



## Review on Biopolymers Based Sodium Ion Batteries

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### Abstract

This review paper is focused on sodium ion batteries prepared with biopolymers. Among the biopolymers, Polysaccharides and the biopolymers like chitosan, cellulose, starch, pectin and other biomaterials are important to prepare energy storage devices. Sodium is inexpensive than Lithium and most abundant material in the earth crust. The overview of this article describes about biopolymers and sodium ion batteries that replace the lithium ion batteries.

### Keywords

Biopolymers; Na ion batteries; Li ion batteries

### Introduction

The development of global energy consumption is a major problem and may be solved by natural renewable energy sources and energy storage technologies [1]. Nowadays energy can be stored by some electrochemical devices such as battery, fuel cell, super-capacitor and electro-chromic devices. Above all the energy storage devices, battery are the highly usable material which is made up of anode, cathode and an electrolyte membrane. Electrolyte membrane is the important material in battery applications to provide better electrochemical performance [2]. There are many polymer electrolytes that conduct lithium ion, magnesium ion, sodium ion and proton conducting electrolytes etc. Lithium ion rechargeable batteries are found in mostly all portable electronic devices. It is a lighter metal with small ionic radius and possesses very low redox potential [3]. In 2019, two electrode lithium ion batteries have reached a global production of 316 GWh by the technology of reversible intercalation for energy storage devices [4]. Lithium ion has some difficulties like limited resources, ever increasing price and some safety issues associated with handling. So, nowadays researchers are searching for new environmental friendly polymer membranes that conduct either sodium (Na), potassium (K), magnesium (Mg) and aluminium (Al) ions [2,5]. In large scale energy storage systems, lithium ion batteries require similar alternative like sodium ion batteries those are low cost energy storage devices having high demand because of increasing growth of population [6,7].

Sodium ion is highly abundant element in the earth and very low cost material compared to lithium [8]. Sodium ion has suitable redox potential -2.71 V of standard hydrogen electrode [6]. This type of active electrode material used to provide possible output for any

battery and true chemical performance [9]. For the past few decades synthetic polymers like PEO (Polyethylene Oxide), PVdF-HFP (Poly Vinylidene Fluoride-hexa Fluoropropene), PEG (Poly Ethylene Glycol) and PVA (Poly Vinyl Alcohol) etc are doped with lithium but in the new technology development, synthetic polymers are doped with sodium [10,11].

Biodegradable polymers are easily available in nature and further these can replace the synthetic polymers [12]. The international issues like global warming, pollution, shortage of fossil fuels and environmental issues are solved by biopolymers. The synthesis and origin of biopolymers can be classified into three main categories. The first one refers that biopolymers are directly extracted from biomass such as chitosan, starch, cellulose and carrageenan etc. The second one refers the biopolymers from bio-derived monomer and the third category is the polymers obtained from microorganisms/bacteria [13]. Generally, biopolymers are produced from biodegradable chemical compounds and organic composites throughout the world [12]. This review paper is focused on overview of bio-based polymers and their applications in sodium ion batteries [14].

### Biopolymers

Recently, researchers concentrate on biodegradable polymers those are good alternatives for synthetic polymers [10]. The energy storage application using biopolymers are very important because of their advantages like eco-friendly, low cost, easily degradable and renewable energy source [15]. Bio based polymers are classified as following categories that is illustrated in Figure 1 [13].

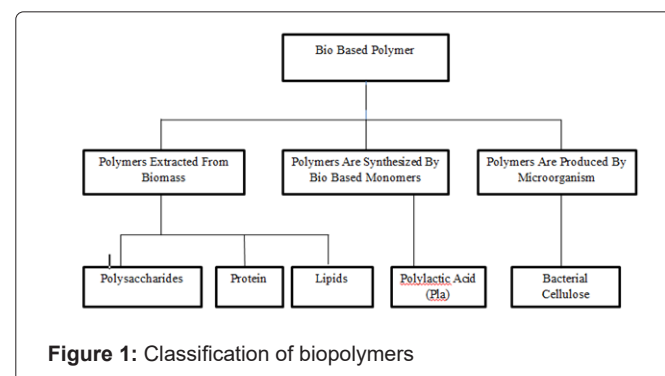


Figure 1: Classification of biopolymers

Biopolymers contain their unique properties and can be easily manufactured into desired shape. Above the bio-based polymers, polysaccharides such as chitosan, cellulose, starch and pectin are demanded more [13].

