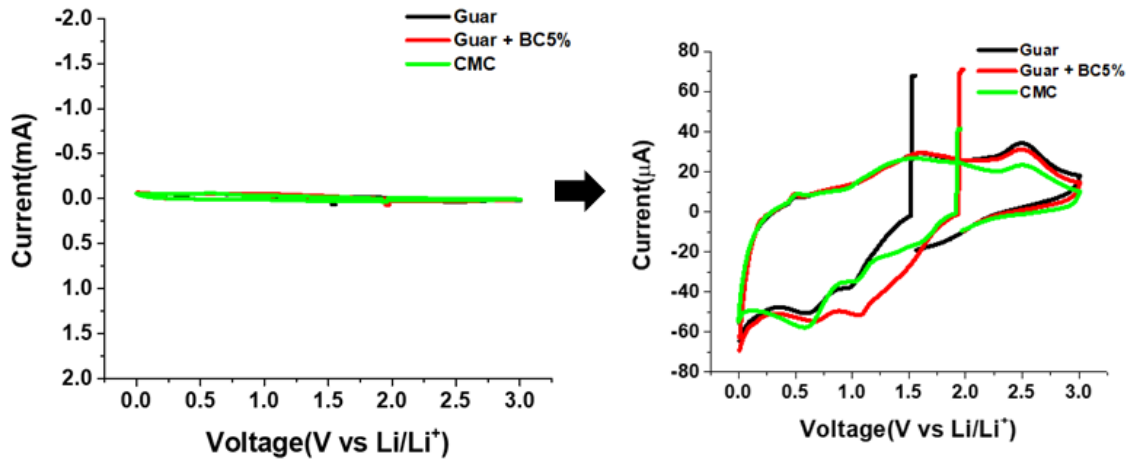


Figure 2.12 Cyclic voltammetry of guar, boronic crosslinker added guar and conventional polymeric binder (CMC) film

Before the electrochemical performance of polymer used electrode as the binder, we measured cyclic voltammetry of polymer binder films to confirm electrochemical stability in the voltage range from 0,01V to 3V (vs. Li/Li+). To apply it as binder, polymer should have high electrochemical stability which prevent continuous reaction with electrolyte and lithium ion. Figure 2.12 shows cyclic voltammetry of reference (guar and CMC) and 5% boronic crosslinker added guar polymer film. All samples have small current range during charge-discharge cycle, which its' current scale is low (μA scale) compared with the electrode (mA scale). This current range of boronic crosslinker added guar is similar to CMC (conventional binder). We assume that this current from the binder is very weak oxidation-reduction than other active material. Therefore this current can be disregardable and acceptable in the electrochemical experiment.

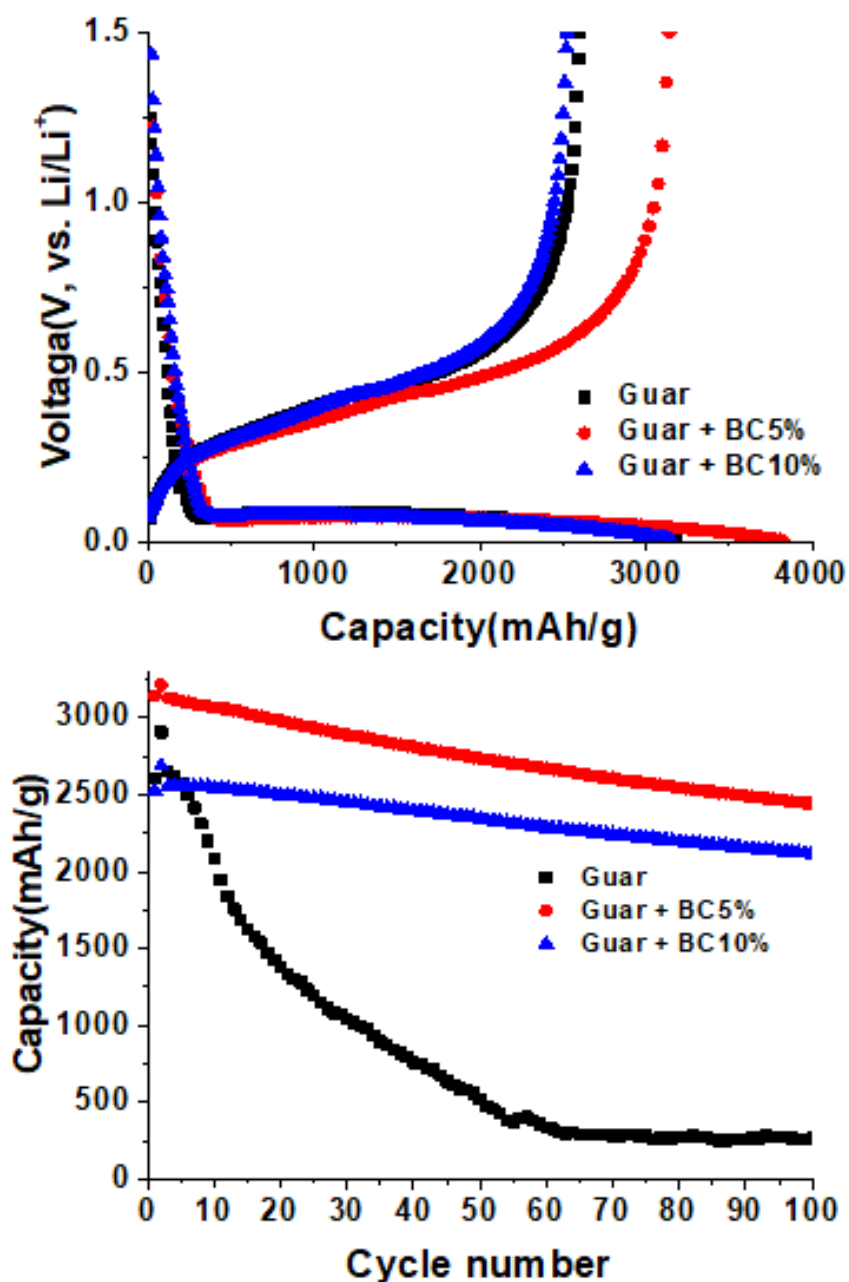


Figure 2.13 Electrochemical performance of guar and boronic crosslinker added guar a) Voltage profile of initial cycle and b) cycle performance

To test electrochemical properties of boronic crosslinker added the polymeric binder, we testing guar without crosslinker as a reference and different ratio crosslinker added binder used electrode. Figure 2.13 shows that high initial coulombic efficiency (81.7 and 82%) of guar and 5% boronic crosslinker added guar binder used electrode. Because guar and 5% boronic crosslinker added guar binder has a similar small oxidation-reduction reaction and similar functional groups which means

interaction with Si particle. In 10% boronic crosslinker has slightly decreased (ICE=80.0%). The capacity of guar binder electrode was rapidly fading during charge-discharge cycle but a cross-linked sample, 5 and 10% boronic crosslinker added guar, maintain capacity during the cycling process.

