Master's Thesis

A bi-polymer-crosslinked binder to improve the kinetics of sodiation,desodiation and reversibility of antimony for sodium ion battery anodes.

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Graduate School of UNIST

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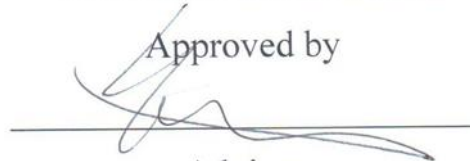Department of Chemical Engineering

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Hyun-Kon Song

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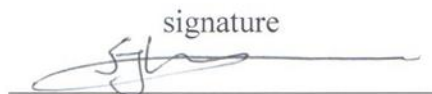
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Abstract

Antimony has been developed as a promising anode material of sodium ion batteries (SIBs) even if its volume is tremendously expanded during the alloying reaction with sodium. Repeated volume changes along sodiation/desodiation cycles encourage capacity fading by triggering pulverization accompanying electrolyte decomposition. Also, low cation transference number of sodium ion is another huddle of SIBs In this work, a binder for antimony in SIB cells was designed to have bifunctionality to improve (1) the mechanical toughness to suppress the serious volume change and (2) the transference number of sodium ion. A crosslinked composite of poly(acrylic acid) (PAA) and cyanoethyl pullulan (pullulan-CN) was presented as the binder. The polysaccharide backbone of pullulan-CN was responsible for the mechanical toughness while the cyanoethyl groups improved by pullulan-CN. The antimony-based SIB cells using the composite binder showed improved cycle life with enhanced kinetics.

KEYWORDS : Na-ion batteries, antimony, polysaccharide binder, cross-linked binder, cation migration

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Nomenclature

EVs	Electric vehicles
HEVs	Hybrid electric vehicles
PHEVs	Plugin hybrid electric vehicles
IoT	Internet of things
LIBs	Lithium ion batteries
Li	Lithium
Na	Sodium/Natrium
Si	Silicon
C	Carbon
Sb	Antimony
Sn	Tin
Ge	Germanium
SEI	Solid electrolyte interface
CMC	Carboxymethyl cellulose
Meldrum's acid	2,2-dimethyl-1,3-dioxane-4,6-dione
SIBs	Sodium ion batteries
PAA	Poly(acrylic acid)
Pullulan-CN	Cyanoethyl pullulan
PVA-CN	Cyanoethyl polyvinyl alcohol
ESS	Energy storage system
PVDF	Polyvinylidene fluoride
η	Coulombic efficiency
$NaBH_4$	Sodium borohydride
$SbCl_3$	Antimony trichloride
NMP	N-methyl-2-pyrrolidone
$NaClO_4$	Sodium perchlorate
EC	Ethylene carbonate
PC	Propylene carbonate
FEC	Fluoroethylene carbonate
CVs	Cyclic voltammograms
t_{Na+}	Sodium ion transference number
ε	Dielectric constant
ECSA	Electrochemical active surface area
FT-IR	Fourier-transform infrared spectroscopy

SEM	Scanning electron microscopy
XPS	X-ray photoelectron spectroscopy
C	C rate
Na_2Co_3	Sodium carbonate
PFM	Poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester)
I_{pc}	Peak current
n	Number of transferred electron
$C_0{}^*$	Concentration of Na+ ion
A	Electrode area
D	Diffusion coefficient of Na^+ ion
v	Scan rate
D.I water	Deionized water

Chapter 1. Introduction

1.1 Importance of secondary batteries in the future

Development of the EVs (Electric vehicles), mobile IT device, IoT (internet of things) devices increased demand of secondary batteries. Moreover, due to the current environmental problems such as energy exhaust, global warming and air pollution, the demand for renewable energy to replace conventional fossil fuel systems has increased dramatically, and secondary batteries, the storage medium of renewable energy, were also of interest. Comparing with other rechargeable secondara batteries (Lead-acid, Nickel-Cadmium or Nickel-Metal-Hydroxide) LIBs (Li ion batteries) have higher energy density and lower weight. [1] **(Figure 1)** Furthermore, LIBs have low self-discharge, dispose easier comparing with lead acid and nickel-cadmium battery due to nontoxic atoms in LIBs. For these reasons, research interests and demands of LIBs will become increased in the future. **(Figure 2)**. [2, 8, 9]
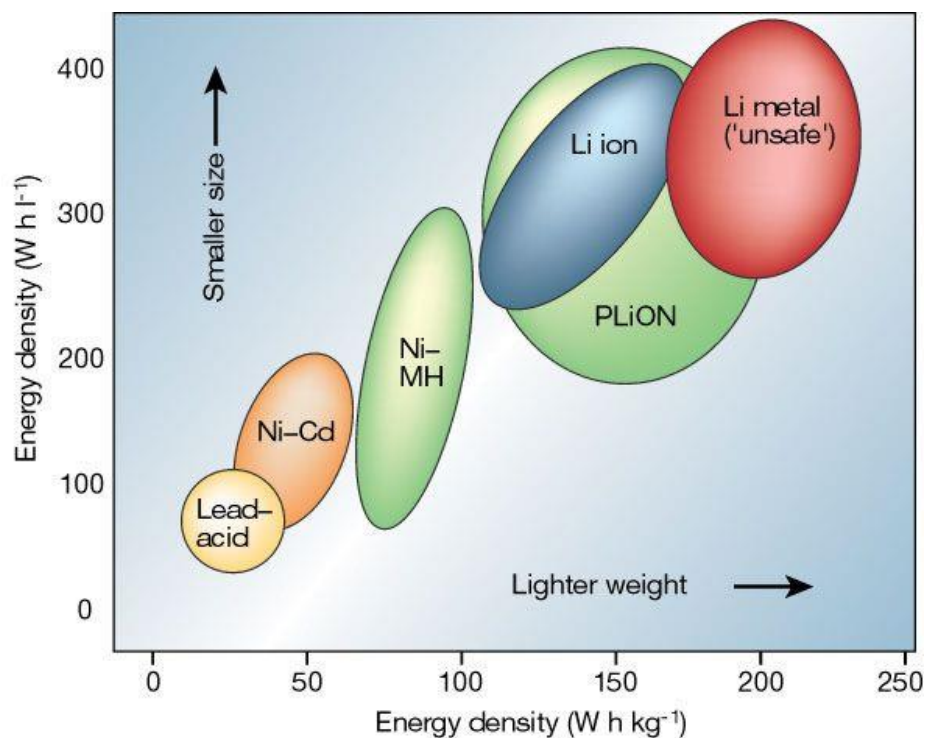
Figure 1. List of rechargeable batteries comparing with volumetric and gravimetric energy density. [1]
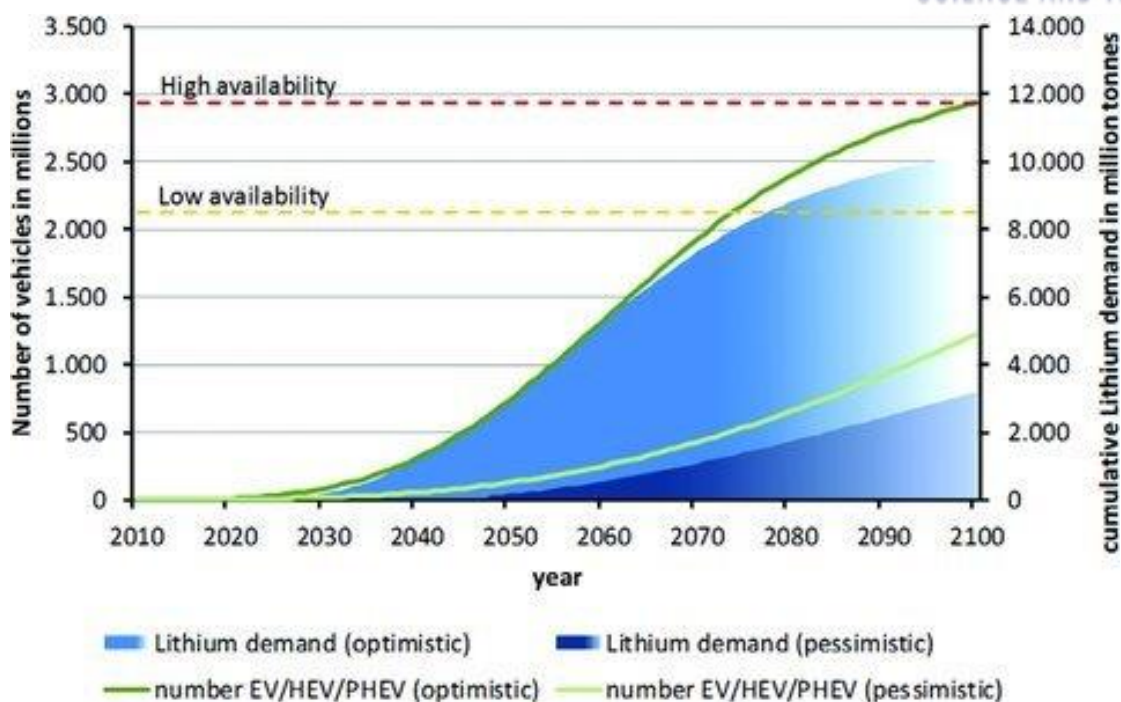
Figure 2. The number of Lithium demand, availability, electric vehicles (EVs), hybrid electric vehicles (HEVs) and plugin hybrid electric vehicles (PHEVs) over time. According to the availability of lithium and demand of EV/HEV/PHEV, run out of lithium the near future could be occurred. [2]

