

Perspectives for solid biopolymer electrolytes in dye sensitized solar cell and battery application

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ARTICLE INFO

Article history:

Received 25 September 2015

Received in revised form

6 May 2016

Accepted 16 June 2016

Keywords:

Biopolymer

Conductivity

Dye sensitized solar cell

Ionic liquid

Battery

ABSTRACT

Photovoltaic technologies represent one of the leading research areas of solar energy which is one of the most powerful renewable alternatives of fossil fuels. In a common photovoltaic application the batteries play a key role in storage of energy generated by solar panels. Although it will take time for dye sensitized solar cells (DSSCs) and batteries based on biopolymer electrolytes to take their places in the market, laboratory studies prove that they have a lot to offer. Most efficient DSSCs and batteries available in market are based on liquid electrolytes. The advantages of liquid electrolytes are having high conductivity and good electrode-electrolyte interface whereas, disadvantages like corrosion and evaporation limit their future sustainability. Biopolymer electrolytes are proposed as novel alternatives which may overcome the problems stated above. In this review, we focus on fabrication, working principle as well as up to date status of DSSCs and batteries using biopolymer electrolytes. The effects of structural and electrical properties of biopolymer based electrolytes on the solar energy conversion efficiencies of DSSCs and their compatibility with lithium or other salts in battery applications are summarized. Biopolymer electrolyte based DSSCs are categorized on the basis of types of additives and recent outcomes of author's laboratory studies on biopolymer electrolyte based DSSCs and batteries are also presented.

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Contents

1. Introduction.....	1099
2. General experimental process followed in the fabrication of DSSCs and batteries.....	1100
2.1. Fabrication of a DSSC.....	1100
2.2. Fabrication of a battery.....	1100

Abbreviations: DMSO, dimethyl sulfoxide; PC, Propylene carbonates; PG, Propylene glycol; 3EG, Triethylene glycol; 4EG, Tetraethylene glycol; MPIL, 1-methyl-3-propylimidazolium iodide; (AElI), 1-allyl-3-ethylimidazolium iodide; (APIL), 1-allyl-3-propylimidazolium iodide; (DALI), 1-3-diallylimidazolium iodide; SDS, Sodium dodecyl sulphate; PVP, Polyvinylpyrrolidone; PEG200, Polyethylene glycol; TW-80, Polysorbate 80-TW-80; NMP, 1-methyl-2-pyrrolidinone; GBL, γ -butyrolactone; PEO-HPC, Poly(ethylene oxide)-2-hydroxypropylcellulose; BmImTf, 1-butyl-3-methylimidazolium trifluoromethanesulfonate; LiTFSI, Lithium bis(trifluoromethanesulfonyl)imide; DES, Deep eutectic solvent; [Amim] Cl, 1-allyl-3-methylimidazolium chloride; BmImPF₆, 1-butyl-3-methylimidazolium hexafluorophosphate; DMAc, N, N-dimethylacetamide; LiCl, Lithium chloride; [BMIM]Cl, 1-butyl-3-methylimidazolium chloride; EC, Ethylene carbonates; PEG, Poly(ethylene glycol); LiTFSI, Lithium trifluoromethanesulfonimide; SPEEK-CS, sulfonated poly(ether ether ketone)-chitosan; DAP, Diethanolamine modified pectin; BC, Bacterial cellulose; TEA, triethanolamine; GA, glutaraldehyde; DTAB, dodecyltrimethyl ammonium bromide; EMImSCN, 1-ethyl 3-methylimidazolium thiocyanate; N3, Cis-Bis(isothiocyanato)bis(4,40-dicarboxyl-2,20-bipyridine)-ruthenium(II), Ru(dcbpy)₂(NCS)₂; N719, Cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)bis-tetrabutylammonium; (AN), acetonitrile; (MOZ), 3-methyl-2-oxazolidinone; (Pr)₄Nl, tetrapropylammonium iodide; TBP, 4-tertiary butylpyridine; MPIm-I, 1-methyl-3-propylimidazolium iodide; DMHIm, 1, 2-dimethyl-3-n-hexylimidazoliumiodide

