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Biomass-Derived Polymeric Binders in Silicon Anodes for Battery Energy Storage Applications

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The demand for portable electronic devices has increased rapidly during past decade, which has driven a concordant growth in battery production. Since their development as a commercial energy storage solution in 1990s, lithium-ion batteries (LIBs) have attracted significant attention from both science and industry due to their long cycle life, high energy density, low self-discharge rate, and high working voltage. Production of LIBs requires large amounts of polymeric binder – commonly polyvinylidene difluoride (PVDF) – for processing and performance purposes. However, since this material is petrochemically-derived, it is far from "green" or sustainable. On the other hand, polymers and their building blocks are found widely throughout nature and can be renewably sourced from biomass at low cost; therefore, replacing PVDF with biomass-derived binders is a promising approach to reduce the environmental footprint of LIBs. Additionally, polymer binders play a critical role in next-generation battery performance. For instance, silicon (Si) is a promising high-capacity anode material for LIBs because of its high theoretical capacity (4200 mAhg^{-1}), low working potential, and high abundance in Earth's crust. However, its huge volume change during charge/discharge tends to result in shortened cycle life, since conventional binders interact only weakly with silicon's native surface and cannot maintain long-term integrity of the electrode. Naturally-derived polymers have found better success in this role due to their high structural advantages. In this review, we summarize recent developments in silicon anode binders derived from various biomass sources, with a focus on polymer properties and their effect on battery performance. We propose various perspectives based on our own assessment of these works, and provide brief commentary on the future outlook of the field.

Introduction

The past decade has seen rapid growth in the demand for cheap, portable energy, while at the same time demonstrating the destructive potential of unchecked, non-renewable energy production [1, 2]. Undeniably, one of the most significant challenges of our time is to develop clean, greener, sustainable and safe energy sources. Lithium-ion batteries have been widely deployed in portable electronics such as smart phones and laptops thanks to their light weight and superior properties. Advances in battery research also benefit the electrical vehicle market, as traditional petroleum systems are expected to be phased out in the near future. Therefore, in recent years, scientific and industrial research on lithium-ion batteries has gained great importance in order to meet the increasing need [1, 3-6]. LIBs are constructed from several major components: an anode, a cathode, an electrolyte allowing the transport of Li$^+$ ions, a separator to prevent internal short-circuit, and current collectors for conducting electricity between the interior and exterior of the cell [7-12]. Notably, each electrode consists of a redox-active material along with conductive additives and a polymer binder for cohesion between discrete particles. Generally, the performance of these devices is highly dependent on the characteristics of individual components, and more importantly, the synergistic effects of the whole composites [10, 13-18]. Various materials for anodes, cathodes, separators, electrolytes, and especially binders have been designed and produced to enhance the performance of LIBs. However, due to the high cost and non-renewable origin of many such materials, investigation of alternative material resources such as biomass has gained special importance in recent years. In order to achieve a truly "green" energy economy using LIBs, there must not only be a transition to environmentally-friendly energy sources, but also to renewable materials of manufacture for the devices themselves.

A typical LIB contains two active materials: graphite at the anode and a lithium-containing ceramic at the cathode. Energy storage is achieved by shuttling electrons between these two materials, accompanied by internal migration of lithium ions to balance charge. Although graphite has been a cornerstone of LIB design since its commercialization, silicon (Si) has attracted great interest from the battery community over the past decade as an alternative active material. Si is seen as a much better anode than graphite due to its high theoretical capacity (4200 mAh/g$_{Si}$ vs. 372 mAh/g$_{Gr}$) at very low potential values (<1V vs. Li/Li$^+$). In other words, one equivalent of silicon can alloy with up to 4.4 equivalents of lithium (Li$_{4.4}$Si / Li$_{22}$Si$_5$), while graphite can only accommodate one lithium atom for each six carbon atoms. However, silicon has a major drawback: it suffers rapid capacity loss due to high volume change (up to 400%) during charge/discharge cycling. This volume change produces cracks in the electrodes and may break the crucial solid-electrolyte interphase

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(SEI) layer, causing a gradual increase of internal resistance and depletion of the electrolyte[19].

Altogether, these effects usually cause Si anodes to suffer from low cycle life, which has prevented their rapid commercialization. However, great research efforts have been made to avoid these capacity losses, with high-performance binder development being one of the most successful strategies. The main function of electrode binders are as inactive materials to assist in electrode fabrication and preservation of its structure during operation. Hence – especially for Si anodes – binders play a key role in maintaining structural stability and contributing to extended cycle life[20].

Biomass can be broadly defined as living organisms and their byproduct matter. Throughout human history, we have obtained raw materials and energy from biological sources such as animal waste and various terrestrial or aquatic plants; this type of energy is called biomass energy [1, 21-23]. For example, the oldest-known biomass energy sources are firewood, charcoal and animal manure. More recently, it has become possible to generate advanced materials from agricultural products, urban wastes, and agricultural industry wastes [23-26]. One emerging use of such biomass-derived materials is to change the unsustainable parts of electrochemical devices such as binders, active materials, and separators in energy storage systems. In recent years, a number of studies have been carried out on the development of biomass-derived materials for LIBs, and some important review papers have been presented [1, 10, 21, 27-30]. Cui et al. showed a bio-based flexible electronic device based on nanomaterials [31]. Nyholm et al. investigated a flexible cellulose-based polymer as a binder for energy storage systems [32]. Furthermore, Jabbour et al. reported the development of cellulose-based binders for LIBs [33]. Other studies have demonstrated energy-storage applications for a wide variety of natural polymers (lignin, alginate and its derivatives, etc.) [34-37].