1.2 Introduction of alloy anode materials for lithium ion batteries (LIB)

The conventional anode material of LIBs is graphite, due to its reasonable cost, non-toxic property, abundance and proper theoretical capacity (372 mAh g^{-1}) by intercalation of Li ions during charge. [8] However, recent papers studied about the advanced anode materials to reach higher capacity comparing with graphite, such as Si (Silicon), Ge (Germanium), Sn (Tin), achieving high capacity by the alloying reactions: e.g, 4200 mAh g_{Si}^{-1} for Li$_{4.4}$Si, 1620 mAh g_{Si}^{-1} for Li$_{4.4}$Ge, 994 mAh g_{Si}^{-1} for Li$_{4.4}$Sn. However, these alloying materials showed huge volume expansion, (420% for Li$_{4.4}$Si, 400% for Li$_{4.4}$Ge, 360% for Li$_{4.4}$Sn) and this volume expansion causes failure of electrode called pulverization. The pulverization of alloying materials causes three problems, (1) material pulverization (2) continuous SEI growth, (3) morphologic change of the entire Silicon electrode. **(Scheme 1)** [10] The repeated volume change along the lithiation/delithiation cycles encourages particle pulverization, isolating particles from electric pathways, breaking electrode integrity, exhausting electrolyte and triggering electrolyte decomposition on the fresh surface of pulverized anode materials. [11-13]
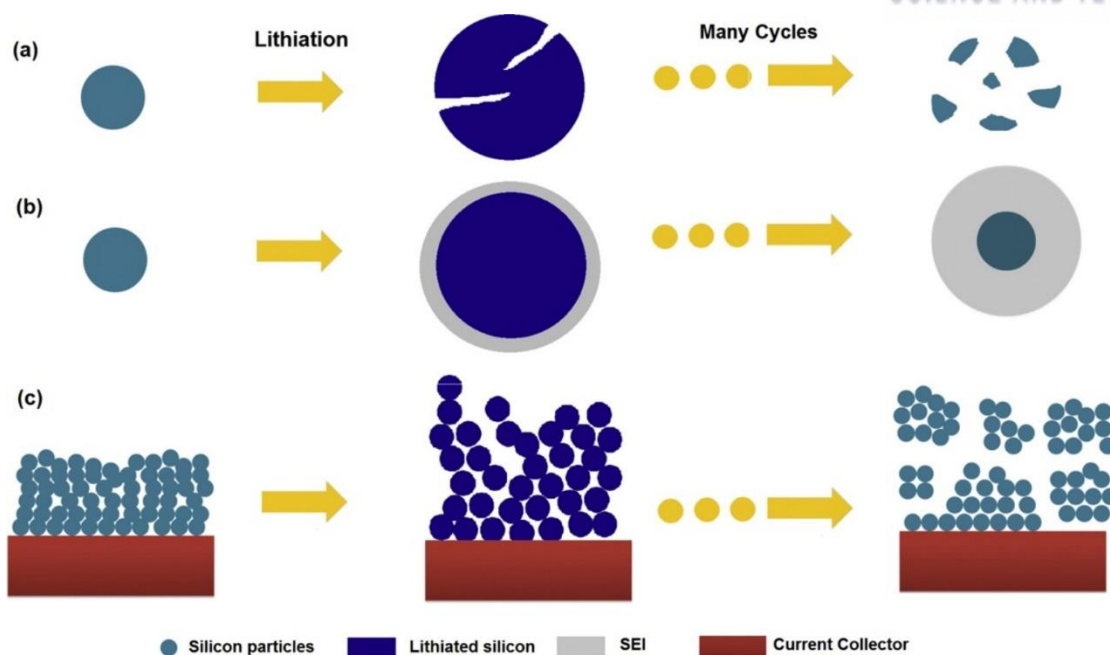
Scheme 1. Failure mechanisms of silicon anode electrode (a)material pulverization, (b) thick SEI growth by continuous SEI layer composition, and (c) morphology and volume change of the entire Si electrode.

Although this huge volume expansion of silicon in LIB anode system, but the merit of abundance, cheap cost and ten times higher theoretical capacity than graphite, pull the interest of researchers. This pulverization issue has been addressed by controlling the characteristic dimension of the anode materials (e.g., introducing porosity or adapting nanodimensional particles) [11, 14-16], coating the active materials with conductive materials[17-21] and hybridizing the active materials with non-active materials.[12, 22-24]

1.2.1 Recent studies for binders to improve alloy anode materials in LIB system

The anode electrode consists of four representative components, current collector, active material, conductive additives and binders. Anode current collector assembles electrons at the outer conductor then supply electron to active materials, active materials make capacities by reacting with Li ions, conductive additives (such as carbon black) increase the conductivity of electrode. Adhesive and cohesive binders mainly used for binder, they connect current collector, active material and conductive agent then keep the integrity of electrode by adhesion (current collector - active material) and cohesion (active material – another active material or conducting agent). [25] **(Scheme 2)**
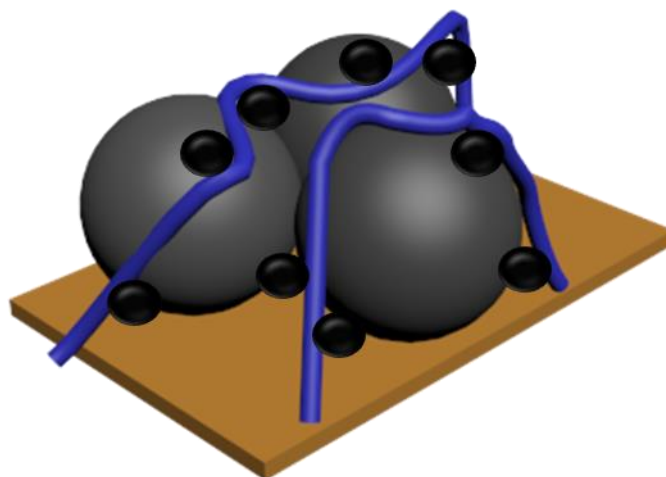
Scheme 2. Four components of anode electrode; Brown plate = current collector, big gray sphere = active material, small black sphere = conductive additive, blue strand = binders.

It has been reported that the volume change of the alloying-reaction-based anode materials and its following effects were suppressed by adopting binders having appropriate properties. Mechanically toughness polymeric binders such as alginate[26], carboxymethyl cellulose (CMC)[27], amylopectin[28] and pullulan[4], are essential for keeping the electrode integrity and suppressing pulverization. Binders which form strong bonding with surface of active material such as poly(acrylic acid) (PAA)[29], guar gum[30] and 5-methyl-5-(4-vinylbenzyl) Meldrum's acid[31] improved the reversibility of silicon due to the covalent bond or hydrogen bond between the binders and surface oxide of active material. Furthermore, the bi-polymer system of mechanically toughness polymer and strong bonding polymer, such as cross-linking of PAA with pectin[3]**(Figure 3)**, CMC[32] or pullulan[4] **(Figure 4)** via condensation is essential to forming branched structure, reinforcing the mechanical strength and reversibility of the silicon. This branched architecture of bi-polymer binder systems provide more improved reversibility of lithiation/delithiation of silicon via interchain cohesion.[33, 34]