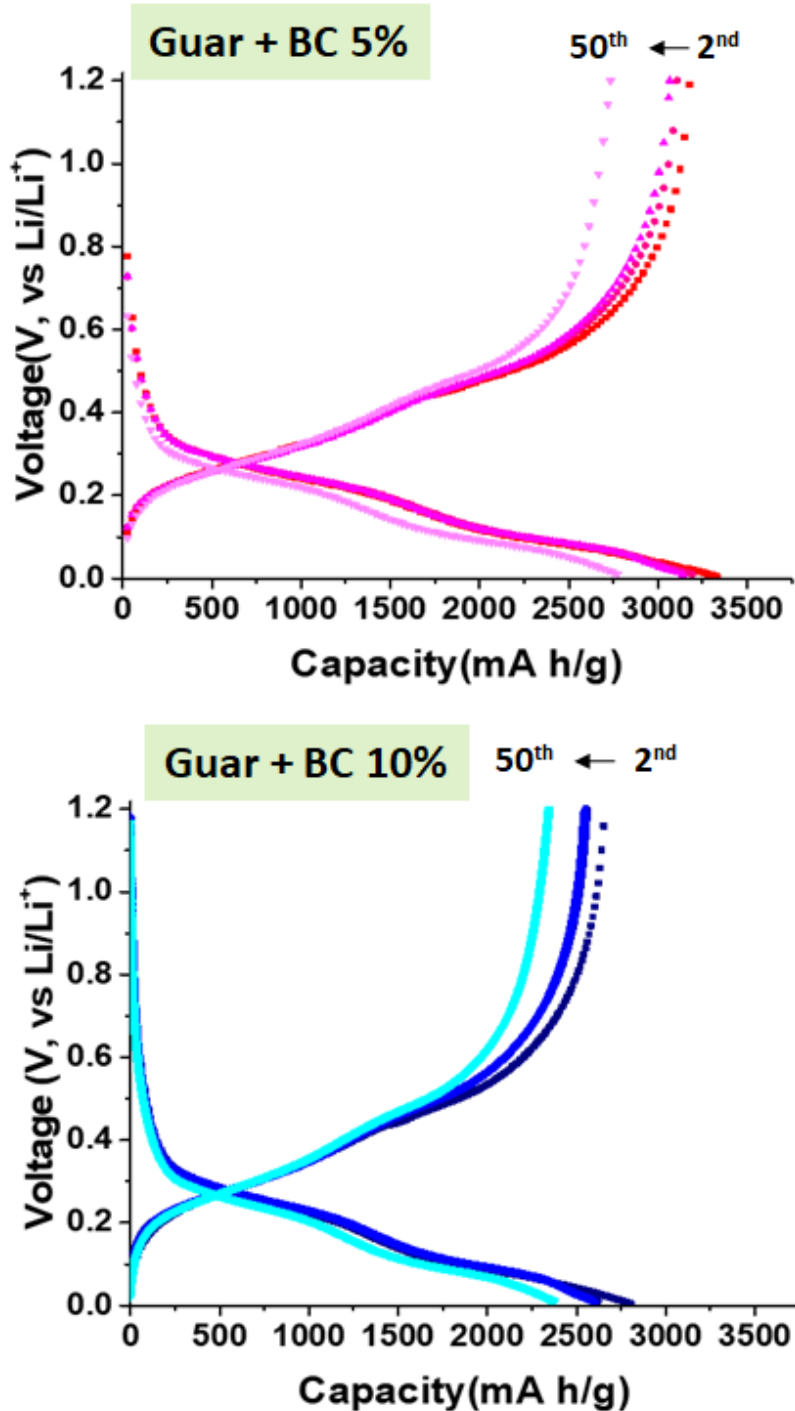


Figure 2.14 Voltage profile of 2, 5, and 10, 50th cycles of 5% and 10% boronic crosslinker added guar binder

5% boronic crosslinker added sample has a highest initial capacity (3139.6mAh/g) and maintain highest capacity value (2441.4mAh/g at 100th cycle) during 100 cycles. 10% boronic crosslinker added sample has a lowest initial capacity (2524.7mAh/g) but maintain highest capacity retention (83.8%). In this result, we determine that by increasing crosslinking density cycle stability increased but initial capacity decreased. Because crosslinking bond between guar and crosslinker can efficiently grasp active material during the volume change but reduced the number of hydroxyl group has lower interaction between silicon and binder, which cause low initial capacity of the electrode. Initial capacity and cycle stability are good properties in electrochemical performance. 5% boronic crosslinker added sample has a high initial capacity and 10% boronic crosslinker added sample has high cycle stability.

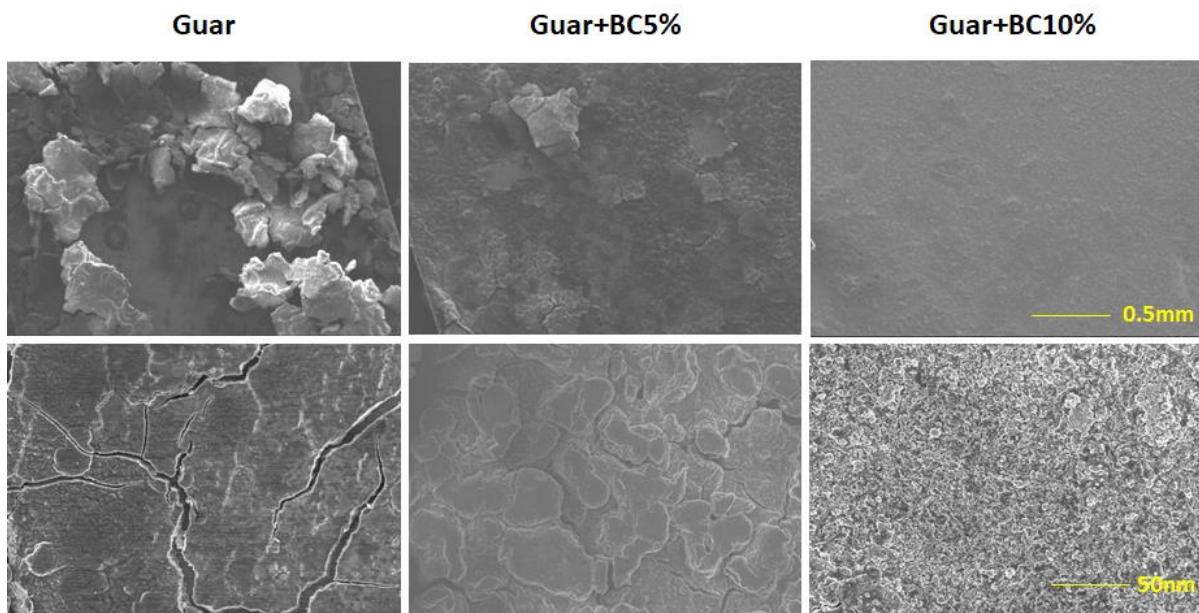


Figure 2.15 SEM image of Electrode surface after 100cycles

To analysis enhanced electrochemical performance of crosslinked guar binder we observed morphology of electrode surface after 100cycles. After cycles guar couldn't maintain the integrity of electrode and current collector exposed due to anode material detached, which cause fast capacity decrease and low retention. 10% boronic crosslinker added guar has smooth surface without any crack. This is reasons that 10% crosslinker added one has higher capacity retention than guar and 5% crosslinker added guar and guar due to stable integrity. 5% crosslinker sample has some active material detaching and crack but still maintain integrity. This means until 100cycles 5% crosslinker cases maintain high capacity but after more cycle it has capacity fading due to loss of electrochemical contact between active materials.

In conclusion, we successfully synthesized boronic crosslinker which can form bonding with vicinal alcohol groups. Crosslinked guar have enhanced G' modulus (16.7Pa of 10% crosslinker added guar and 13.8Pa of 5% crosslinked added guar) and changed to the gel state. This polymer has electrochemical stability in 0.01~3.0 Voltage range which is cell operating region. In electrochemical testing, crosslinked guar have high capacity retention and stable cycle life. However initial discharge capacity is decreased in 10% crosslinker added sample due to reducing the number of hydroxide group of guar. We expect that cycle stability and initial discharge capacity will improve by controlling crosslinker ratio. This boronic crosslinker can apply to many areas which use alcohol contained polymers for changing mechanical properties or using thermal responsive properties.