In the following review, we provide a brief primer on the role and processing of binders for LIB applications, as well as materials production from biomass. We then give an overview of research, focusing on the latest advances in biomass-derived polymer binders and their effects on battery performance. Finally, we summarize these results and provide perspective on the current outlook of this field.

LIB Binder Basics for Silicon Anodes

Polymeric binders are critical to LIB design, and they can exert significant effects on electrode stability and capacity loss according to recent studies. Binder formulation plays an active role in balancing charge-discharge cycling performance, especially in regards to resisting electrode disintegration due to volume changes over time [38-43]. Many novel (synthetic) binders have been proposed in the scientific literature which are often block or graft copolymers [44-54], particularly those that are electrochemically inactive and designed to give mechanical reinforcement to the active materials. In general, the role of the binder is to maintain the mechanical integrity of the electrode i.e. promote continuous contact between active material, conductive additives, and the current collector. In order to design optimum polymer binders for LIBs, a given polymer must be considerably resistant to dimensional changes during charge-

discharge cycles, be electrochemically stable, and require only small amounts to preserve cohesion in order to maintain overall energy density [2, 55-61]. LIB electrodes are prepared by dispersing solid particles in a solvent solution of the binder, and both the homogeneity and viscosity of the resulting slurries are crucial.

LIB electrodes are porous composites containing active material particles and conductive carbon additives, which form an electron percolation network. This network must remain intact for the battery to function and therefore an adhesive component i.e. binder is required.

Binders for LIBs in particular, the following features are desirable:

(i) The binder material should contain polar functional groups such as -OH, -COOH, -O(CO)R, -SO$_3$H, -CN, etc. to promote strong adhesion of particles to the current collector metal foil and each other, so that a charge percolation network is maintained [5].

(ii) The binder must remain chemically and physically stable in contact with an electrolyte, such as ethylene carbonate, propylene carbonate, etc.[36]

(iii) The binder must have high electrochemical stability at low potential values[5].

(iv) The binder should not have a negative effect on cell impedance, whether by hindrance of Li$^+$ diffusion to the electroactive interface or in terms of redox reaction kinetics.

(v) The binder must be thoroughly soluble in solvent prepared with the active material and the conductive additives to produce a paint-like viscosity. Additionally, it needs to be uniformly dispersed for better interaction with the materials [55].

(vi) The binder should be low-cost, eco-friendly, and non-hazardous.

Additionally, the solvents required for slurry preparation necessitate further delineation between organic-solvent-based or water-based binders.

Interactions between binders and active materials at their interface are critical to many of the above characteristics. Binders may be divided into three types based on their interaction mode: [21, 62]

1) Point-surface contact binders (such as polytetrafluoroethylene [PTFE], SBR, polyacrylate latexes)

2) Segment-surface contact binders (PVDF, PAA, CMC, PVA, and PAN, etc.)

3) Network-surface contact binders, such as three-dimensional (3D) networks used as a cross-linked binder [56, 57, 63-66]

Organic solvents are more expensive and more harmful to the environment because of their flammability, toxicity and contribution to volatile organic compound (VOC) content in Earth's atmosphere. As a result of their environmental and cost advantages, water-based binders have gained a great interest over the last decade [57, 63, 66-70].

As an example of an organic-solvent-based binder, polyvinylidene difluoride (PVDF) is the conventional choice for preparation of commercial LIB electrodes due to its electrochemical stability and excellent bonding strength with active materials such as graphite [62]. However, although polyvinylidene difluoride (PVDF) is widely used in traditional designs, it is not appropriate for Si anodes with high

capacity due to its poor interaction with Si particles. Its relatively weak van der Waals forces cannot stand the large volume expansion during the lithium insertion[71]. PVDF also has other drawbacks, starting with its solubility properties: PVDF is poorly soluble in most solvents and requires use of N-methylpyrrolidone (NMP) for processing. This solvent, like PVDF itself, is petroleum-derived, and also a known reproductive toxin. Therefore, much recent effort has been dedicated to replacing NMP with less-harmful solvents, like water, which necessitates replacement of the binder as well. Additionally, when PVDF is used along with lithium salts, Li may directly react with the PVDF binder. Because of the formation of LiF during their reaction with lithium and electrolyte precursors can easily decline the charge-discharge cycle of LIBs [72]. Finally, the reaction between Li and fluorinated polymers is exothermic and may initiate thermal leakage and self-heating reactions, contributing to LIB safety concerns. Altogether, these drawbacks have incentivized new research into eco-friendly and low-cost binders to replace PVDF.

Biomass Materials

Since biomass is a vast resource and can be obtained nearly anywhere, it may be seen as an appropriate and significant source of energy and materials when harvested sustainably. Its utilization can also help the socio-economic development of rural areas, which tend to possess it in abundance[73]. Plants such as corn, wheat, herbs, and algae, maritime wastes, animal feces, fertilizer, industrial wastes, *etc.* can all be viewed as a source of biomass materials, in addition to the organic wastes discharged from households such as fruit and vegetable residues. Another advantage of biomass materials is that their usage costs are low due to their high abundance in nature[74]. Approximate costs of biopolymers that can be used as binders in LIBs are given in **Table 1**. Thanks to these advantages, the use of biomass is becoming increasingly important to solve global energy problems due to the limited fossil fuel resources [31, 75-77].