### Polysaccharides

The backbone of polysaccharides is repeated units of sugar that can determine the exact saccharide. Saccharide contains nominal formula (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) [13]. Polysaccharides are studied in energy storage applications due to their excellent physiochemical properties, abundance, low cost and easily renewable sources [12,13].

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Received date: November 05, 2020; Accepted date: November 20, 2020

Published date: November 27, 2020

## Chitosan

The second most abundant natural polysaccharide named as chitin which are found in insect exoskeletons, fungus cell walls, shells of crustaceans such as crab, shrimp and crawfish [16]. Chitin has named as chitosan in later 1894 by Hoppe seyley [1]. Chitosan can be prepared by deacetylating chitin and it consists of 1,4 linked-2-deoxy-2-aminoglucose [17]. In functional groups, chitosan can serve electron donor by amino and hydroxyl group [18]. Chitosan can be extracted by the following process like demineralization, deproteinization and deacetylation. Another process to extract chitosan is microwave technology. This method can provide chitosan in just 12 minutes [1]. Chitosan contains a heterogeneous distribution of acetyl groups along the chain and because of semi-crystalline morphology of chitin [12].

The prepared chitosan is used for many applications for example separators in medicine and biotechnology, food packaging material and polymer electrolyte has been studied for potential application in electrochemical device such as batteries [19]. In polymer electrolyte application, the chitosan is the first biopolymer reported in 1995. The ionic conductivity is improved by the variety of salts and acid dopants [20]. The outstanding electrochemical performance with high specific capacitance and energy density were reported in chitosan [13]. In the past decades, chitosan can be doped with lithium or ammonium based salts to improve the conductivity but recently sodium contains similar or equal amount of increasing conductivity value [21].

## Cellulose

Cellulose is the most abundant material that can be extracted from plant cell walls. It has structural and skeletal functions. It contains high molecular weight and a linear homo polysaccharide polymer consists of  $\beta$ -D-glucopyranose confirmation joined by (1 4) glucosidic linkage [13]. Cellulose derivative has reacting with three hydroxyl groups present in the anhydroglucose unit. It has many types which can be studied such as methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, cellulose acetate and carboxymethyl cellulose. Mechanical robustness, hydrophilicity, biocompatibility, high sorption capacity and alterable optical appearance are the qualities of cellulose [12].

Many Research reports show cellulose as host in polymer electrolyte membrane. The first solid polymeric electrolyte based on cellulose was reported in 1995, after adding of salt it deserves the ionic conductivity of  $10^{-4}$  S/cm [22]. Recently improving the possibility of solution casting film by its mechanical properties and electrical properties will improve the stability also. On literature review of cellulose doped lithium salt gave a good ionic conductivity. A similar or alternative salt of lithium is sodium and is used to prepare a film with same ionic conductivity value [23].

## Starch

Starch is one of the polysaccharides that extracted from natural carbohydrate and it is the end product of photosynthesis in plant [13]. It is a mixture of two molecules: linear and helical amylose and branched amylopectin [1]. Starch amylose is complex with small ligands like fatty acid, alcohols and aromatic compounds [22].  $\alpha$ - 1, 4-glycosidic bonds linked with polymer chains of amylopectin and glucose units are linked with glycosidic bonds. The biopolymer of starch contains presence of amylose to easily form a film with good mechanical strength, elongation and also physiochemical properties [13].

Extraction of starch can harvested from corn, potato, wheat, tapioca and rice etc. the starch is a low cost biopolymer, easily degradable, solubility in organic solvent and hot water. The first starch based electrolyte reported in 2002 using lithium salt and it produced high efficiency for the electrolyte and easily degradable [22]. Adding various types of salts, filler and plasticizer can be improving the ionic conductivity of the polymer electrolytes [1].