Chapter III. Amphipathic binder for stable cycle in Graphite/Silicon oxide composite anode

3.1 Introduction

3.1.1 Polymeric binder for composite anode

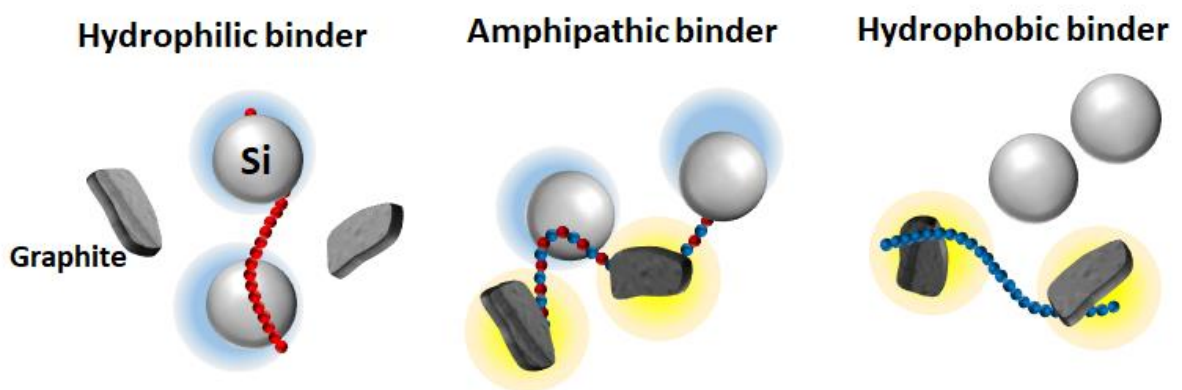


Figure 3.1 schematic description of different philicity effect of binder

The other for making high energy battery is making the composite of graphite and high theoretical capacity material. Graphite is the conventional active material which has little volume expansion but low theoretical capacity (372mAh/g). High theoretical capacity materials have high volume expansion example Si, Ge and Sn. ^[12-14] Therefore these are the big problem for practical use. One solving method is mixing the small amount of high capacity material (silicon or silicon oxide) to the conventional material (graphite). ^[31-33] That composite has higher theoretical capacity than graphite and lower volume expansion than silicon. Although the small amount of high capacity material was added in the electrode, it makes higher volume expansion than graphite. ^[34, 35] Therefore a new polymeric binder needs for grasping active material during charge-discharge cycle process. Because graphite has hydrophobic property and Silicon has hydrophilic property. PVDF, Conventional polymeric binder, has low interaction with silicon and can't hold particle during the cycle. Otherwise polymeric binder for silicon anode has low adhesion with graphite due to hydrophilic properties of binder. To hold two active material which have different properties, polymer binder need interactable functional group with each material. Interaction between binder and active material give enduring ability for volume expansion and detachment of active material to electrode. Figure 3.2 explains different interaction between different active material (silicon and graphite) and CMC, which is also conventional binder materials.

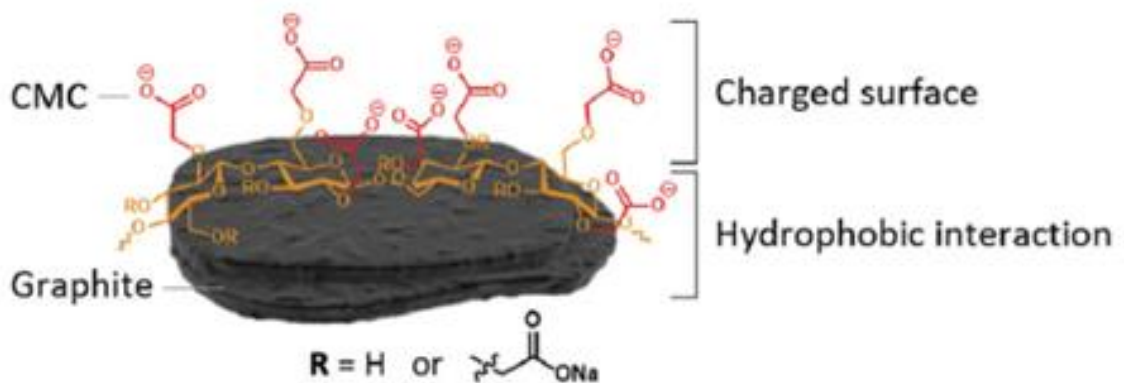
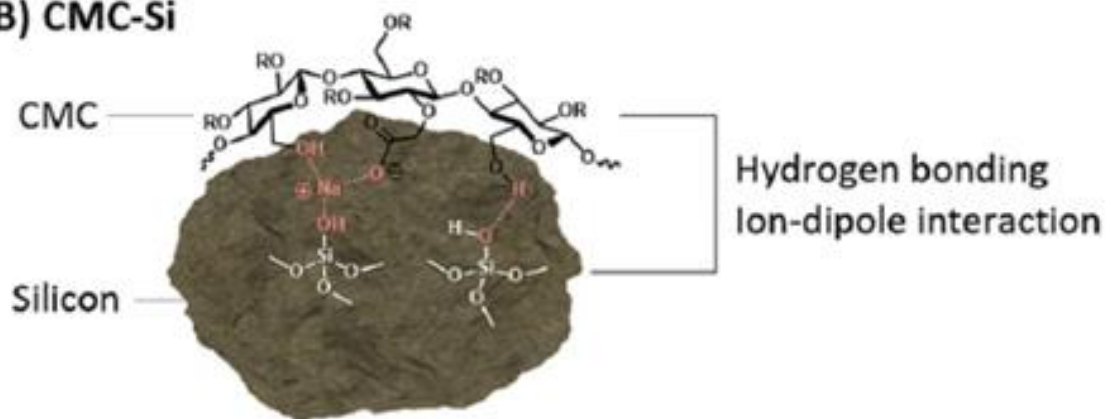
(A) CMC-Graphite**(B) CMC-Si**

Figure 3.2 schematic description of interaction between binder and active materials ^[10]

CMC has hydrophilic acrylic group in side chain and hydrophobic backbone. When mixed with graphite, backbone has hydrophobic interaction with graphite and charged side chains were positioned on the other side. However, in the silicon material case, side chains have hydrogen bonding and ion-dipole interaction with hydroxyl groups on the silicon surface. To make interaction with silicon and graphite, different parts of CMC work and effect. Through interaction between active material and CMC, we can get a clue for polymeric binder structure in graphite and silicon composite anode. We designed PS-PAA-PVA (poly(styrene-co-vinyl alcohol-co-acrylic)) which is added hydrophobic styrene monomer to poly(vinyl alcohol-co-acrylic) binder for silicon anode in previous work of our group. ^[36] Figure 3.3 is the chemical structure of PS-PAA-PVA binder. Styrene monomer can provide high interaction with graphite and the hydrophilic group, vinyl alcohol and acrylic, give interaction with silicon, high theoretical capacity material. Among candidates of hydrophobic functional groups, we chose the styrene group because it also contained in SBR, which is a conventional binder. And for giving hydrophilic properties to the binder