Figure 3. Polysaccharides polymeric binders characterized by glycosidic linkages between their monomeric units and functional moieties on side chains. (a) Molecular structures of polysaccharides: CMC, pectin. (b) Schematic figure of morphological changes of two polysaccharides binders and silicon particles along lithiation and delithiation: white strands = polymeric binders; red points = covalent bonds between hydroxyl and carboxylate moieties of binder; blue points = condensation reaction of between carboxylate of binders and hydroxyl moieties of silicon oxide films on the silicon particles. [3]
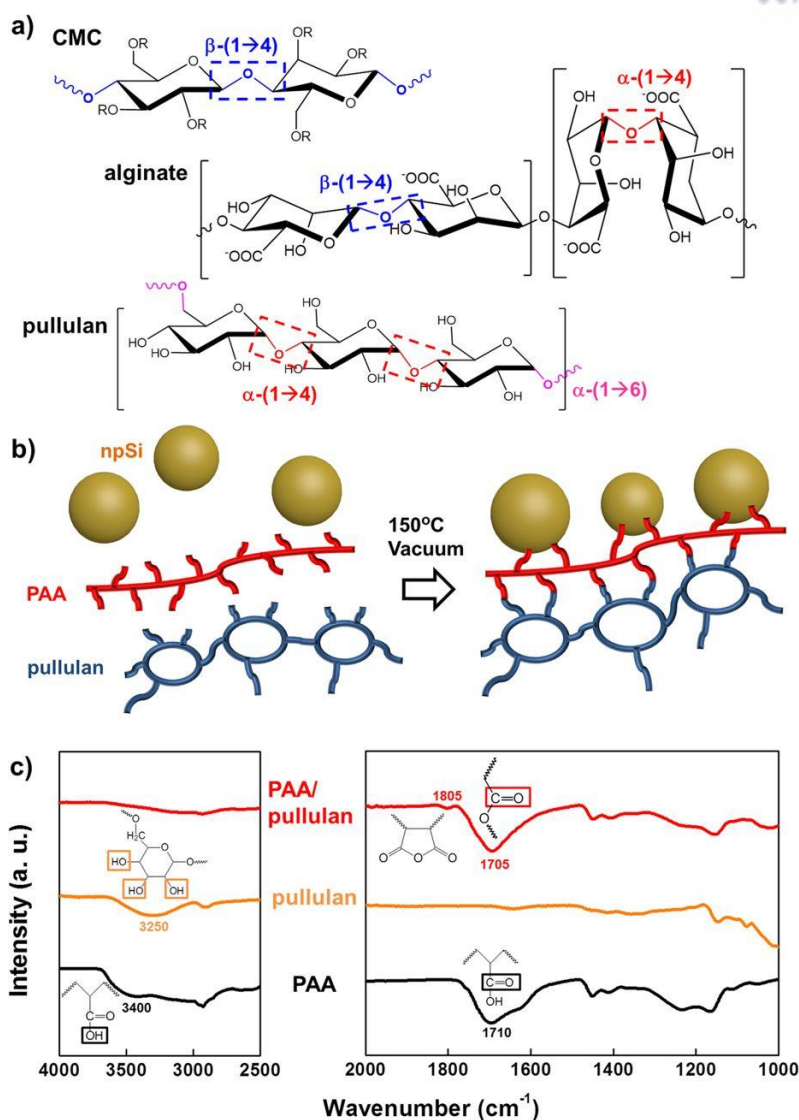
Figure 4. (a) Structure of alginate, CMC and pullulan. Glycosidic linkages (α, β) of each polymeric binder were indicated. (b) Covalent condensation between surface oxide of Si and carboxylate of PAA as well as between pullulan and PAA after thermal heating at 150 °C. Dehydration reactions are induced at 150 °C between carboxylic moieties of PAA and hydroxyl moieties of pullulan and surface oxide of silicon. (c) FT-IR spectra of PAA, pullulan and PAA/pullulan, confirming the cross-linking of two binders by disappearance of hydroxyl moiety and appearance of ester moiety [4]

1.3 Comparison of LIB and sodium ion batteries (SIB)

The demands for LIBs were increased in past years, but the atomic ratio of Li in the crust of earth is not abundant. Moreover, the markets for large scale applications such as ESS (Energy storage system) were developed in present, but the expensive cost of LIBs are difficult to used for large-scale applications. Therefore, it is essential for developing alternative secondary batteries, which is free to abundance and cost problem, to replace the LIBs. Sodium is one of alkali metal, similar with Li, but it has low cost, infinite abundance in the earth. These characteristics of sodium triggers developing SIBs as an alternative to LIBs.[2, 35] **(Figure 5 and Table 1)**
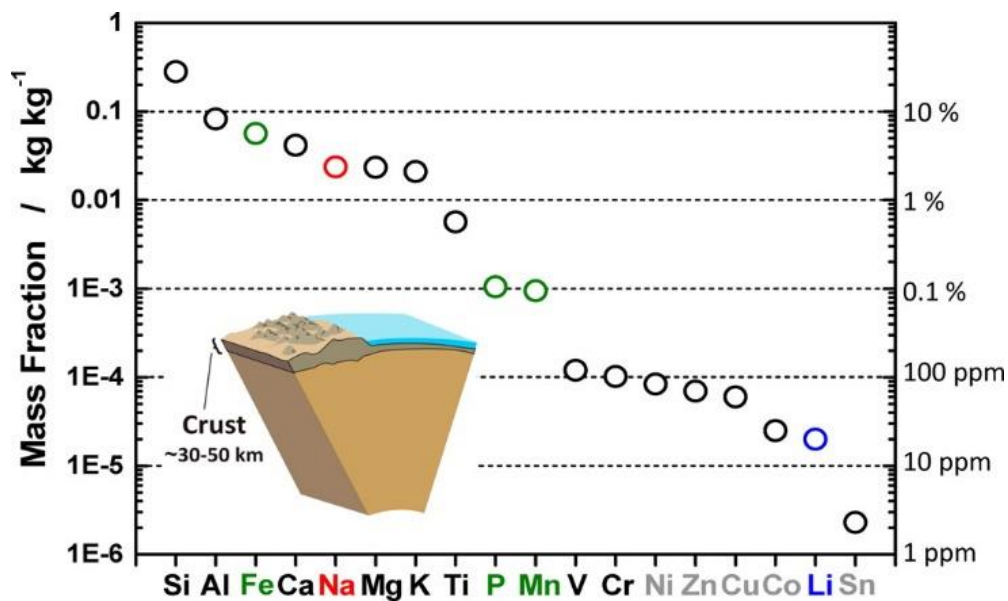
Figure 5. Natural abundance in the crust of earth. [5]

	Na	Li
Prices(for carbonates)	0.08 − 0.42 $/kg	4.7 − 5.1 $/kg
Voltage (vs SHE)	-2.71 V	-3.02 V
Capacity, metal	1165 mAh g^{-1}	3829 mAh g^{-1}
Cation radius	1.06 Å	0.76 Å

Table 1. Comparing properties of Na(sodium) and Li(lithium) in secondary batteries

1.4 Introduction of anode materials for SIB

However, because of the larger ionic radius of sodium, (1.03 Å versus 0.73 Å for Li$^+$) sodium ions can't intercalate into the basal plane of graphite. [36] **(Scheme 3)** Therefore, SIB cannot use graphite as anode, require other anode materials.
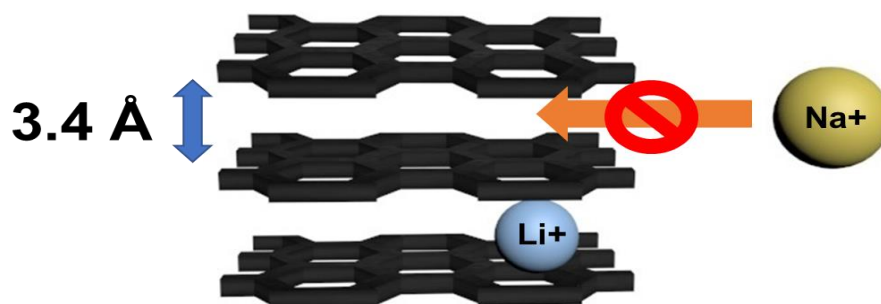
Scheme 3. Intercalation comparison of Na+ ion and Li+ ion in the graphite.

Recent papers studied about the replacement of graphite, such as hard carbon, silicon, tin and antimony. However, there have been some problems reported for each of these alternative anode materials. The hard carbon can absorb sodium ion in its nanopores, but it was supper with low volumetric capacity (450 mAh cm^{-3}) due to its low density. (1.5 g cm^{-3}). The tin forms binary alloy with sodium ion to Na$_{15}$Sn$_4$, showing very high gravimetric capacity. (847 mAh g^{-1}) However, tin suffers from pulverization during sodium alloying. [37] The Antimony (Sb) is promising alloying material for SIB anode, showing high gravimetric capacity through alloy reaction (660 mAh g^{-1}) and volumetric capacity (1120 mAh cm^{-3}) by forming Na$_3$Sb. However, like silicon and tin, too large amount of alkali metal is incorporated into the metals and metalloids so that severe volume expansion is inevitable: e.g., 393 % volume expansion from Sb to Na$_3$Sb. [38, 39]