## Sodium ion batteries

In early, 1980's and 1990's several electrochemical devices were assembled by sodium based batteries but commercially lithium based batteries are arrived because of its possibilities [8]. Nowadays limited source of lithium ion is a drawback to face the upcoming issues of energy storage [2]. So that later sodium ion batteries are started in the year 2010 with similar properties which is equal to lithium ion and also inexpensive material.

Special benefits of sodium ion batteries which compared to lithium that is very less expensive aluminium current collectors can be used for both positive and negative electrode [9]. In sodium, positive electrodes can be cycled with sodium salt electrolyte in sodium ion cells but negative electrode do not employed in sodium ion cell because negative electrode is oxidized when discharge [24]. The two electrodes are interacting with both to create a true performance of stability of the electrolyte. The performance can be tested by certain properties and the sodium ion properties are follows as:

## Chemical properties

During cell operation there is no chemical reactions including the current collectors and packaging materials employed.

## Thermal properties

In operation temperature both boiling and melting points should be well outside the (internal) temperature. Properties are optimized by certain characterization like DSC (Differential Scanning Calorimeter), TGA (Thermo gravimetric analysis) and DTA (Differential thermal analysis).

## Conductivity

The cell operation of ion transport and minimize of self-discharge can be obtained by ionic and electrical conductivity. Above requirements are generally optimized by the electrolyte [9]. Biopolymer electrolytes are classified as following categories,

1. Solid biopolymer electrolyte of sodium ion based which contains sodium salt and a biopolymer that can dissolved in water or organic solvent
2. Blend biopolymer electrolyte membranes are prepared by two polymers that can be dissolved in same solvent and a sodium salt
3. Gel biopolymer electrolyte of sodium ion which contain viscous solution and a sodium salt
4. Composite biopolymer electrolyte has their interaction with polymer matrix and sodium salt [25].

## Sodium salt

For solid biopolymer electrolyte based sodium batteries that important one is salt [26]. The sodium salt has been selected by the following characteristics such as: (i) chemical stability, (ii)

solubility, (iii) non toxicity in nature and safely related aspects and electrochemical stability should be used for select type of salt for electrolyte membrane [9]. The sodium salt which are used in early stage of solid polymer electrolytes like sodium iodide (NaI), Sodium yttrium tetrafluoride (NaYF<sub>4</sub>), Sodium perchlorate (NaClO<sub>4</sub>) and Sodium trifluoromethane sulfonate (NaTf) etc [25]. For example, Na conducting ion using sodium triflate for flexible supercapacitor were reported by Jingwei wang et al. [11]. Thivagar sugumaran et al. reported that iota-carrageenan with sodium iodide and it give enhance conductivity of 10-2 S/cm for DSSC application [27].

In recently researchers have attention in Na-S and Na-NiCl<sub>2</sub> batteries because they are aimed for consumer electronics and large scale energy storage applications [9].

### Biopolymer based sodium batteries

Nowadays Na based ions are used in biodegradable polymers and have a great interest in modern research of energy storage device [28]. Selected biopolymer based on sodium ion batteries are reported such as chitosan, cellulose, starch, carrageenan, pectin etc.

### Chitosan

Recently, chitosan based biopolymer electrolyte have a great interest to improve the conductivity of the electrolyte. Especially sodium salt is alternative to the lithium ions of limited resources and low cost [1]. Biopolymer electrolyte can be prepared by solution casting technique. Film with Chitosan and sodium salt is prepared that can be characterized by ac impedance, XRD, FTIR and other thermal studies are optimized. Devesh et al. prepared a sodium ion based biopolymer electrolyte at maximum conductivity of  $1.2 \times 10^{-4}$  S/cm at room temperature [20]. Noriah Abdul et al. reported a film using O-nitrochitosan and sodium hydroxide as a salt which obtain conductivity of  $10^{-6}$  S/cm [21].

### Cellulose

Cellulose is a derivative which has high molecular weight and a polysaccharide material. It is a biodegradable, biocompatible and renewable source [1]. Cellulose has low ionic conductivity and it can be doped with salt to raise the conductivity for battery in energy storage application [10]. Sodium salts were selected for recent research to alternative for lithium and also provide similar conductivity for the electrolyte [13].