Biomass is used for different purposes in various fields, and the application type depends on its chemical and physical properties. For instance, the polysaccharide cellulose, which forms the skeletal structure of plants, is an important polymeric raw material due to its chemical structure. Cellulose consists of pyranose D-glucose molecules connected linearly through β-(1,4) linkages, and it has a versatile, semi-crystalline fibrous morphological structure. Cellulose nanocrystals are rod-shaped particles with high crystallinity and are obtained from lignocellulosic raw material sources [78-82]. In recent years, the production of cellulose nanocrystals from roots, stems, straw, leaves, and shells, etc. has significantly increased. Therefore, the use of plant waste as a source of lignocellulosic raw materials has accelerated due to its economic and environmental benefits. Cellulose-based nanomaterials are divided into two classes according to their extraction method and fiber dimensions; (i) cellulose nanocrystals, cellulose nanocrystallites or nanocrystalline cellulose; (ii) cellulose nanofibrils, microfibrillated cellulose or nanofibrillated cellulose. The latter material is made directly from wood [83, 84]; micro-fibril cellulose obtained from wood fiber tracheid has a multi-channel, mesoporous structure which enables intracellular transport of water and mineral salts.

Microfibrillated cellulose is produced by delaminating the wood pulp with mechanical pressure before chemical or enzymatic treatment. Plants and microorganisms can form cellulose macromolecules with different conformation and polymerization degrees; extraction from wood, bacteria or *Cladophora algae* can produce materials with different crystallographic forms and degrees of crystallinity (**Figure 1**) [78, 83].

CMC, alginate and chitin are a few examples of water-soluble binders. Derived from abundant biomass such as plants and bacteria CMC has received significant attention as a water-soluble, inexpensive, green chemical that can avoid disposal problems [33, 83, 85, 86]. Chitin is also a biopolymer, formed by the linkage of 2-acetamido-2-deoxy-β-D-glucose monomers through β-(1,4) bonding. Chitin is characterized by a polysaccharide structure with a large number of polar organic moieties, and it is the second-most-common biopolymer in nature after cellulose, being readily found in marine life, fungi, and arthropods [36, 87-90]. Carboxylic acid functional biopolymers such as CMC, alginic acid, etc. are generally modified with a base solution to make their salt form (CMC-Na, sodium alginate, etc.) which will be more water-soluble. Natural biological polymers are generally abundant in biomass and are easily accessible from a range of sources, such as forest products, grasses, tunicates, crustacea, and stalks[91].

Besides cellulose, many polysaccharides like alginate, carrageenan, agar or chitin can be isolated from various marine source such as algae, arthropods or corals. Since these organisms live in different marine environments, they can be used in a high range of applications such as bioengineering, pharmaceutical, chemical industries, and food technology. Other useful polysaccharides include amylopectin, a highly-branched polymer commonly found in plants, and β-cyclodextrin, a cyclic molecule formed by enzymatic treatment of starch. Many researchers have also produced novel polymeric materials based on dopamine, a catechol-bearing amino acid found in bioadhesive proteins.

Among all synthetic binders from the petrogenic sources, PVDF has a high electrochemical stability and is commercially employed as binder for LIBs. However, limitation remains. Primarily, PVDF is expensive due to complicated synthesis process. Furthermore, NMP is generally used as solvent to dissolve PVDF, that increases the cost and contaminate the environment. Lastly, PVDF solution is quite delicate to humidity in air that affect the viscosity, this seems same as few biomass-based polymers. Hence, the improvement of cheaper, greener, and better performance binders is significant for battery technology. Concordantly, some natural polymers or their derivatives, such as alginate, CMC, polycatechols, amylopectin, β-CD and polydopamine have been discovered to provide as green and vigorous binders to overcome the above mentioned deficiencies of PVDF or huge volume change of Si-based materials.

All of the above materials have been investigated as LIB binders. The advantages/disadvantages of some typical biomass-derived binders and the comparisons between them are presented in

Table 1. Natural polymers such as CMC, alginate, polycatechols, amylopectin, β-CD and polydopamine share the common advantages of being eco-friendly and abundant. Cells using these "green" binders typically display long cycle life, high energy density, and/or better safety compared to conventional designs, not to mention the low cost and inherently-sustainable production of these materials. Additionally, many biomass-based polymers can be engineered to be water soluble and support electrode aqueous processing, which can lower fabrication cost and reduce the safety/environmental impact of manufacturing.

A final advantage of using biomass-derived binders in comparison to PVDF is their stronger adhesion to silicon surfaces thanks to carboxylic acid and hydroxyl functionality. In other words, higher performance can potentially be achieved by using less binder, which means a higher ratio of active material. Like PVDF, the majority of biomass polymers mentioned here fall into the category of segment-surface contact binders: after coating, the polymer segments adhere to the surface of the active materials. In some cases, these polymers may be cross-linked network through chemical or thermal processes to produce three-dimensional (3D) networks. Although 3D network binders lead to high adherence, they are more difficult to manufacture while maintaining overall flexibility[92].

Recently-Reported Biomass-Derived Binders

Carboxymethylcellulose. Carboxymethylcellulose (CMC) is a synthetic, water-soluble cellulose ether derivative that is white-to-yellowish in color and fibrous. This polymer and its salts are commonly used as viscosity enhancers, emulsion stabilizers, and thickeners in food, pharmaceutical and cosmetic products [33, 36, 93]. CMC is soluble in hot and cold water, insoluble in most organic solvents, and compatible with water/alcohol systems. It increases aqueous solution viscosity without gelling, but it can also be cross-linked very easily. CMC is stiffer than PVDF: the Young's moduli of CMC and PVDF are 4100 and 650 MPa, respectively [20].