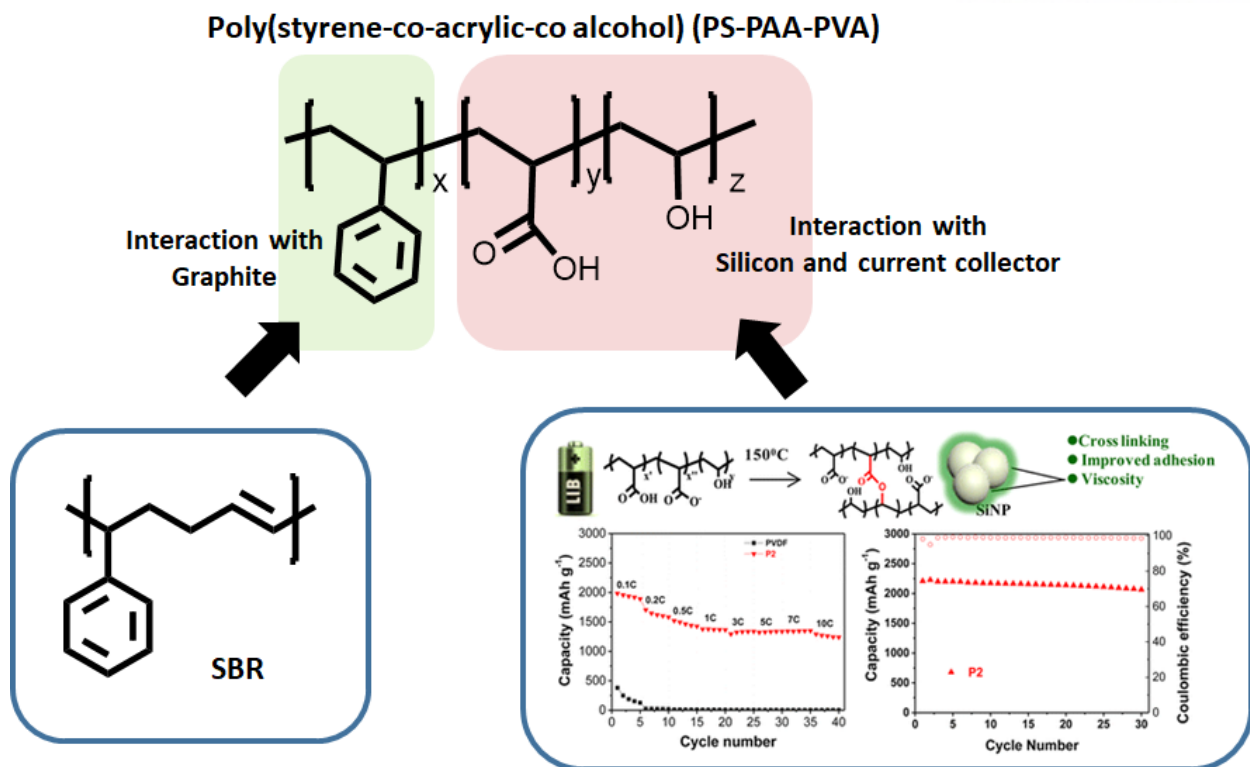


Figure 3.3 Chemical structure and properties of PS-PAA-PVA binder

we use hydroxyl and acrylic group as hydrophilic unit in polymer.^[37] Hydroxyl group has hydrogen bond and acrylic group has ion-dipole interaction with silicon which is same interaction between CMC and silicon. We expect PS-PAA-PVA binder has higher interaction with silicon and graphite than CMC due to more flexible functional groups in the side chain. This amphipathic random-co-polymer has similar functional group with CMC/SBR, conventional binder in anode. However we guess higher stability by combining two binder to one polymer which can give higher cohesion to two active materials.

3.2 Experimental

3.2.1 Material

Methyl acrylate (stabilized with MEHQ), Vinyl acetate monomer (stabilized with HQ) was purchased from Tokyo Chemical Industry (TCI), Tokyo, Japan. Styrene and aluminum oxide were obtained from Sigma Aldrich, Korea. Potassium persulfate, sodium dodecyl sulfate were obtained from Samchun pure chemical co., Korea. Carboxymethyl cellulose (CMC), SBR, graphite and silicon oxide were obtained from LG chemical, Korea.

3.2.2 PS-PAAPVA synthesis

Monomers were filtered with aluminum oxide for removing inhibitor. Potassium persulfate 1mg was added to styrene (0.12g, 1.15mmol) and 12g Distilled water in well dried 25ml round bottom flask. And Sodium dodecyl sulfate 150mg was added. Vinyl acetate (4g, 46.5mmol) and Methyl acrylate (2.67g, 31mmol) added to mixture. After then close tightly with parafilm and purging with Ar gas for 30min to remove oxygen. Than mixture was heated at 70°C for 3day with stirring. After the water was evaporated and polymers were solved THF and purified by precipitation in hexane two times. The polymers were characterized using 400 MHz ¹H-NMR spectroscopy and GPC. Synthesized polymer, random poly (styrene-co-methyl acrylate- vinyl acetate) dissolved THF and KOH added in solution. This mixture was stirring for 2day at 25°C. Separated solid is filtered from solution and dissolved distilled water. Deprotected polymers were purified by precipitation in ethanol and characterized using 400 MHz ¹H-NMR spectroscopy, FT-IR spectroscopy.

3.2.3 Electrochemical measurement

The electrochemical properties of graphite and silicon oxide anode with different polymer binder were measured using a 2032 R-type coin cell. The counter electrode was lithium metal and the working electrode was composed of 92% Active material (graphite: silicon oxide = 7:3), 5% polymer binder and 3% super-P. The loading mass of slurry was about 1.5mg cm⁻². Used electrolyte consisted of 10w% fluoroethylene carbonate and LiPF₆ (1.3M) in ethylene carbonate and diethyl carbonate (3:7 volume ratio). The half-cell were tested in the voltage range of 0.005 to 1.5 V at 0.1 C for formation cycle and 0.01 to 1.2 V at 0.5 C for cycle performance. The cells were tested with WBCS-3000 battery cycler (Wonatech Co.) at 25°C. After cycles electrode surfaced was observed using scanning electron microscopy (Hitach High-Technologies, S-4800)

3.2.4 Mechanical property of polymer binder

Polymer films were prepared by drying 0.5w% polymer solution at 50°C after then sample was prepared by dog bond shape (short width = 4mm) using metal frame. To determine mechanical properties of polymer were measured using a tensile strength measurement (DA-01, Petrol, Korea) as 10mm/min velocity.

3.3 Result and Discussion

3.3.1 Polymeric binder synthesis and characterization.

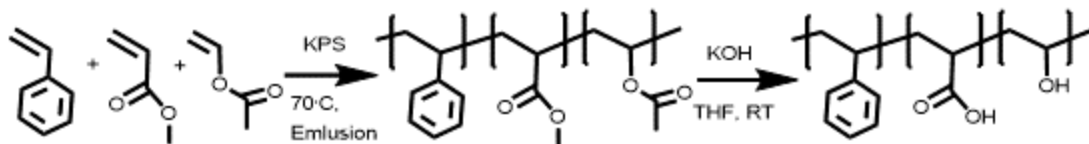


Figure 3.4 PS-PAA-PVA binder synthesis process

PS-PMA-PVA (poly (styrene-co-methyl acrylate-co-vinyl acetate)) binder, which is protected structure of PS-PAA-PVA, was synthesized by free radical emulsion polymerization and deprotected from acrylate and acetate group to acrylic and alcohol group. This polymer has random-co-polymer of styrene, alcohol and acrylic functional group which are also maintained in the conventional binder (SBR/CMC). Figure 3.3 Shows monomer ratio in the polymer after polymerization. We prepare three different styrene ratio polymer for checking electrochemical properties of styrene functional group as the polymeric binder. And figure 3.4 Shows molecular weight distribution of synthesized polymers. Three polymers have similar molecular weight ($M_n \approx 700k$ Da) and distribution regardless of styrene ratio. Figure 3.5 Shows FT-IR spectra PS-PAA-PVA binder after acetate and acrylate group deprotection. After deprotection, acetate groups were changed to alcohol group and acrylate groups were changed to acrylic group. Stretching O-H peak of alcohol groups and stretching O=C-O peak of acrylic groups appeared at 1556cm^{-1} and $3200\text{-}3700\text{ cm}^{-1}$ wavenumber.