1.4.1 Recent studies for binders to improve alloy anode materials in SIB system

Like the binder works for LIBs silicon anode mentioned at the previous page, [3, 4, 26, 28, 29, 31, 32, 40] binder works for sodiation alloy materials are in interest. Komaba et al. [6] introduced about the polyacrylate binder for Tin anode electrode, and Gao et al. [41] introduced about the cross-linked chitosan and glutaraldehyde for antimony. This binder works suppress the volume expansion of alloy materials, showing better cyclabilities comparing with conventional binders such as PVDF (Polyvinylidene fluoride) or non-crosslinked chitosan. **(Figure 6)**
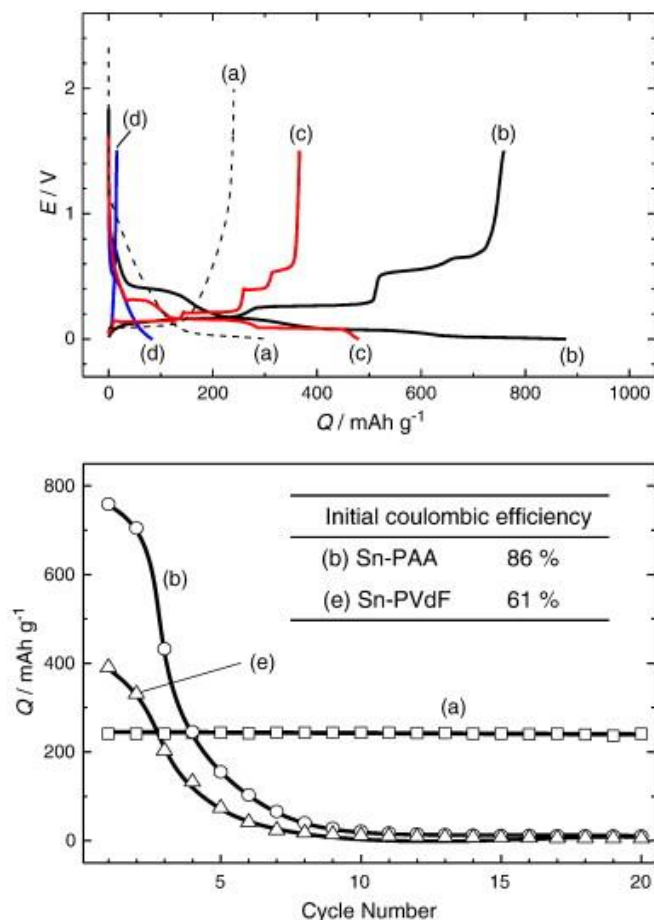
Figure 6. (upper) Initial charge and discharge profiles and (bottom) cyclability of (a) hard-carbon with PVdF binder, (b) Sn-PAA, (c) Pb-PAA, (d) Si-PAA, and (e) Sn-PVdF. The hard-carbon electrodes were characterized in beaker-type Na cells at 25 mA g^{-1}, and Sn, Pb, Si and Sn based electrodes were tested in coin-type cells at 50 mA g^{-1} in 1.0 M NaClO$_4$ PC. [6]

1.4.2 Other problems of SIBs anode and strategies to solve this problem

The size of sodium ion bigger than that of lithium ion (1.03 Å for Na$^+$ versus 0.73 Å for Li$^+$) limits its mass transfer and charge transfer kinetics.[36, 42, 43] In addition to suppressing pulverization, therefore, it is useful to install an active transport mechanism of sodium ion into active materials. Dai et al. [44] introduced electroactive binder, PFM (Poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester)), to enhance the kinetics of tin nanoparticles in SIBs anode. For LIBs system, Hwang. et al.[7] demonstrated that cyanoethyl polyvinyl alcohol (PVA-CN) crosslinked with PAA played a role of increasing lithium ion transport number (t_{Li+}) to get better transfer kinetics comparing with PAA/CMC binder (good adhesion strength but no transfer kinetic enhancement).[45] **(Figure 7)** If

these approaches are applied at SIBs system, limited mass transfer and charge transfer kinetics will be solved.
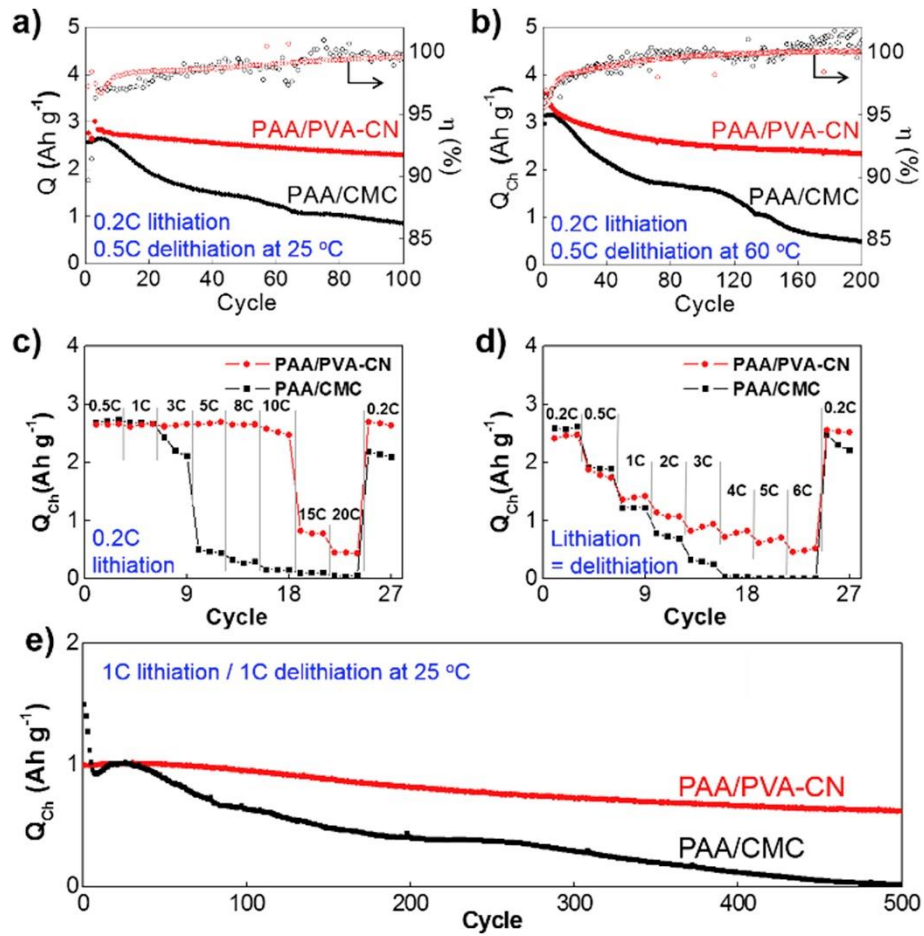
Figure 7. Electrochemical performance of PAA/PVA-CN or PAA/CMC binder-based silicon anodes. Cyclability and coulombic efficiency along continous cycles of lithiation and delithiation at 25 °C (a) and 60 °C. (b) Rate performance of silicon anodes. Controlling delithiation of silicon anodes with lithiation fixed at 0.2 C (c) Same lithiation/delithiation C-rate were used for (d). Cyclability at 1 C/1 C cycles. (e) [7]

Chapter 2. A crosslinked binder to enhance the performance of antimony anode for sodium-ion batteries

2.1. Introduction

In this work, we present a novel binder system composing of cyanoethyl pullulan (pullulan-CN) crosslinked with PAA for antimony-based SIBs. The polysaccharide backbone of pullulan-CN provides mechanical toughness to suppress the volume expansion of antimony during sodiation while the cyanoethyl groups of pullulan-CN facilitate sodium ion transport (high sodium ion transport number t_{Na+}). The dissolution of pullulan-CN in electrolyte was prevented by crosslinking pullulan-CN with PAA. The bi-polymer composite binder system (PAA/pullulan-CN) was compared with PAA and PAA/pullulan to decouple the effects of the mechanical toughness factor and transference number factor on cell performances. Resultantly, PAA/pullulan-CN drove antimony-based SIBs to work most reversibly along sodiation/desodiation cycles.