Electrodes made using CMC often show higher performance than PVDF[93]. In fact, the sodium carboxylate salt of this material (NaCMC) is very commonly studied as a binder for Li-ion negative electrodes, especially those based on Si. As an illustrative study, two NaCMCs with different degrees of carboxymethyl substitution DS = 0.6 and DS = 1.27 were compared as binders by Li *et al.* [82]. In another study, Lee *et al.* discovered that NaCMC (DS = 0.6) provides better adhesion of the electrode to current collector and more uniform dispersion of the electrode slurry than DS = 1.27 [79]. Curiously, little difference between initial coulombic efficiency was observed, which the authors explained by proposing that the -OH groups are not involved in irreversible reactions with Li. Drofenik *et al.* demonstrated that increasing the amount of NaCMC did not increase the capacity of Si electrodes, meaning the number of -OH groups had no effect on the irreversible capacity loss [93]. In this study, NaCMC binder produced better performance than other polymers when electrodes were cycled between 0.18 and

0.9 V. More than 1100 mAh g^{-1} discharge capacity was observed after 66 cycles in a cell at 0.1 C (**Figure 2**).

Alginate. Alginic acid, a copolymer of β-(1-4)-D-mannuronic acid and α-(1-4)-L-guluronic acid in varying ratios (**Figure 3A**), is a major constituent of brown algae (Phaeophyta). Alginates are hydrophilic colloidal substances which, in recent years, have been widely studied for biochemistry and Li-ion battery applications. One of the best examples comes from Kovalenko and colleagues, who obtained high-performance Si anodes for Li-ion batteries using sodium alginate as a binder [94]. Compared to the commercially available PVDF, the alginate binder (structurally characterized by NMR (**Figure 3B**)) showed much better cell performance and mechanical strength. Importantly, the Young's modulus of PVDF was severely reduced when swelled with electrolyte, but no change in the hardness of the alginate is observed. The mechanical robustness of alginate is considered to be one of the main factors that enables long cycle life in Si anodes, due to its tolerance of large volume changes from the active material. Although alginate shares many structural features with CMC, carboxylate groups on the polymer chain provides great advantages, especially for Li$^+$ ion transport with the formation of lithium carboxylate through the binder layer. In addition, carboxylates are known to provide specific binding interactions with the Si surface, forming covalent and/or hydrogen bonds with naturally-present silanol groups [95, 96]. Due to this critical blend of characteristics, the alginate along with Si nanopowder was able to reversibly store 1200 mAh g^{-1} discharge capacity for more than 1300 cycles at 1.2 A g^{-1} (**Figure 3C**). When fully charged/discharged at a high rate of 4.2 A g^{-1} (**Figure 3D**), the reversible capacity of such an anode was much higher than that of cells produced with the other binders such as PVDF and CMC, even for the 100th cycle [94]. Notably, the observed capacity was ~5x higher than the theoretical limit of graphite, and 9-13x higher than its experimentally-observed capacity at such high rate.

β-Cyclodextrin. Propounded first in 1891 by French chemist Villier, who observed crystals in waste alcohols, cyclodextrins(CDs) are oligosaccharides consisting of six or more glucopyranose units bound by α-1,4 glycosidic bonds. They are produced from an intermolecular transglycosylation of starch, aided by the glycosyltransferase enzyme [97, 98]. In the so-called β-CD molecule, consisting of 7 repeat units, each glucopyranose can form hydrogen bonds with neighboring hydroxyl groups. With the help of these bonds, a secondary structure forms in the molecule to give the β-CD a very robust shape. In fact, β-CD has poor solubility in water due to intramolecular hydrogen bonding, since these bonds reduce the ability of β-CD to interact with water molecules in the environment. However, β-CD is the still most widely used and preferred type of CD due to its low cost.

Although its low solubility restricts its applications, chemical modification of β-CD enables uses of the derivatives as binders. Choi and colleagues have demonstrated that a β-CD-based (β-CDp) binder is very effective for Si nanoparticle anodes in lithium cells because it reduces the decomposition rate in silicon during the lithiation-delithiation process [98]. In this study,

it was found that pristine β-CDp aggregated promptly due to intramolecular hydrogen bonding, which weakened the overall mechanical durability of the Si electrode. However, when combined into a hybrid complex with alginate, β-CDp lent ductility to the network structure owing to its interaction with carboxylate groups (COO⁻) (**Figure 4A**); such interactions have the ability to repair damaged structures [41, 99, 100]. Thus, compared to the pristine β-CDp, it was observed that the hybrid complex produces better capacity and retention (**Figure 4B**). The low cost and ease of modification for β-CD makes it a promising choice for lithium-ion electrode binders.
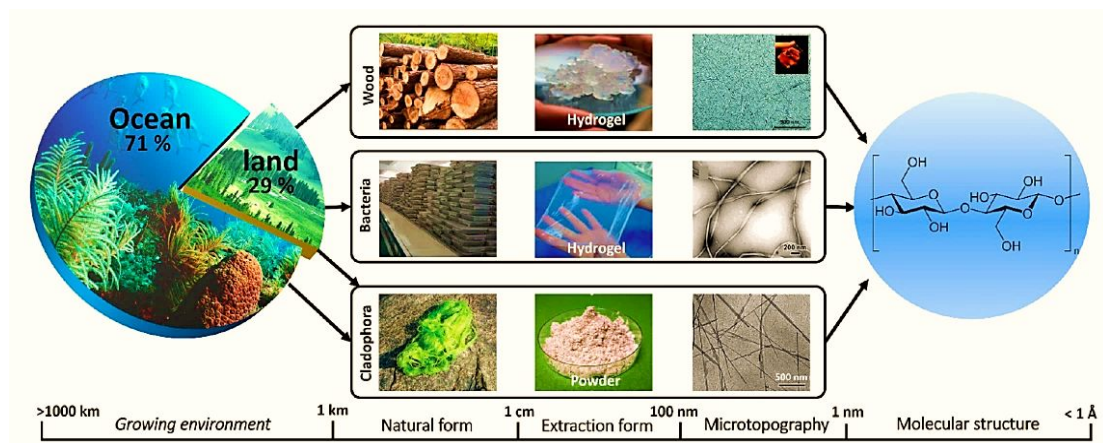
Figure 1. Overview of different forms of cellulose extractable from biomass, showing the range of scales for the different growth environments. *Copyright (2019) American Chemical Society*