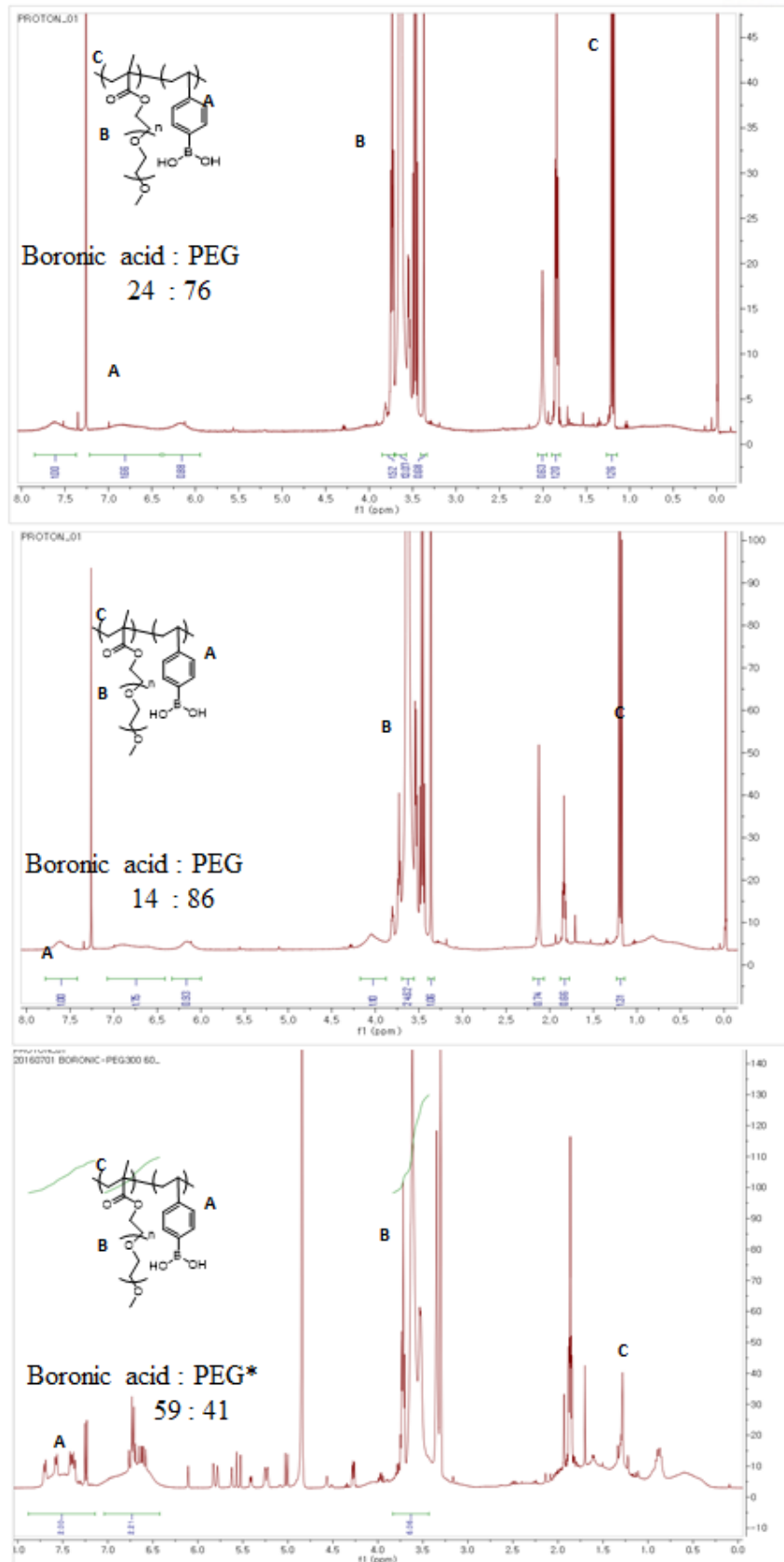


Figure 3.5 H-NMR spectra of 14.8%, 39%, 48% styrene contained polymeric binder

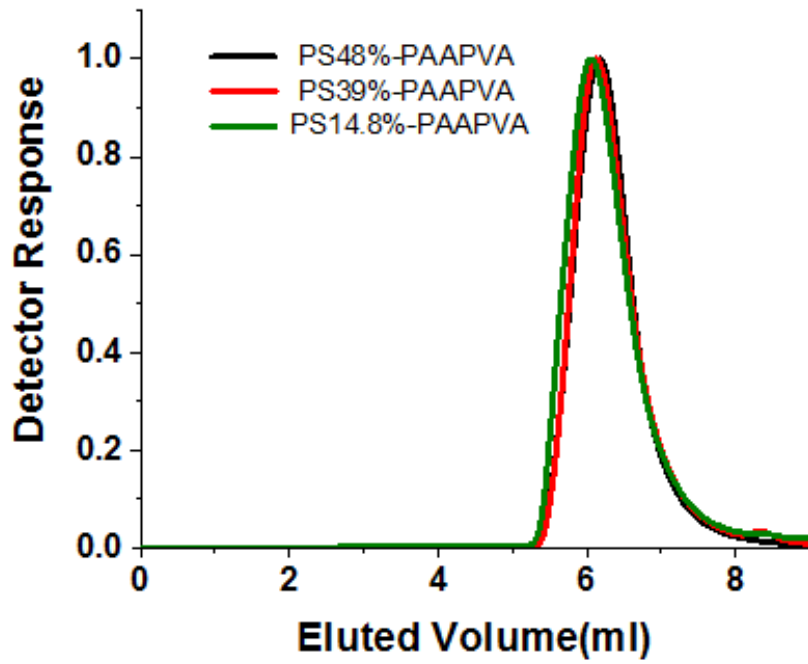


Figure 3.6 GPC spectra of 14.8%, 39% and 48% PS-PMAPVA binder.