For example Shetty et al. reported that sodium bromide doped with carboxymethyl cellulose which the conductivity is  $5.15 \times 10^{-4}$  S/cm [10]. Baharun et al. can develop a film based on sodium-carboxymethyl cellulose with polysulphide for QDSSC and reported conductivity of  $10^{-1}$  S/cm at room temperature [29].

### Starch

It is a carbohydrate based polymer and a mixture of amylose based material [13]. Starch can be easily blended or doped with polymers or salt to improve their ionic conductivity for further electrochemical application [1]. The starch was doped with sodium salt because it contains the glycosidic groups that can react actively in the electrolyte. Sometimes starch possesses alpha glucose monomer and its films are

similar to characteristics of synthetic polymers like transparent and semi-permeable membrane [14]. Few of research works are reported that starch with sodium salts improve the conductivity similar to lithium based ions [30,31].

### Conclusion

This review paper is focused on biopolymer based sodium ion batteries in energy storage applications. In recent research, biopolymers are selected because of biodegradable, easily available, very inexpensive and less harmful for our ecosystem. Sodium ion battery is a good alternative because of limited resources of lithium ions. The main point is that biopolymer based sodium ions produce similar ionic conductivity of lithium ions and further the performance can be improved by using filler or plasticizer.

### References

- Selvaraj T, Perumal V, Khor SF, Anthony LS, Gopinath SCB, et al. (2020) The recent development of polysaccharides biomaterials and their performance for supercapacitor applications. *Mater Res Bull* 126: 110839.
- Zhang J, Yao X, Misra RK, Cai Q, Zhao Y (2020) Progress in electrolytes for beyond-lithium-ion batteries. *J Mater Sci Technol* 44: 237-257.
- Chawla N, Safa M (2019) Sodium batteries: A review on sodium-sulfur and sodium-air batteries. *Electron* 8: 10.
- Qiao L, Judez X, Rojo T, Armand M, Zhang H (2020) Review—polymer electrolytes for sodium batteries. *J Electrochem Soc* 167: 7.
- Oh SM, Myung ST, Yoon CS, Jun Lu, Hassoun J, et al. (2014) Advanced Na[Ni<sub>0.25</sub>Fe<sub>0.5</sub>Mn<sub>0.25</sub>]O<sub>2</sub>/C-Fe<sub>3</sub>O<sub>4</sub> sodium-ion batteries using EMS electrolyte for energy storage. *Nano Lett* 14: 1620-1626.
- Kim H, Hong J, Park YU, Kim J, Hwang I, Kang k (2015) Sodium storage behavior in natural graphite using ether-based electrolyte systems. *Adv Funct Mater* 25: 4.
- Yang YQ, Chang Z, Li MX, Wang XW, Wu YP (2015) A sodium ion conducting gel polymer electrolyte. *Solid State Ionics* 269: 1-7.
- Che H, Chen S, Xie Y, Wang H, Amine K, et al. (2017) Electrolyte design strategies and research progress for room-temperature sodium-ion batteries. *Energy Environ Sci* 10: 1075-1101.
- Ponrouch A, Monti D, Boschini A, Steen B, Johansson P (2015) Non-aqueous electrolytes for sodium-ion batteries. *J Mater Chem A* 3: 22-42.
- Shetty SK, Ismayil, Shetty G (2020) Enhancement of electrical and optical properties of sodium bromide doped carboxymethyl cellulose biopolymer electrolyte films. *J Macromol Sci Part B Phys* 59: 235-247.
- Park CW, Ryu HS, Kim KW, Ahn JH, Lee JY, et al. (2007) Discharge properties of all-solid sodium-sulfur battery using poly (ethylene oxide) electrolyte. *J Power Sources* 165: 450-454.
- Yazdi MET, Amiri MS, Darroudi M (2020) Biopolymers in the synthesis of different nanostructures. *Encycl Renew Sustain Mater* 2: 29-43.
- Rayung M, Aung MM, Azhar SC, Abdullah LC, Ahmad A, et al. (2020) Bio-based polymer electrolytes for electrochemical devices: Insight into the ionic conductivity performance. *Materials (Basel)* 13: 838
- Nur NF, Shyuan LK, Mohamad AB, Kadhum AAH (2013) Review on biopolymer membranes for fuel cell applications. *Appl Mech Mater* 291-294: 614-617,
- Perumal P, Selvin PC, Selvasekarapandian S (2018) Characterization of biopolymer pectin with lithium chloride and its applications to electrochemical devices. *Ionics (Kiel)* 24: 3259-3270.
- Manjuladevi R, Selvin PC, Selvasekarapandian S, Shilpa R, Moniha V (2018) Lithium ion conducting biopolymer electrolyte based on pectin doped with Lithium nitrate, *AIP Conf Proc* 1942: 140075
- Buraidah MH, Arof AK (2011) Characterization of chitosan/PVA blended electrolyte doped with NH<sub>4</sub>I. *J Non Cryst Solids* 357: 3261-3266.
- Ma J, Sahai Y (2013) Chitosan biopolymer for fuel cell applications. *Carbohydr*