Table 1. Comparison of typical biomass-derived binders with PVDF.

| Binder	Scope	Advantages	Disadvantages	Cost ($/kg)	Structure	Performance	Ref.
PVDF	Cathodes, Si anodes	Electrochemical stability	Expensive/ sensitive to moisture/ low cycling capacity	25-32		260 mAh g^{-1} after 50 cycles at 0.1C	101-104
CMC-Na	Carbon based and Si, Sn, Ge anodes	High source/ high viscosity/ little required/ cheap/ environmentally-friendly/ stiff	Low flexibility/ variable chemical structure/ viscosity can be limiting	2-4		1200 mAh g^{-1} after 80 cycles at 0.2C	82, 84, 105, 106
Alginate	Si and Sn anodes	High stiffness electrolyte/ Algae sources/ low ionic impedance/ evenly distributed carboxyl groups	Variable molecular structure/ unpredictable slurry viscosity	11-15		1200 mAh g^{-1} after 1250 cycles at 1C	34, 94, 107, 108
β-CD	Si anodes	Starch sources/ eco-friendly	Low viscosity	3-5		1500 mAh g^{-1} after 50 cycles at 0.2C	97, 98, 109
Polycatechols	Si anodes	High source/ cheap/ environmentally-friendly	Low viscosity	2-3		2100 mAh g^{-1} after 400 cycles at 0.5C	87, 110-113
Amylopectin	Si and Ge anodes	Eco-friendly/ starch sources	Easily degraded/ low viscosity	5-8		800 mAh g^{-1} after 50 cycles at 0.4C	114, 115
Polydopamine	Si anodes	Eco-friendly/ obtained from plant and animals/ cheap	need to use another precursor/ variable slurry viscosity	4-7		1074 mAh g^{-1} after 300 cycles at 0.5C	116-120
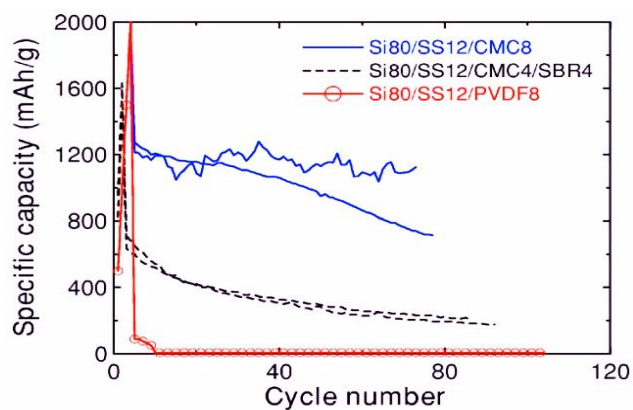
Figure 2. Cycling performance of cells each having Si80/SS12/CMC8, Si80/SS12/SBR4CMC4, and Si80/SS12/PVDF8 electrodes. *Copyright 1997, Electrochemical Society*

Polycatechols. Mussels are marine bivalves composed of double shells interlocked with very strong bonds. These creatures firmly anchor themselves on all kinds of surfaces such as pier posts, dock walls, and rocks using bio-adhesive byssus fibers; a medium-sized mussel has approximately 150 of them [110, 111]. Different studies have shown that these protein fibers owe their adhesion to surface catechol groups, which has led to the development of bio-inspired materials

from this functionality [63, 121]. Park *et al.* investigated the use of a catechol-functionalized-alginate complex as a binder In 2013 (**Figure 5A**) [111]. Si and catechol-alginate interaction enabled better electrochemical performance compared to the electrodes with alginate alone (**Figure 5C**). Importantly, the catechol molecular group can be easily attached to different functional substrates *via* dopamine to achieve stronger secondary interactions, resulting in improved adhesion and mechanical strength against the volumetric changes of Si [110, 111, 122]. For instance, Zhao *et al.* have synthesized a conductive adhesive using mussel-inspired catechol (**Figure 5B**) [110]. This polymer was incorporated as a Si-anode binder, providing both conductivity and strong mechanical integrity. The biomimetic conductive polymer binder with Si active material enabled very stable cycling performance of a thick electrode >3 mAh cm^{-2} (1000 mAh g^{-1}) at 0.1C (**Figure 5D**) [110].