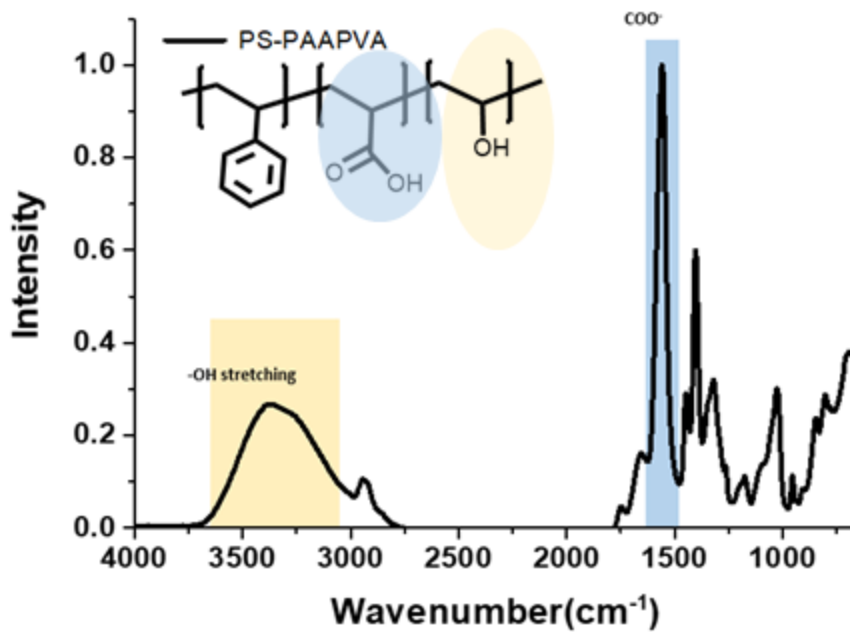


Figure 3.7 FT-IR spectra of PS-PAA-PVA binder film

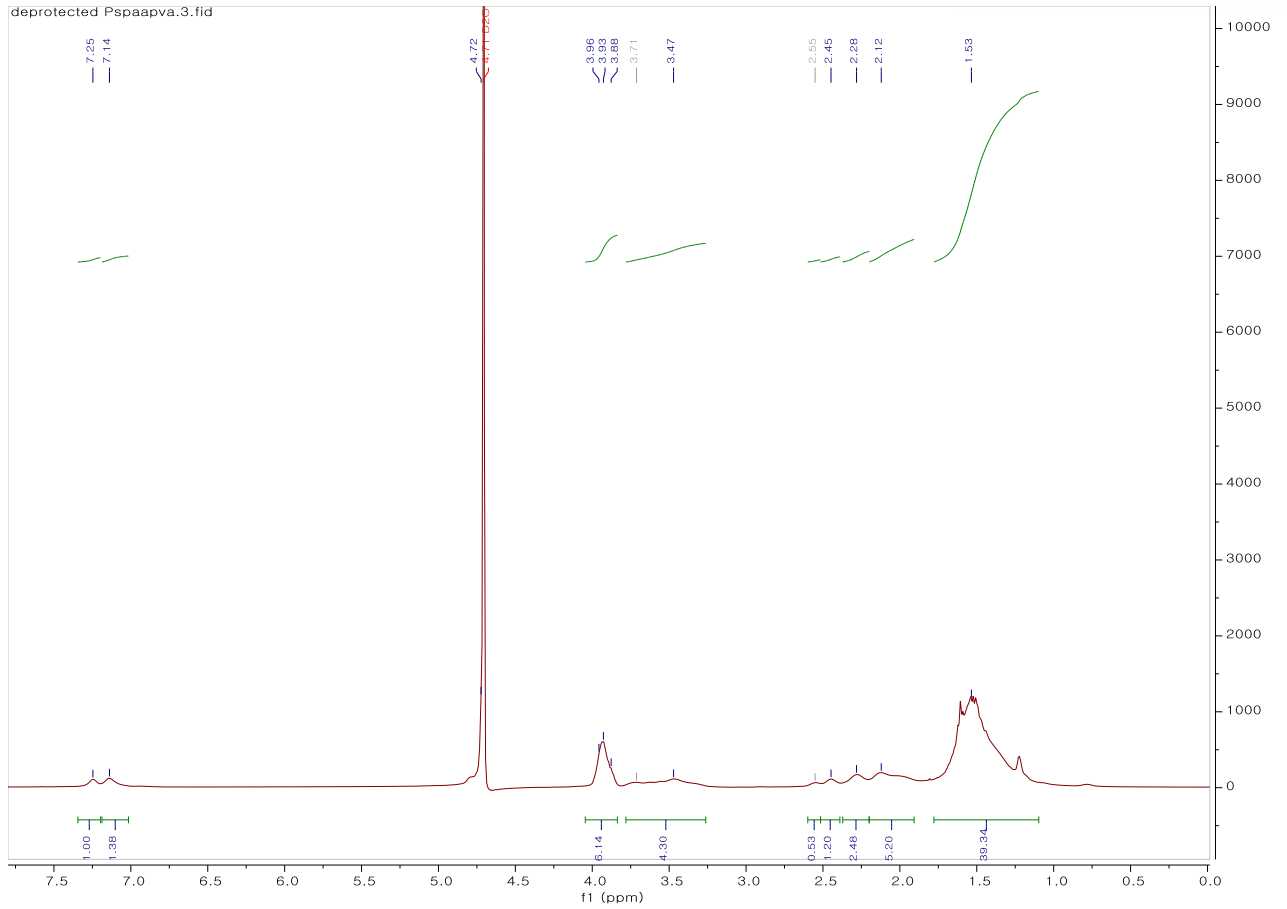


Figure 3.8 $^1\text{H-NMR}$ PS-PAA-PVA after deprotection

3.3.2 Electrochemical performance and surface morphology

To test electrochemical properties of different styrene monomer containing the polymer, different polymers used electrode prepared by following with experiment section. Figure 3.6 shows that low initial coulombic efficiency (ICE=75.6%) of 48% PS-PAA-PVA and low initial discharge capacity (582.5 and 553.1 mA h/g) of 48% and 39% PS-PAA-PVA sample, compared with lower styrene ratio

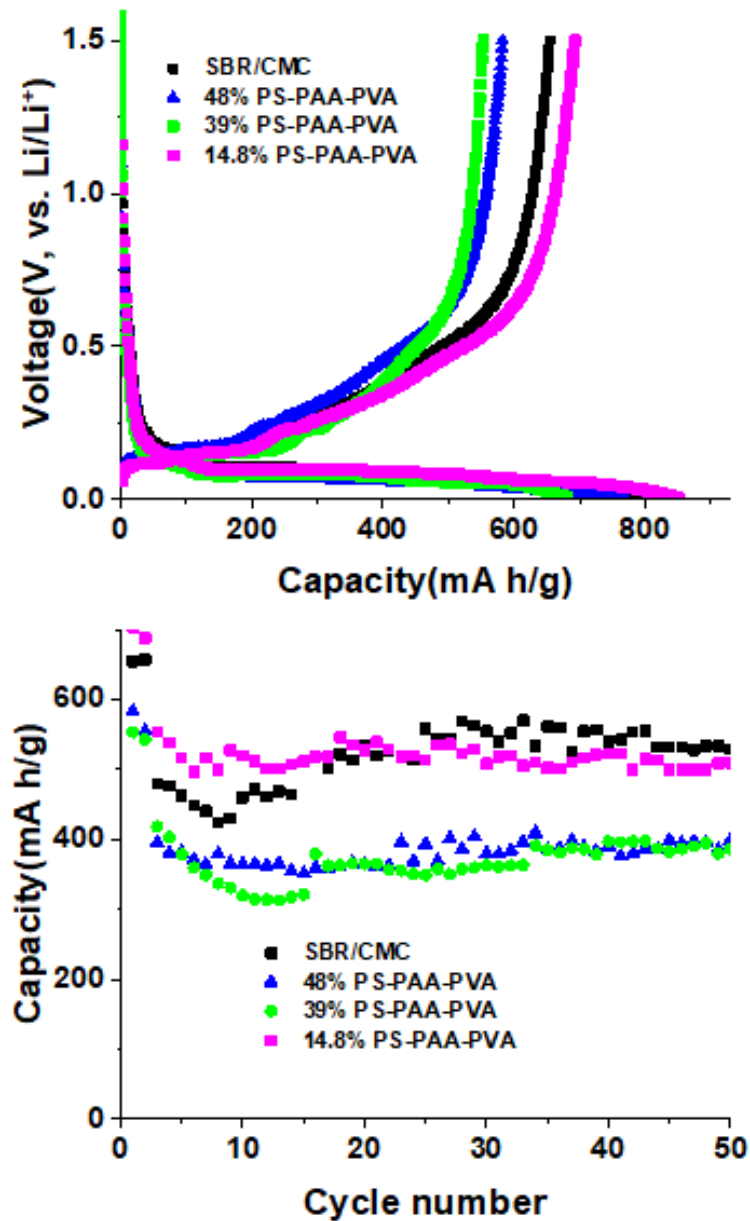


Figure 3.9 Electrochemical performance of different hydrophobic group ratio polymer binder and reference a) Voltage profile of initial cycle and b) cycle performance

polymer sample (ICE=80.2 and 692.7 mA h/g). By increasing, styrene amount of polymer, alcohol and acrylic group amount were decreased. We guess results that by decreasing two functional group, alcohol and acrylic group, polymer loses high interaction with the current collector or silicon oxide which have hydrophilic properties. The low interaction between active material and binder cause losing integrity during the volume expansion of silicon oxide. But 14.8% PS contained PAA-PVA binder has slightly higher coulombic efficiency and capacity retention than conventional binder (SBR/CMC). Because PS-PAA-PVA has higher interaction between polymer than SBR and CMC which are physical mixture.

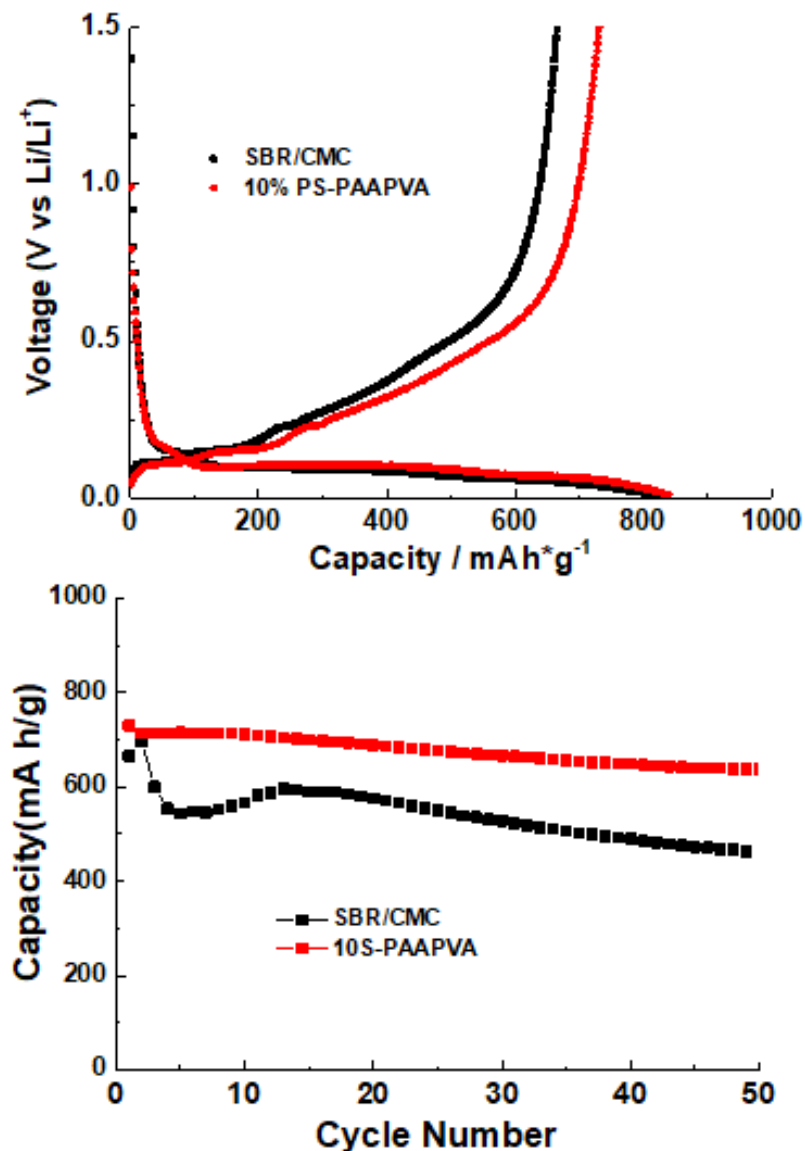


Figure 3.10 Electrochemical performance of conventional binder and 10% PS-PAAPVA binder a) Voltage profile of initial cycle and b) cycle performance