2.2 Experimental method and materials

2.2.1 Binder & Antimony preparation.

Nano-size antimony (~200 nm) was prepared by reducing Sb^{3+} **(Scheme 4)**. 0.6 g $NaBH_4$ was introduced into 1 g $SbCl_3$ in 50 ml ethanol for reduction reaction. The solution was stirred at 150 rpm for 3 h at room temperature. Sb particles were recovered and washed through vacuum filtration with excess ethanol and deionized water. The Sb particles were dried under vacuum at 120 °C and then freeze-dried at -120 °C (Operon FDCF-12012). Two different polymeric binder solutions were prepared. Pullulan (MW = 200,000; Sigma-Aldrich) or pullulan-CN (MW =316,000; Shin-Etsu Chemical) was mixed with PAA (MW = 250,000; Sigma-Aldrich) at 8:2 wt. ratio in N-methyl-2-pyrrolidone (NMP) solvent at 80 °C.
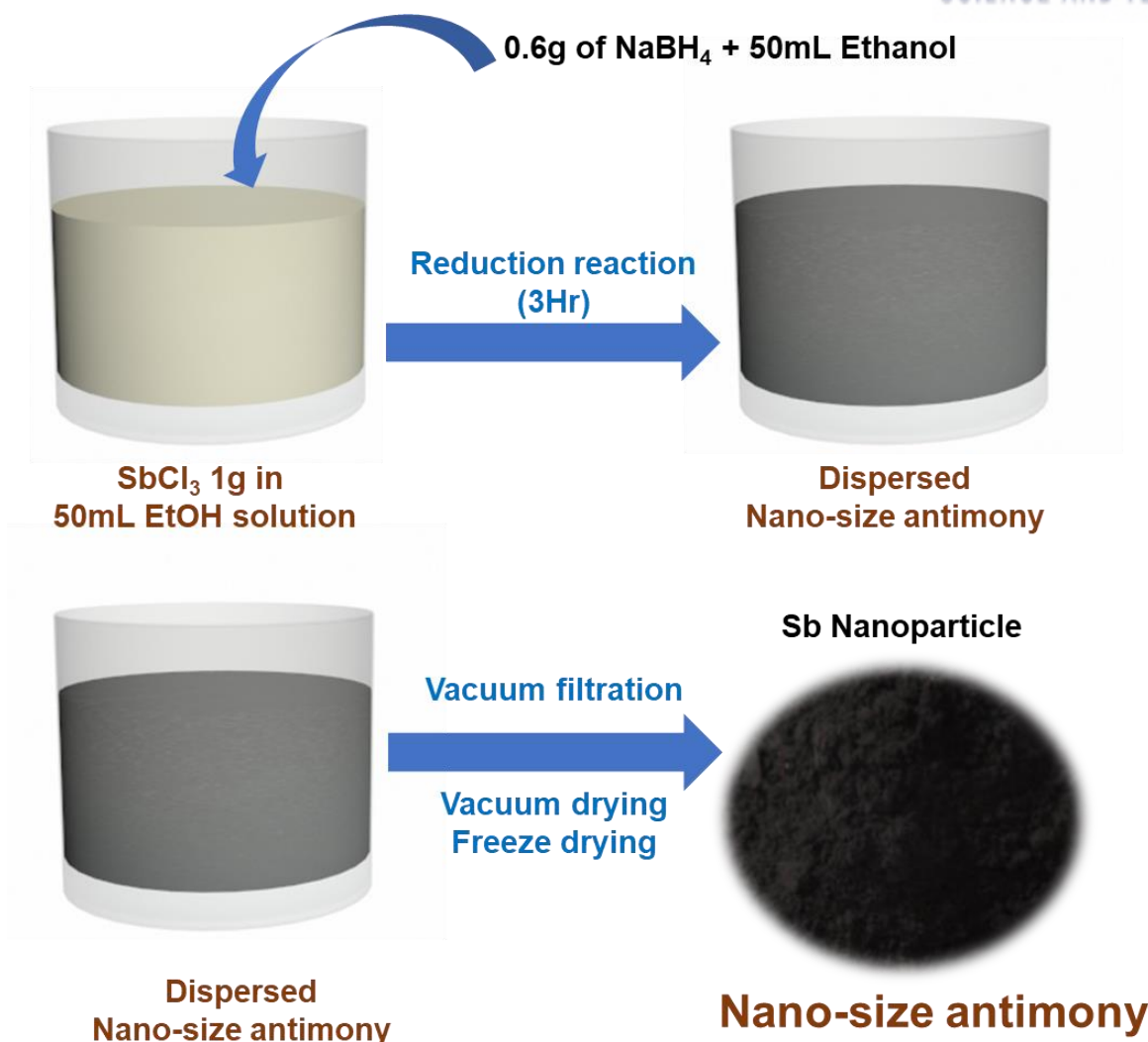
0.6g of NaBH$_4$ + 50mL Ethanol

**SbCl$_3$ 1g in
50mL EtOH solution**

**Reduction reaction
(3Hr)**

**Dispersed
Nano-size antimony**

**Dispersed
Nano-size antimony**

Vacuum filtration

**Vacuum drying
Freeze drying**

Sb Nanoparticle

Nano-size antimony

Scheme 4. The nano-sized antimony particles were synthesized by chemical reduction reaction of SbCl$_3$. [41] 1.0 g of SbCl$_3$ is dissolved by 50 mL of ethanol, then mix it with 0.6 mg of NaBH$_4$ in ethanol solution at room temperature, at 150 rpm stirring. The reduction reaction lasts for 3 hours, then took vacuum filtration with D.I water and ethanol to harvest the resultant. After the filtration, dry antimony particles for 80 °C, vacuum condition, then insert the powder in the freeze dryer at -120 °C condition.

2.2.2 Cell preparation

The 2032-coin-type configuration was used for the antimony-based SIB half cells, having sodium metal for counter electrode with the glass fiber membrane (Wattman) as the separator. The slurry of antimony particles, binder polymer and carbon black at 7 : 1.5 : 1.5 wt. ratio in NMP was loaded on copper foil at 1.0 mg cm^{-2}. Then, the antimony electrodes were dried at 150 °C for 3 h in vacuum.

Thin sodium foil was used for counterpart of the antimony anode, by cutting and rolling sodium metal chunk (Sigma-Aldrich) about 10 um thickness. Glass-fiber separator (Wattman) was used for effective ion transport and prevent short circuit of cell. 1.0 M $NaClO_4$ in EC/PC (1:1 v/v) with 10 wt. % FEC additive was used as electrolyte (EC = ethylene carbonate; PC = propylene carbonate; FEC = fluoroethylene carbonate). The assembled cells were located at 45 ℃ for 3 h before electrochemical characterization. Assembling coin type cells were assembled in Ar-filled glove box (MOTEK).

2.2.3 Mechanical characterization

Adhesion strength of 10 μm-thick antimony composite electrodes was measured by 180° adhesive peel strength test described in ASTM D1876. Tensile strength of 50 μm-thick binder films was measured by stretching the films by the tensile strength machine (Petrol LAB DA-01).

2.2.4 Electrochemical characterization.

The antimony-based SIB cells were charged/discharged between 0.01 and 2.0 V (WonATech WBCS3000). The first cycle was operated at 0.05C (33 mA g^{-1}) to form the stable SEI layer. Cyclic voltammograms (CVs) and Electrochemically active surface area (ECSA) were obtained by scanning potential at various scan rates (Biologic VMP). The transference number of sodium ion (t_{Na+}) were measured by the potentiostatic polarization method (VSP-300, BioLogic). Sodium metal symmetric cells were constructed with the glass fiber separator (Wattman) used in the SIB cells between the metals. The separator was coated with one of the tested binders (PAA, PAA/pullulan or PAA/pullulan-CN) by soaking the separator in the corresponding 10 wt. % binder solution and then drying at 150 ℃ for 3 h. **(Scheme 5)** The electrolyte used in SIB cells was injected to the sodium symmetric cells.
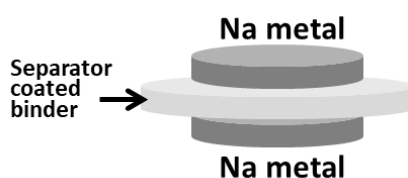
Scheme 5. schematic figure of binder-coated separator for measuring transference number.

2.2.5 Material characterization.

Functional groups of the binders were spectroscopically characterized by infrared (Bruker ALPHA). The microstructural morphology of antimony electrodes was investigated by the scanning electron microscopy (SEM; S-4800 Cold FE-SEM). The SEI layer of electrodes was characterized by the X-ray photoelectron spectroscope (XPS; ESCALAB 250XI) with C1s peak focusing.