Amylopectin. Amylopectin has a branched polysaccharide structure, where each branch consists of 20-30 glucose units. The branched and linear regions of this structure are connected to each other by α-(1,6) and α-(1,4) bonds, respectively. Amylopectin is the major essential component of nearly all starches found in nature. It is considered one of the most important biomass resources in terms of its functional properties.
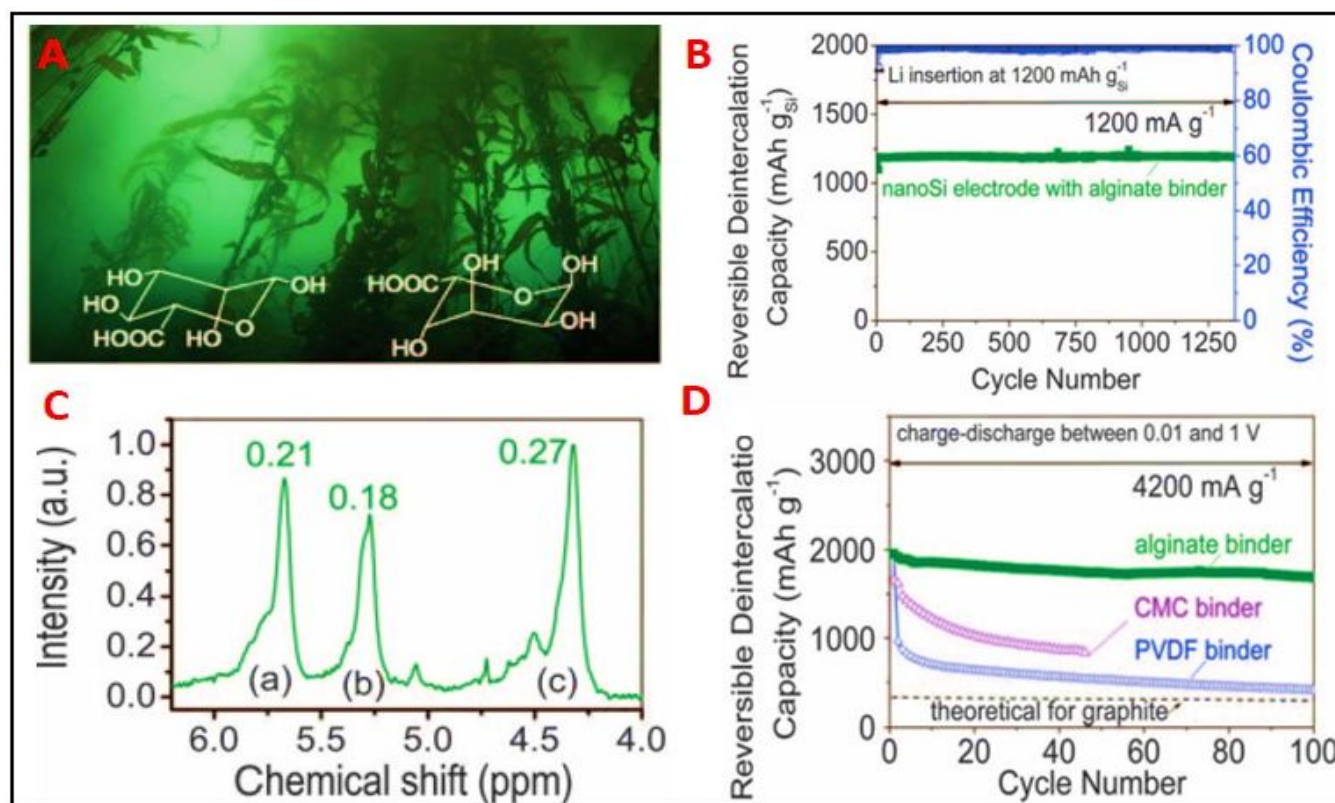

Figure 3. Alginate, a natural polysaccharide extracted from brown algae **(A)**. Specific capacity and coulombic efficiency of alginate based silicon anode **(B)**. ^{1}H NMR spectrum of alginate **(C)**. Comparison of reversible capacity of alginate binder with CMC, PVDF **(D)** [41]. *Copyright © 2011, American Association for the Advancement of Science*
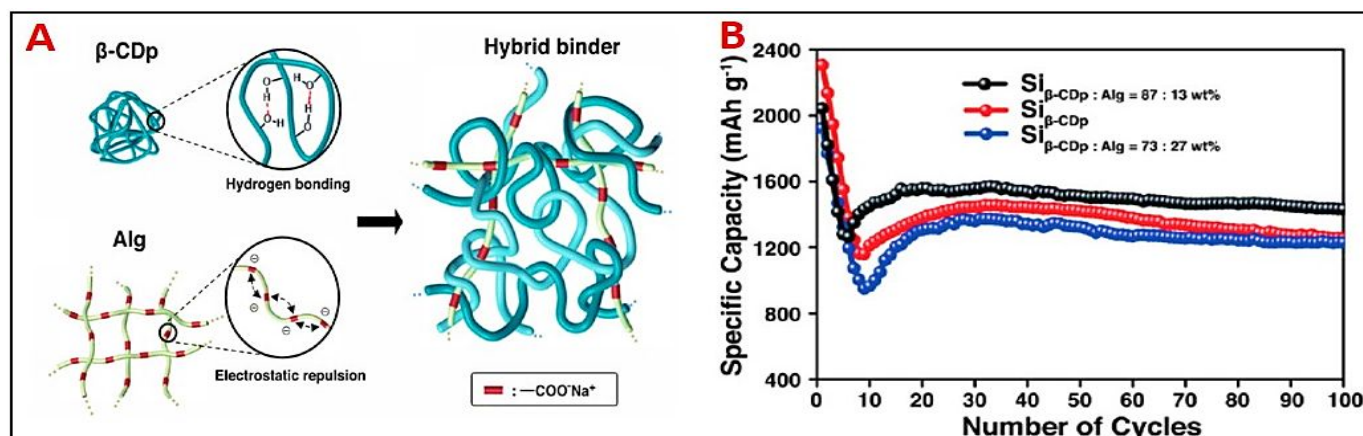
Figure 4. Illustration of β-CDp-and-alginate-based binder structure **(A)** Cycling performance of Si electrodes based on a hybrid binder approach employing different ratios of β-CDp and Alg. **(B)** *Copyright (2014) American Chemical Society.*