As a result of the electrochemical performance of different styrene ratio polymer binders, we prepared the new polymer, 10% styrene contained PAAPVA binder, for improved electrochemical properties of the electrode. Figure 3.7 shows high initial coulombic efficiency (ICE=81%) and retention (89.2%) of 10% PS-PAAPVA binder used electrode compared conventional binder used one (ICE=80%, retention= 72.1%) This result means that 10% PS-PAAPVA binder has more stable cycle-ability and lifetime than SBR/CMC in electrode. We guess that 10% PS-PAAPVA has a proper ratio for interact graphite and silicon oxide and it has resulted in maintenance of the integrity of electrode and hindrance of continuous SEI formation.

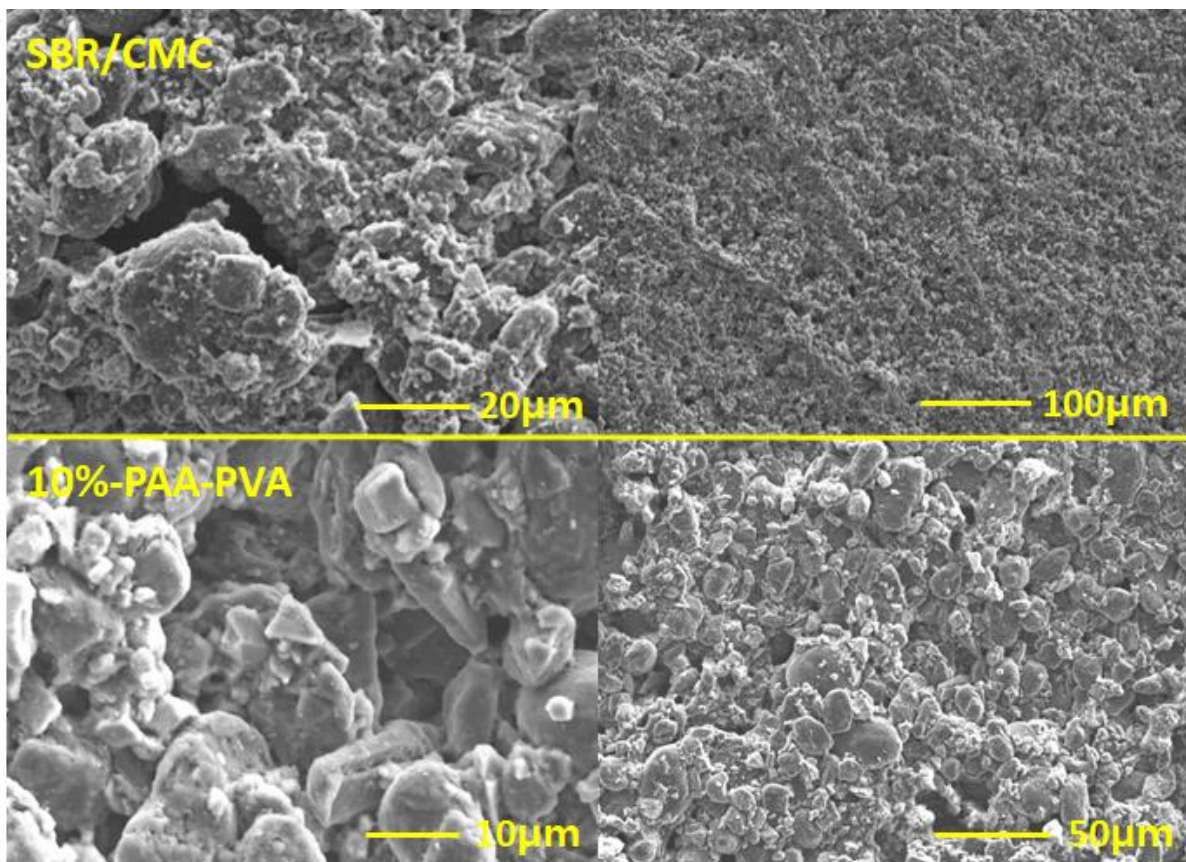


Figure 3.11 scanning electron microscope image of SBR/CMC and 10% PS-PAA-PVA binder electrode surface after 50 cycles

Figure 3.8 shows the morphology of 10% PS-PAA-PVA and conventional SBR/CMC binder used electrode surface after 50 cycles. We want to determine different SEI formation between conventional binder and PS-PAA-PVA binder used electrode. But both electrodes show active material particle in high magnification. It means that there were formed thin SEI in electrode surface and maintained integrity without a crack at both electrodes

3.3.3 Tensile test of polymeric binder film

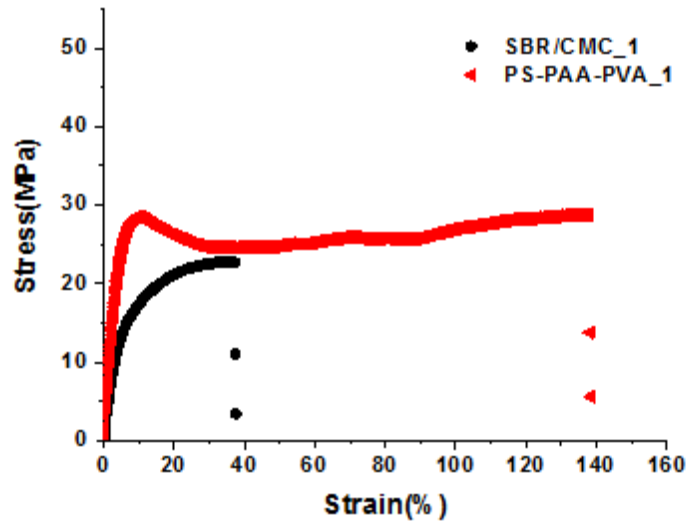


Figure 3.12 Stress-strain curve of conventional binder (SBR/CMC) and 10% PS-PAAPVA film

To determine mechanical properties of the polymer, strain-stress curves were measured by tensile strength measurement. Figure 3.9 shows that conventional polymer binder (SBR/CMC) had fracture point in 40% strain but PS-PAA-PVA binder maintained the integrity of polymer film over 130% strain compared the initial length of the polymer film. PS-PAA-PAA had a lower elastic point (about 10% elongation) than SBR/CMC but it needs high strength for elongation. This property can explain that how 10% PS-PAA-PVA gave enhanced electrochemical properties in half-cell test. The 10% elastic region of PS-PAA-PVA can accept volume change of electrode because graphite (64% content of electrode) has 10% volume expansion to C-axis during the lithiation process. And the high hardness of PS-PAAPVA property can stand a pressure of volume expansion during the charging process.