Polym 92: 955–975.

19. Kadir MFZ, Aspanut Z, Majid SR, Arof AK (2011) FTIR studies of plasticized poly(vinyl alcohol)-chitosan blend doped with  $\text{NH}_4\text{NO}_3$  polymer electrolyte membrane. *Spectrochim Acta-Part A Mol Biomol Spectrosc* 78: 1068–1074.
20. Bharati DC, Kumar H, Saroj AL (2020) Chitosan-PEG-Nal based bio-polymer electrolytes: Structural, thermal and ion dynamics studies. *Mater Res Express* 6: 31
21. Rahman NA, Hanifah SA, Mobarak NN, Su'ait MS, Ahmad A, et al. (2019) Synthesis and characterizations of o-nitrochitosan based biopolymer electrolyte for electrochemical devices. *PLoS One* 14: 1–17.
22. Pawlicka A, Donoso JP (2010) Polymer electrolytes based on natural polymers. *Polym Electrolytes Fundam Appl* pp: 95–128.
23. Monisha S, Mathavan T, Selvasekarapandian S, Benial AMF, Aristatil G, et al. (2017) Investigation of bio polymer electrolyte based on cellulose acetate-ammonium nitrate for potential use in electrochemical devices. *Carbohydr Polym* 157: 38–47.
24. Ellis BL, Nazar LF (2012) Sodium and sodium-ion energy storage batteries. *Curr Opin Solid State Mater Sci* 16: 168–177.
25. Sudhakar YN, Selvakumar M, Bhat DK (2018) Methods of preparation of biopolymer electrolytes. *Biopolym Electrolytes* pp: 35–52.
26. Wang J, Chen G, Song S (2020) Na-ion conducting gel polymer membrane for flexible supercapacitor application. *Electrochim Acta* 330.
27. Wang J, Chen G, Song S (2020) Na-ion conducting gel polymer membrane for flexible supercapacitor application. *Electrochim Acta* 330.
28. Sugumaran T, Silvaraj DS, Farhana NK, Ramesh S, Ramesh K, et al. (2019) The conductivity and dielectric studies of polymer electrolytes based on iota-carrageenan with sodium iodide and 1-butyl-3-methylimidazolium iodide for the dye-sensitized solar cells. *Ionics (Kiel)* 25: 763–771.
29. Lundstr R (2018) Anthracite based amorphous carbon anode for sodium-ion batteries pp: 50.
30. Baharun NNS, Mingsukang MA, Buraidah MH, Woo HJ, Teo LP, et al. (2020) Development of solid polymer electrolytes based on sodium-carboxymethylcellulose (NaCMC)-polysulphide for quantum dot-sensitized solar cells (QDSSCs). *Ionics (Kiel)* 26: 1365–1378.
31. Xu D, Chen C, Xie j, Zhang B, Miao L, et al. (2016) A Hierarchical n/s-codoped carbon anode fabricated facilely from cellulose/polyaniline microspheres for high-performance sodium-ion batteries. *Adv Energy Mater* 6: 1–7.

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