The chain distribution of amylopectin, which varies based on source, is the major determinant of its characteristics [114, 123, 124]. Although amylopectin has not been reported much in the literature as a silicon anode binder in LIBs, a couple of studies have been published. Recently, Komaba *et al.* have examined the use of amylopectin as a binder in silicon anode Li-ion batteries and demonstrated Si-based electrodes with much-higher capacity and better cycling performance compared to

PVDF binder (800 mAh g^{-1} after 50 cycles) **(Figure 6)**. The most important factor in amylopectin's binder performance is its degree of branching [114]; however, its reduced adhesion and smaller number of hydroxyl groups compared to other biomass-derived binders may limit its potential in this area. We suggest that it may find better use as a minor component of polymer composites, perhaps functioning as a branched cross-linker.
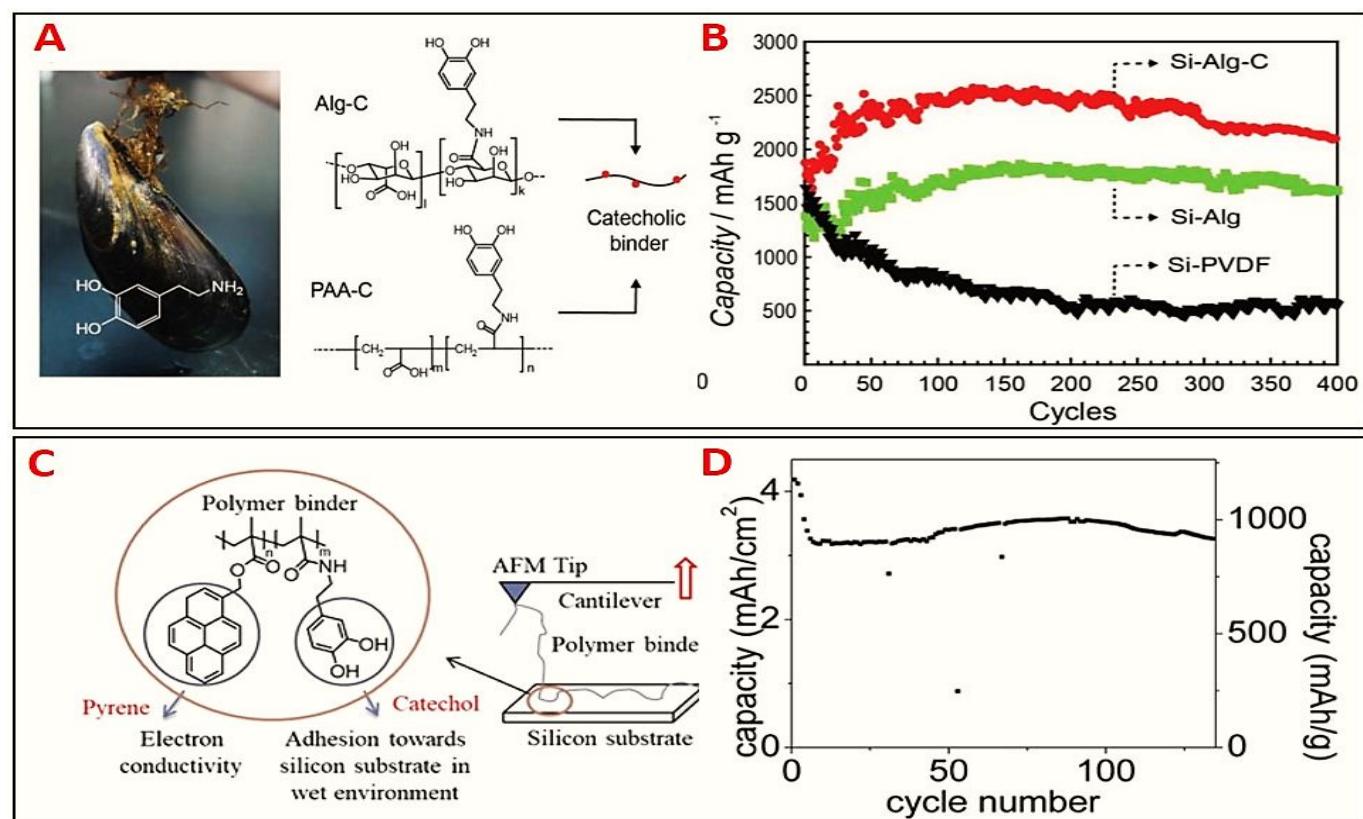