3.3.4 Cross-linked PS-PAA-PVA binder

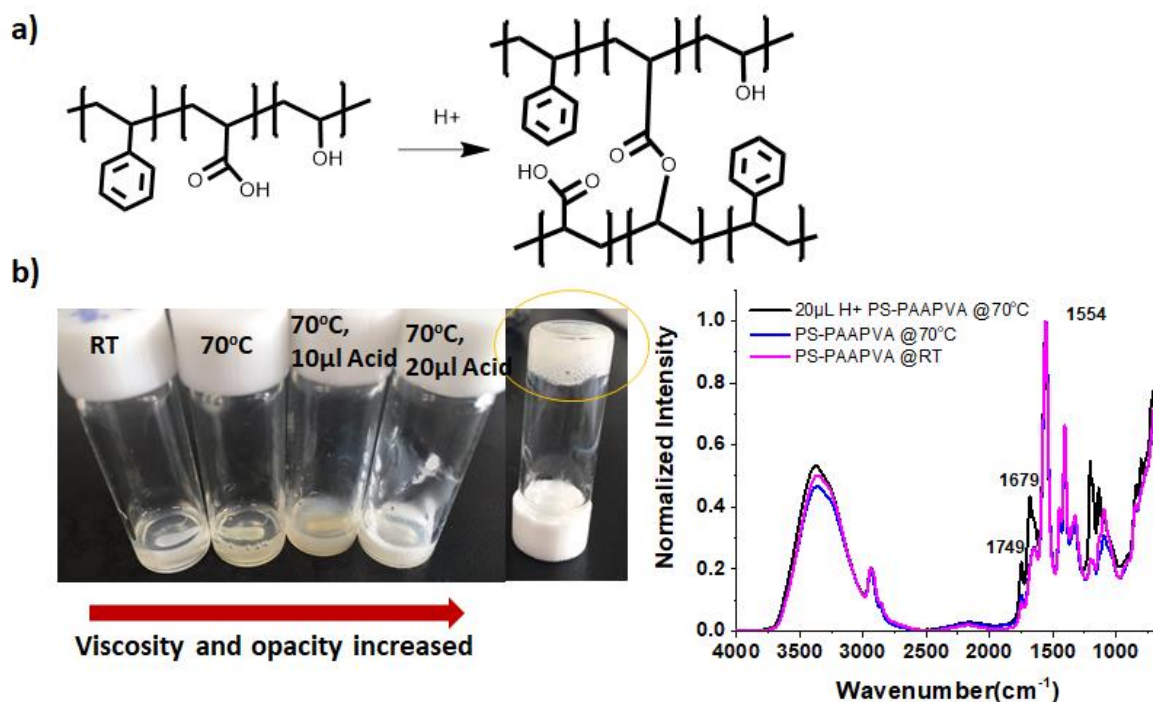


Figure 3.13 a) crosslinking reaction of PS-PAA-PVA binder, b) photographic image and FT-IR spectra of polymer solution after reaction

For the more improved electrochemical performance of 10% PS-PAA-PVA polymer, we tested cross-linked 10% PS-PAA-PVA binder. To make crosslink bond between polymers, we used acid catalyzed esterification reaction between acrylic and alcohol group.^[38] For checking crosslinking bond, we prepare difference reaction condition (temperature and acid amount). Esterification of alcohol and acrylic group occurred by adding the acid. The Acid makes acrylic acid by giving proton to acrylic and also make protonated acrylic acid which accelerated esterification between alcohol and acrylic acid group. After adding acid, solution change to high viscosity and opacity (Figure 3.10 b photographic image). FT-IR spectra in Figure 3.10 b shows that after adding acid, 1749 cm^{-1} (COOH) and 1679 (COOR) cm^{-1} wavenumber peak increased. The COOH peak means that acrylic groups were changed to acrylic acid by acid and the COOR peak is evidence of crosslinking bond between COOH and OH group of 10% PS-PAA-PVA.

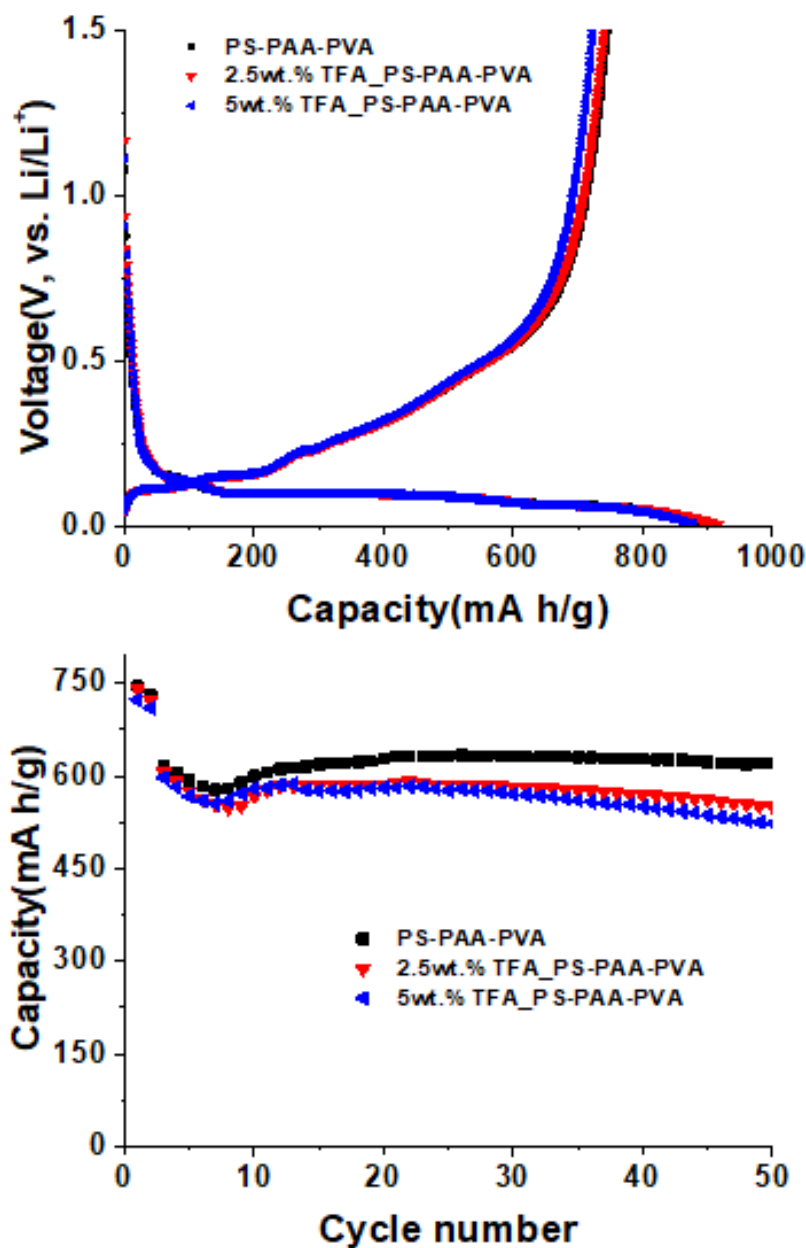


Figure 3.14 Electrochemical performance of 10% PS-PAA-PVA binder and acid added one a) Voltage profile of initial cycle and b) cycle performance

To determine the electrochemical performance of cross-linked 10%PS-PAA-PAA binder, we experimented 10%PS-PAA-PVA without crosslinking and cross-linked sample as the binder. The initial coulombic efficiency of each sample is similar with others. We guess cross-linked and without cross-linked 10%PS-PAA-PVA have a similar functional group and that is giving similar stability in initial cycle. However, in cycle performance, the cross-linked binder has slightly lower cycle stability than

one without crosslinking. We guess reasons that by increasing crosslinking bond polymer binder has harder properties and lower elasticity. 10% PS-PAA-PVA has elastic resin about 10% strain which can acceptable in graphite electrode but crosslinking bonding between alcohol and acrylic group gives decreased elastic resin and hard properties. Crosslinked polymer continuously have damage because of stress resulted from electrode volume expansion and lose holding property. It cause continuous capacity losing in cycle performance.

In summary, PS-PMA-PVA (poly (styrene-co-methyl acrylate-co-vinyl acetate)) synthesis was confirmed by NMR and GPC and then polymer deprotected to PS-PAA-PVA (poly (styrene-co-acrylic-co-alcohol)). In electrochemical performance, we confirmed tendency, which increases electrochemical stability and cycle ability as decreasing styrene ratio. Initial capacity and retention of electrochemical performance are improved in 10% PS-PAA-PVA. In stress-strain curve, 10% PS-PAA-PVA binder file has higher fracture point in 140% strain and strength for stretching than conventional binder. These properties give high tolerance to volume expansion of active material.

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