2.3. Results and Discussion

The PAA/pullulan-CN-based antimony anodes were prepared to have the cross-linkage between PAA and pullulan-CN and strong bonds between PAA and antimony. The anode slurry containing antimony particles with PAA/pullulan-CN was coated on copper current collectors. Then, the anode was aged at 150 ℃ for 3 h. PAA was strongly bound to antimony surface as the condensation reaction of the carboxyl side chain of PAA and the hydroxyl moieties of the surface oxide of antimony[16, 46] proceeded at the aging temperature.[29, 32, 47] At the same time, PAA and pullulan-CN were crosslinked via the condensation reaction between the carboxyl moieties of PAA and the hydroxyl moieties of pullulan-CN **(Scheme 6a)**.[4] Furthermore, the sodium ion (yellow balls at **Scheme 6b**) is strongly bound by the cyanoethyl moieties around the glucopyranosides. As a result, the ion transport around the electrode was improved.
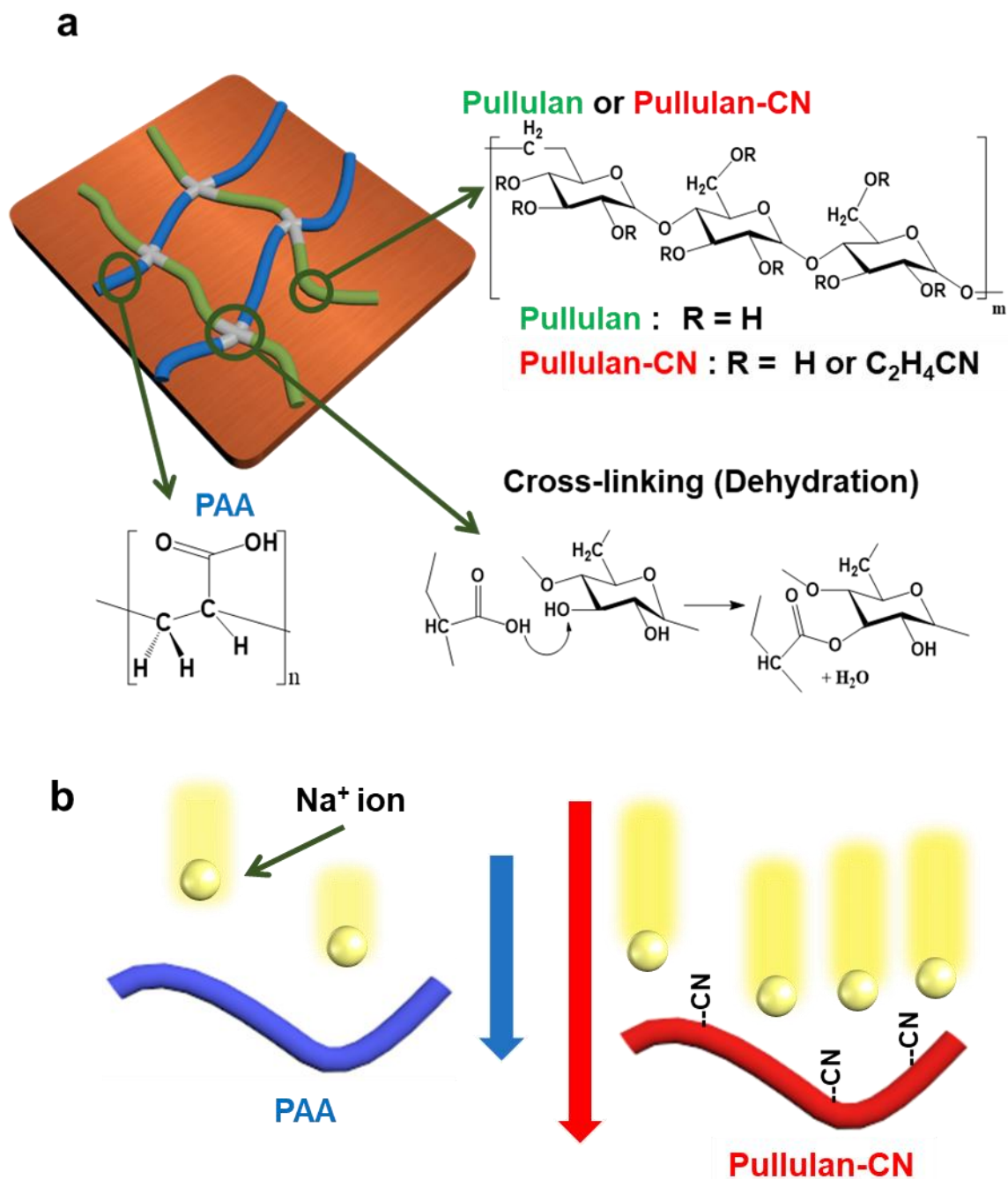
Scheme 6. Graphical showing of the three binders and their cross-linking. (a) Chemical structures of three different polymer binder and their crosslinking dehydration reaction; Blue strands = Poly-acrylic acid (PAA); Red strands = Two kinds of polysaccharides, Pullulan or Pullulan-CN; White intersection = Crosslinked polymer binder network formed by dehydration reaction between Poly-acrylic acid and Pullulan or Pullulan-CN. (b) Increasing of sodium ion transfer around the electrode facilitated by pullulan-CN binder, comparing with PAA.

The chemical structure of binders and bipolymer condensation reaction were confirmed by IR spectra. Hydroxyl peak of the pullulan was observed, (dispersed around wavelength 3304 cm^{-1}) and smaller hydroxyl group peak of pullulan-CN was observed, (dispersed around wavelength 3460 cm^{-1}) because of replacing hydroxyl group to cyanoethyl groups. Nitrile functional groups of pullulan-CN and PAA/pullulan-CN were observed at the wavelength 2250 cm^{-1}. The carboxylate peak of non-crosslinked PAA at 1695 cm^{-1} is observed. When the bipolymer mixture of PAA and pullulan or pullulan-CN had gotten 150 °C under vacuum, carboxylate peak of PAA converted to ester group peak with the hydroxyl groups of pullulan or pullulan-CN. Thus, shifted ester group peak of PAA/pullulan or PAA/pullulan-CN was observed at 1703 cm^{-1}, and hydroxyl group peak of pullulan or pullulan-CN was disappeared during the condensation reaction. [4] Moreover, two carboxylate moieties in the PAA react each other, making anhydride peak at 1801 cm^{-1} (**Figure 8**). [32]
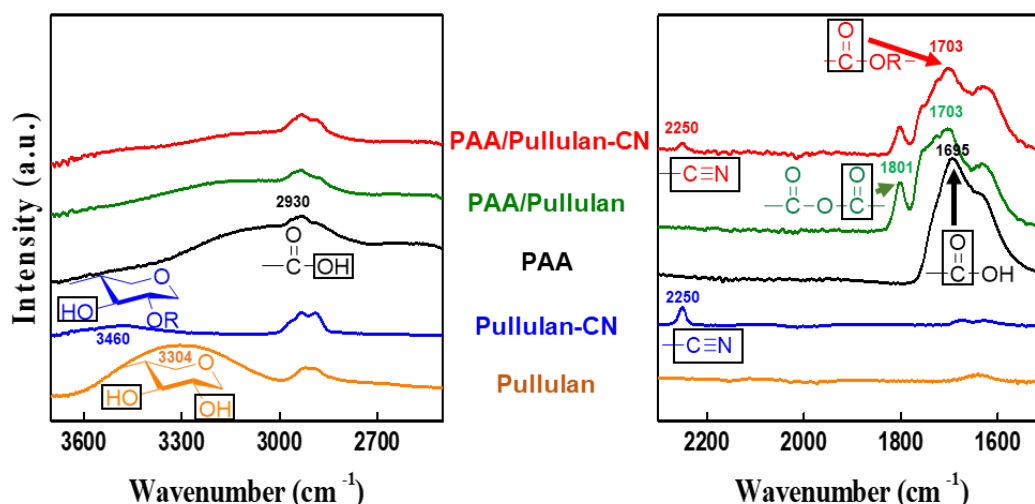
Figure 8. Structural informations about three polymers and their cross-linked bipolymers. The disappearance of hydroxyl and carboxylate moieties in the crosslinked polymers, appearance of ester moieties of cross-linked bi-polymer binders and remained nitrile groups measured by FT-IR spectra.

Mechanical properties of binders, such as stiffness and elasticity, were investigated since they affect the events of volume expansion and pulverization significantly (**Figure 9a**). The PAA film was easily elongated even by a small stress. The elastic modulus of PAA (1.03 MPa) was too small to resist against the volume expansion of antimony during sodiation. The PAA became mechanically stiffer after being cross-linked with polysaccharide: elastic modulus = 1.75 MPa for PAA/pullulan and 4.68 MPa for PAA/pullulan-CN. Both cross-linkage and higher elastic moduli of pullulan and pullulan-CN are responsible for the increase in mechanical stiffness. Dipole-dipole interaction of

nitrile groups encouraged PAA/pullulan-CN to be stiffer than PAA/pullulan.[48] However, both of the pullulan-based composite binders were less stiff than PAA/CMC (6.75 MPa) that is the binder popularly used for silicon anodes. The elasticity of pullulan backbone of pullulan-CN originates from the reversible chair-to-boat transition of pyranose unit of the polysaccharide on elongation.[3, 49] The α-glycosidic linkages of pullulan allows the molecular-level conformational change while the conformation of polysaccharide based on β-glycosidic linkages such as CMC is fixed at chair even after elongation. In our previous work, a more durable operation of silicon LIB was demonstrated by using pullulan crosslinked with PAA (PAA/pullulan) instead of the popularly used PAA/CMC. The PAA/pullulan let antimony anodes breathe in and out lithium ions with volume change rather than by fixing their dimensions.