Figure 5. Mussel-inspired catechol polymer binder **(A)** The cycling performance of the Si electrodes based on the Alg-C, Alg and PVDF binders measured at C/2 **(B)** A catechol and pyrene-based conductive polymer backbone **(C)** Electrochemical performance of PPy-Cat-C-Si anode **(D)**. *(A-B) Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, (C-D) Copyright 2018 American Chemical Society*
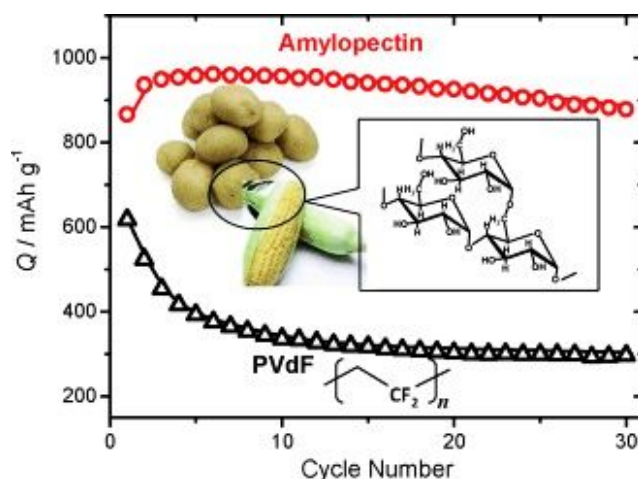
Figure 6. Cycling performance of a silicon anode using crop-derived amylopectin as a binder. *Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim*
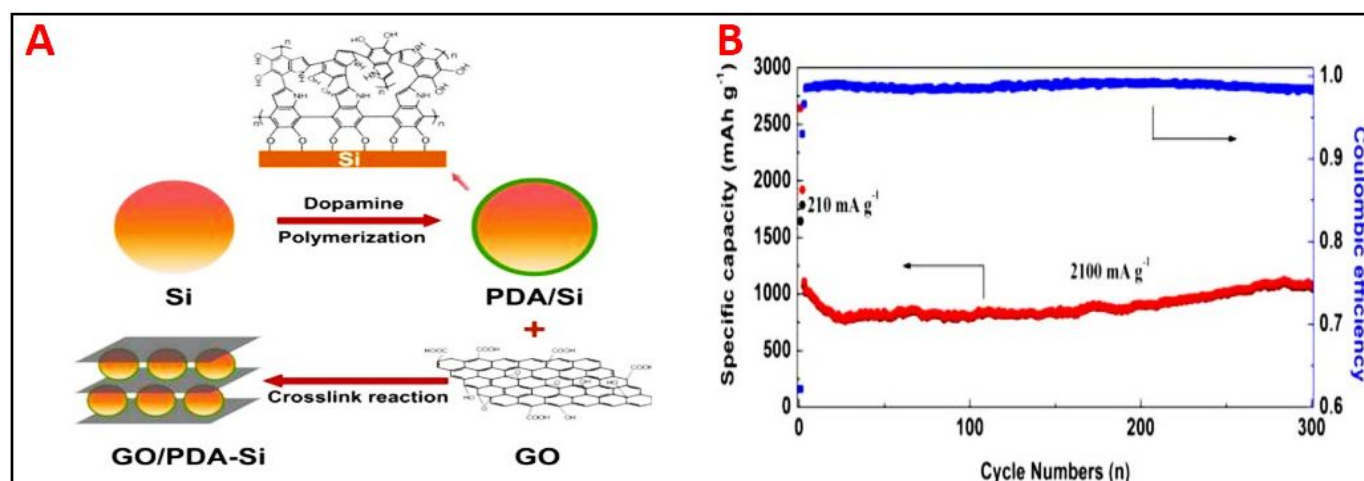

Figure 7. Schematic illustration of the synthetic procedure for polydopamine-Si based nanomaterials **(A)** Specific capacity of a silicon anode using polydopamine based binder **(B)**. *Copyright 2014 American Chemical Society.*

Dopamine. Dopamine is a naturally produced chemical in the body. In the brain, it acts as a neurotransmitter by activating dopamine receptors. Various plants can produce dopamine and the maximum concentrations of dopamine have been found in bananas which is about 40 to 50 ppm. Broccoli, potatoes, and avocado can contain at levels of 1 ppm or more; tomatoes, orange, beans, spinach have concentrations of less than 1 ppm. Polydopamines have been used for variety of applications including silicon anode material for LIBs. Chen et al. reported that a polydopamine-based nanocomposite **(Figure 7A)** shows 1074 mAh g^{-1} specific discharge capacity after 300 cycles and good cycling stability as an anode material for LIBs **(Figure 7B)**[116].

Conclusions

In this review, we introduced several of the most popular biomass resources – cellulose and its derivatives, alginates, cyclodextrins, polycatechols, amylopectins, and polydopamines – and

summarized their application as electrode binders for silicon anodes in Li-ion batteries. According to existing research on next-generation LIBs, polymer binders play a significant role in device performance, and biomass-derived binders pose a promising alternative to the conventional ones used in lithium-ion batteries. However, biomass-derived binders have several critical disadvantages which must be overcome such as low adhesion to nonpolar (*i.e.* carbon) surfaces, high moisture uptake, varying quality, and stiffness.

Biomass-based materials are expected to find wider use, not only for silicon anodes, but also in Li-S or Li-air batteries within the coming years. Additionally, many such materials can be sourced from existing biomass waste streams. In other words, eco-friendly, low-cost, sustainable, recyclable and reusable biomass-derived polymers may enable the development of more environmentally-friendly, cost-effective, and higher-performing battery systems. Note that biomass-derived binders supported

with certain other functional materials may improve adhesion and flexibility on the current collector. In the future, other biomass materials with different functional properties such as lignin, melanin, marine-environment polysaccharides, and biomass from environmental wastes, etc. can potentially find use in battery systems. The reusability of biomass waste for battery production provides a low-cost and eco-friendly path to meet the energy needs of the 21st century.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

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