Adhesion and cohesion of PAA/pullulan-CN were investigated by peeling off the Sb-containing active layers loaded on copper foil from the foil by using the 3M Magic tape (**Figure 9b**). The active layer containing PAA/pullulan-CN was most hardly detached, indicating the strongest adhesion. The minimum strength after the peel-off point was: 0.65 N/mm for PAA/pullulan-CN; 0.41 N/mm for PAA/pullulan; 0.18 N/mm for PAA. All the mass of active layer based on PAA/pullulan-CN was detached from the foil and found on the 3M Magic tape after the peel-off. It confirmed that the PAA/pullulan-CN guaranteed the strong cohesion between electrode components (antimony and carbon black) and therefore the electrode integrity. However, the pullulan-absent and cyanoethyl-absent binders (PAA and PAA/pullulan, respectively) showed lower and uneven peel strength. Only a portion of the mass of the active layer left on the 3M Magic tape confirmed their poor cohesion strength. It was reported that the nitrile pendants of polyarylene ether nitrile played a role of enhancing its adhesion ability due to their polar interaction. [48, 50, 51]

From the viewpoint of ionics, the PAA/pullulan-CN showed the highest transference number of sodium ion (t_{Na+}; **Figure 9c**): 0.68 for PAA/pullulan-CN versus 0.49 for its cyanoethyl-absent counterpart (PAA/pullulan) and 0.38 for its pullulan-absent counterpart (PAA). The cyanoethyl groups would be partly responsible for the high t_{Na+} value. It was reported that the solvated sodium ion is more loosely bound to the cyanoethyl groups than its counter-anion, perchlorate.[45, 52-57] The high t_{Na+} supports high concentration of sodium ions nearby antimony particles during sodiation. The concentration polarization observed especially at the end of fast charging is possibly relieved because the lack of charge carriers nearby electrodes is solved in such a high t_{Na+} environment. Also, high dielectric constant of pullulan-CN ($\varepsilon = 19$ for pullulan-CN[58, 59] versus about 9.4 for pullulan [60] at 20 °C) possibly encourage the desolvation of sodium ions. The cyanoethyl side chains of the pullulan-CN binder plays an important role to increase the dielectric constant. This mechanism to reduce the

desolvation activation energy possibly improves the charge transfer kinetics of sodiation, guaranteeing good rate performances.

The superiority of transference number and desolvation capability of PAA/pullulan-CN supported full utilization of active mass of antimony in composite electrodes. Cyclic voltammograms of antimony anodes in half cells were compared between binders (**Figure 10**). Two cathodic processes of sodiation of antimony were identified at 0.39 V and 0.65 V. [61, 62] Higher currents were obtained from the PAA/pullulan-CN-based antimony anode than its controls. Electrochemical active surface area (ECSA) was calculated by Randles-Sevcik equation,

$$I_{pc} = (2.69*10^5)n^{2/3}C_0^*AD^{1/2}v^{1/2}$$

where I_{pc} = peak current at a given potential, $n^{2/3}$ = number of transferred electron (1 for Na^+), D is diffusion coefficient of Na^+ ion, C =concentration of the Na^+ ion.estimated from the slope of Randles-Sevcik plots (peak current at 0.39 V versus the root square of scan rate).

The ECSA of PAA/pullulan-CN-based electrode is about 1.5 times larger than that of PAA/pullulan or PAA-based electrode. The control binders showed the similar value of ECSA.   (**Figure 9d**)

Figure 9. Mechanical behaviors of electrodes and different binders, (a) Stress-strain measurement of the binder film on the slide glass, measuring the mechanical strength of PAA, PAA/Pullulan, PAA/Pullulan-CN, and PAA/CMC. (b) Adhesion characteristics of those binders in the electrode on the current collector, measured by peel test method. (c) The transference number of sodium ion (Na^+) in each sodium symmetric cells containing 1.0 M $NaClO_4$ with EC/PC (1:1 v/v) 10% FEC additive , Wittman^{tm} glass fiber separators which are coated with different binders, reference(not coated, raw separator) , PAA/pullulan-CN , PAA/pullulan, and PAA, respectively. (d) The Electrochemically active surface area (ECSA) and cyclic voltammograms of antimony electrodes were indicated the relationship between cathodic peak currents at **Figure 10a, b and c** (Ipc) and the square root of the scan rate.

Figure 10. The cyclic voltammograms of antimony electrodes were indicated, with PAA, PAA/Pullulan and PAA/Pullulan-CN at the scan rate of (a) 0.2, (b) 0.6, and (c) 1.0 mV s-1

Considering its balanced mechanical properties between stiffness and elasticity, strong adhesion/cohesion, high transference number and high dielectric constant, we tested SIB half cells

galvanostatically by using the PAA/pullulan-CN binder. The sodiation and desodiation plateaus were found at 0.6 V and 0.9 V in all cells independent of binders **(Figure 11a)**. The highest initial coulombic efficiency was obtained from PAA/pullulan-CN when compared with the controls: 70% for PAA/pullulan-CN > 69% for PAA/pullulan > 63% for PAA. The PAA/pullulan-CN was also superior to its controls in terms of cyclability at both 0.2C and 1C **(Figure 11b and c)**. The cells containing pullulan-CN showed good capacity retention at least up to the 200th cycle. However, the cells based on the other two binders did not work at the cycle. The effects of high transference number and high dielectric constant of the binder were clearly shown. The capacity difference between the pullulan-CN-present and absent binders became more emphasized as the current (C-rate) increased **(Figure 11d)**. The capacity decay of the pullulan-CN-containing cells was not very serious along C rates: 55.9 % of the capacity at 0.2C was achieved at 20C. On the other hand, a meaningful capacity was not extracted at 20C from the control binder cells.

Figure 11. Electrochemical performances of Sb electrodes with three different binders. (a) The first galvanostatic charge/discharge cycle of three electrodes with the condition of 0.05 C rate, potential range of 0.01 – 2.0 V (vs Na/Na+) showing with calculated initial coulombic efficiencies respectively. Cyclabilities of three electrodes which contain different binder each, by plotting cell discharge

capacities versus cycle number during 200 cycles, at (b) 0.2 C/0.2 C charge/discharge or (c) 1 C/1 C.(d) Rate performances of three electrodes, plotting discharge capacities versus specific C rates, all C rate conditions were operated for same value of charge/discharge C rates during 5 cycles each, and after highest value of 20 C rate, return the C rate as 0.2 C. (1C = 660 mA g-1)

The rate capability obtained from the PAA/pullulan-CN cells is considered most excellent when compared with those of previously reported works **(Table 2 and Figure 12)**.

Materials	Initial capacity (mAh g^{-1})	C rate	Capacity at Higiest C rate (mAh g^{-1})	Capacity retention (%)
Sb electrode with PAA/Pullulan-CN binder (This work)	571.46	20	319.17	55.85 %
Sb@C coaxial nanotubes[18]	948	21.10	310	32.70 %
Sb nanorod array[62]	~950	21.05	557.7	58.71 %
Sb hollow nanosphere[11]	~628	2.42	315	50.16 %
Nanoporous antimony[15]	~610	5	420	68.85 %
Cypress leaf-like Sb porous hollow microsphere[14]	639	4.85	312.9	48.96 %
Bulk Sb[63]	~600	4	491	81.83 %
Sb/C fibers[64]	405	9.1	88	21.73 %
Nanocomposite Sb/C[65]	624	3.03	309	49.52 %

Sb-C nanofibers[66]	631	5	337	53.41 %
Rod-like Sb-C composite[67]	499.8	0.38	259.1	51.84 %
Antimony/graphitic carbon composite[68]	310	10	202	65.16 %
Spherical nano Sb@C composites[69]	420	15.15	146	34.76 %

Table 2. The comparison with our works and other reported electrodes which containing antimony in the sodium ion battery anodes.
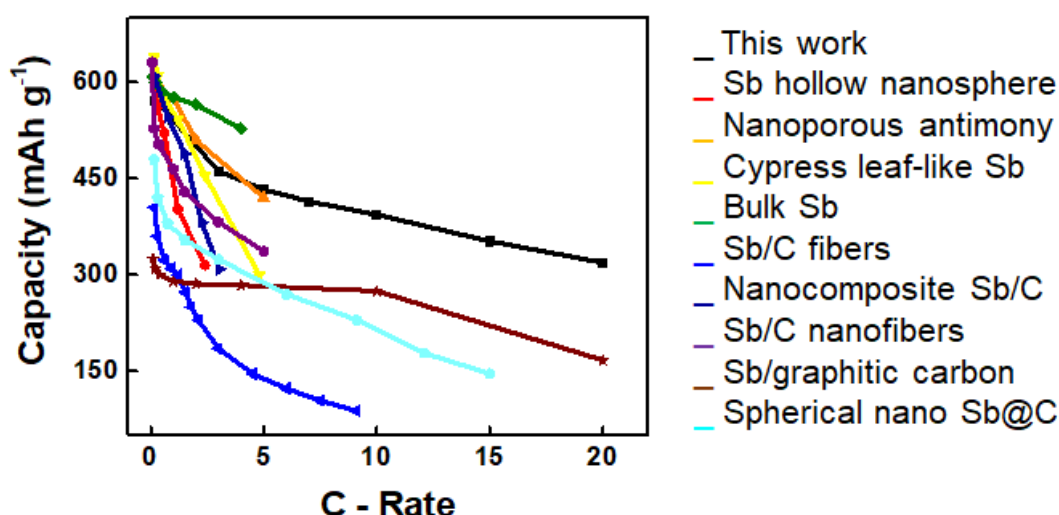
Figure 12. The comparison of rate performance which contains antimony electrodes were indicated, with different experimental method, mentioned in **Table 1**.

The morphological change of antimony electrodes was traced along sodiation and desodiation (**Figure 13**). In the presence of PAA as the binder for antimony electrode (**Figure 13a**), the 11.8 μm-thick electrode was thickness-expanded more than 2 times after the first sodiation. The original thickness was not fully recovered after the following desodiation. The thickness expansion at 123% (14.5 μm/11.8 μm) was not reversible. After 100 times repeated sodiation followed by desodiation, the thickness of PAA electrode reached 21 μm with macroscopic cracks developed. As expected from its

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low elastic modulus and weak cohesion capability, the PAA did not keep the electrode integrity and therefore showed poor electrochemical performances. On the other hand, the thickness expansion of the bi-polymer-crosslinked binders after the first sodiation was not as serious as that of the PAA electrode **(Figure 13b and c)**. Their original thicknesses were almost or fully recovered (especially for PAA/pullulan-CN) after the following desodiation. The electrodes based on the pullulan-related binders (thinner than 14 μm) were much thinner than the PAA electrode (thicker than 20 μm) after the 100th sodiation/desodiation cycles.
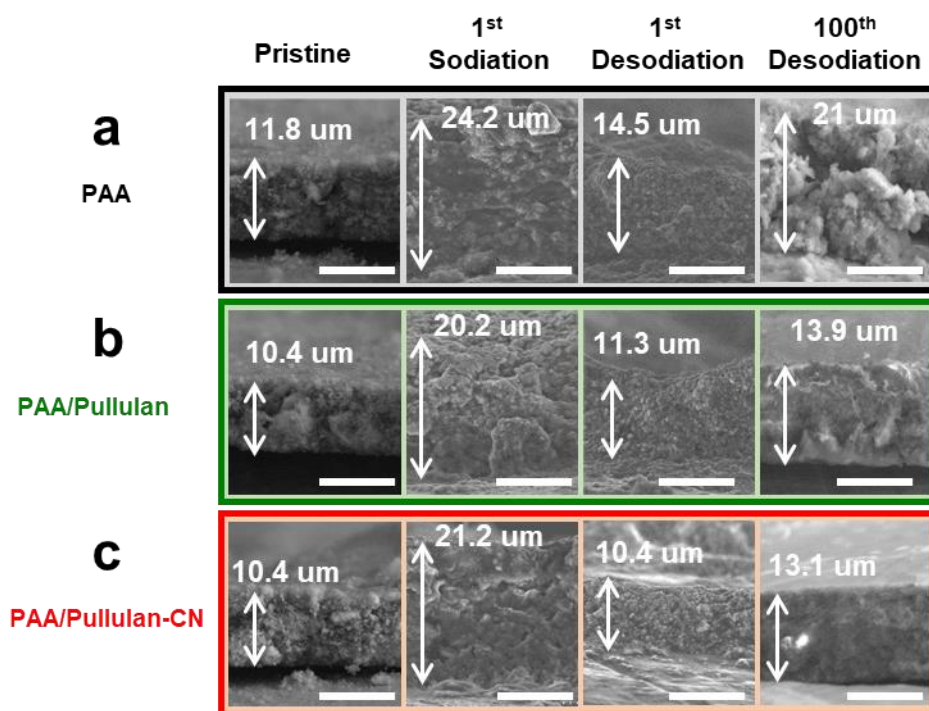
Figure 13. SEM images of Sb anode surfaces. The pristine SEM images of electrodes were captured after 12 hours in manufacturing. 1 C rate charge/discharge cycles containing different binders of (a) Poly-acrylic acid (PAA), (b) crosslinked PAA/Pullulan and (c) crosslinked PAA/Pullulan-CN at initial state, for Pristine, 1st sodiation, 1st desodiation, and 100th desodiation images. (1C = 660 mA g^{-1})

For better understanding on the excellent capacity retention even at fast charge and discharge performance, X-ray photoelectron spectroscopy (XPS) was performed to identify the components of the SEI layer at the electrode after the cycle used in each binder. The component of SEI layer was compared with after formation and 10 cycle. **(Figure 14a and b)** The surface of the electrodes featured five split peaks at C1s (the C-C single bond at 284.8 eV, the ether bond (-COC-) at 286.15 eV, the ester bond (-COOR-) at 288.4 eV, the carboxylate group (-COOH) peak at 289.5 eV and/or the Na2CO3 peak at 290.3 eV. [70-72] The surface of PAA/Pullulan-CN based electrode featured less

carbonated contents in its SEI layer (288.4 and 290.3 eV), compare with PAA and PAA/Pullulan: % area of the carbonate peak = 14.30 % for PAA/pullulan-CN, 14.91 % for PAA/pullulan and 18.71 % for PAA after 10 cycle (**Figure 14**). The carbonate components were formed in SEI layer form EC molecules existing in electrolyte are reduced. The initial SEI layer was made of FEC (fluorinated EC), which was used as an SEI layer forming additive in this operation, so lower levels of carbonate are involved. Therefore, a relatively high carbonate content indicates decomposition of additional EC molecules. The new surface of antimony exposed to EC-based electrolytes developed with cracking during repetitive cycles accounts for the high carbonate content observed in PAA and PAA/Pullulan based electrodes. Basis of the results, the high t_{Na+} help to guarantee health SEI layer, resulting in stable and fast electrochemical performance. [71, 73, 74]
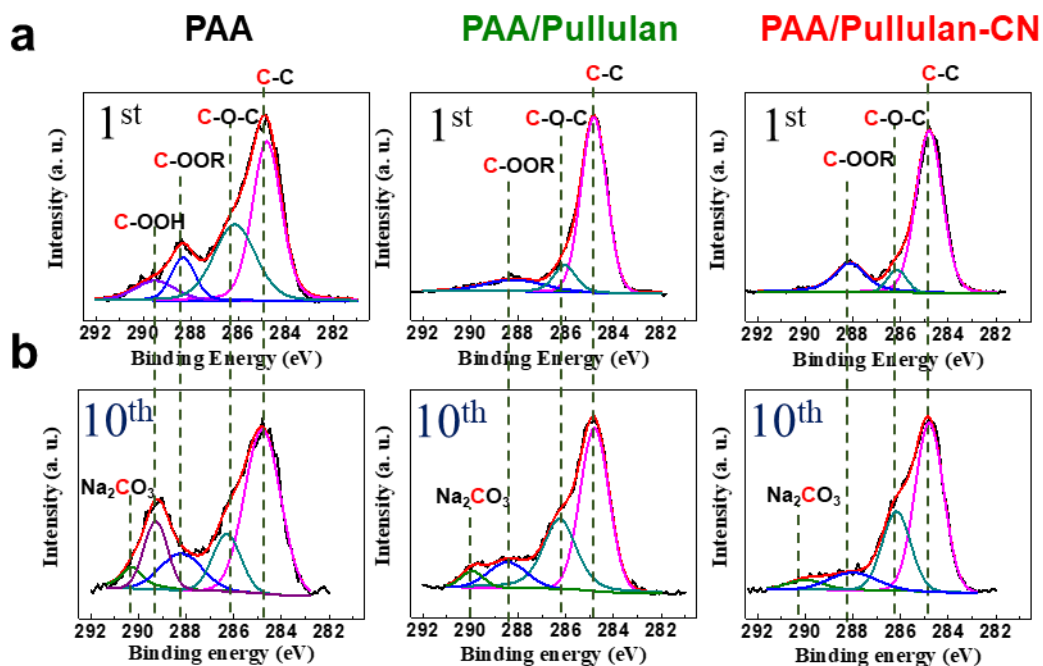
Figure 14. XPS analysis of three Sb electrodes vs Na metal, precycled for several numbers, measured by ESCALAB XPS. C 1s XPS spectra of Sb electrodes containing PAA, PAA/Pullulan, and PAA/CRS binder each, cycled after (a) 1cycles (b) 10 cycles for 0.05C/0.05C formation step then 1C/1C charge/discharge step (1C = 660 mA g^{-1}).

2.4 Conclusion

In this work, we presented PAA/pullulan-CN as the effective binder for antimony anode of SIBs. Two characteristics (bond formation of PAA and ion transport, proper mechanical strength of pullulan-CN) of the bi-polymer-crosslinked binder system improved the reversibility and kinetics of sodiation/desodiation of antimony. Its balanced mechanical strength between stiffness and elasticity inhibited the volume expansion (thickness change <130% for PAA/pullulan-CN versus 180 % for PAA at the 100th cycle of 1C/1C) as well as pulverization, guaranteeing the capacity retention along cycles (*reversibility* gain: capacity at the 200th cycle of 1C/1C = 400 mAh g^{-1} for PAA/pullulan-CN versus meaningless capacity for PAA). Also, its high sodium ion transference number (t_{Na+} = 0.68 for PAA/pullulan-CN versus 0.49 for PAA/pullulan) provided the sodium-ion-rich environments around antimony with lower desolvation activation required, supporting high rate performance (*kinetic gain*: capacity at 20C = 320 mAh g^{-1} for PAA/pullulan-CN versus 122 mAh g^{-1} for PAA/pullulan).

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