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2.3.	Preparation of biopolymer electrolyte	1100
3.	Solid biopolymer electrolyte used in electrochemical devices	1101
3.1.	Development of solid biopolymer electrolytes for electrochemical devices	1101
3.1.1.	Agarose/Agar	1101
3.1.2.	Carrageenan	1101
3.1.3.	Alginate	1101
3.1.4.	Pectin	1101
3.1.5.	Cellulose	1101
3.1.6.	Plant seeds, plant tuber & root, cereal starch	1101
3.1.7.	Chitin and chitosan	1102
3.1.8.	Gum Arabic	1102
3.1.9.	Gum Tragacanth	1102
3.1.10.	Xanthan gum	1102
3.1.11.	Gellan gum	1102
3.1.12.	Carboxymethyl cellulose (CMC)	1103
3.2.	Gelatinization and ion transport mechanism in biopolymer electrolytes	1103
3.2.1.	Gelatinization	1103
3.2.2.	Ion transport mechanism	1103
3.3.	Dye sensitized solar cell using solid biopolymer electrolyte	1104
3.4.	Batteries using biopolymer electrolytes	1104
4.	Recent works by authors	1109
4.1.	Structural measurements	1110
4.1.1.	FTIR studies	1110
4.1.2.	XRD studies	1110
4.2.	Electrical measurements	1110
4.2.1.	Electrical conductivity measurements	1110
4.2.2.	Temperature dependent conductivity measurement	1111
4.2.3.	Ion dissociation factor	1112
4.2.4.	Dielectric studies	1112
4.2.5.	Ionic transference number measurement using DC polarization method	1112
4.3.	Dye sensitized solar cell performance (I–V curve)	1112
5.	Conclusions	1112
	Acknowledgments	1112
	References	1112

1. Introduction

Polymer electrolytes are one of the most important materials used in fabricating many electrochemical devices [1–5]. Polymers are classified into two main categories (1) synthetic and (2) natural. Most of the electrochemical devices available in market are based on liquid electrolyte. However solid polymer electrolytes (SPEs) which come into the category of synthetic polymers, offer more advantages over liquid electrolytes, such as higher energy density, flexible geometry, higher operating temperatures and safety, no-leakage of electrolyte and ease of application. The most commonly studied polymer electrolytes are the complexes of metal salts with high molecular weight polymer polyethylene oxide (PEO) [1–3]. However, one of the major drawbacks of PEO-based solid polymer electrolytes is their low ionic conductivity (10^{-7} S/cm) at ambient temperature, which limits their practical applications [4,5]. To date, a large number of other synthetic polymers, such as polymethyl methacrylate (PMMA), polyacrylonitrile (PAN), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), polyvinyl alcohol (PVA), and polyvinylpyrrolidone (PVP) etc, have been studied in electrolyte applications [6–9].

Especially in developing countries, environmental pollution caused by synthetic polymers is becoming a serious threat. Petroleum-derived plastics are not biodegradable; they do not undergo microbial degradation and hence accumulate in the environment. Together with the environmental concerns, tremendous increase in the prices of fossil fuel derived products force the scientist to focus on biodegradable polymers. Biopolymers fall into the natural polymers category, and represent one of the hot topics of polymer research. Since their introduction in 1980s, a vast number of

biodegradable polymers have been synthesized [10–14] with the major goal of development of stable biopolymeric systems with excellent electrical and mechanical properties. Biopolymer electrolytes (BPEs) are solid ion conductors formed by dissolving salts in polymers having high molecular weight. They can be prepared in semi-solid or solid form through cheap and reliable processes [15–27]. BPE materials possess high ionic conductivity (10^{-2} to 10^{-4} S/cm), high energy density, wide electrochemical stability window, provides solvent-free and leak proof condition, easy processability and light weight which are essential for any kind of electrochemical device, e.g. fuel cells [28], supercapacitors, batteries [29–32], dye sensitized solar cells (DSSCs) [33–290], etc. Due to the large variety of energy related BPE applications, the scope of this review is limited to the application of BPEs in DSSCs and batteries.

Since the introduction of DSSC technology by O'Regan and Grätzel in 1991, it represents one of the most studied photovoltaic technologies [46]. The conversion efficiencies vary between 6% and 13% depending on the size of active area, preparation conditions and the type of electrolyte [33]. Although the highest conversion efficiency has been achieved by using liquid electrolytes due to the stability problems generate mainly from the leakage of electrolyte, quasi gel electrolytes are introduced. However this kind of electrolytes could not solve the stability problem and also caused efficiency reductions generating from the low ionic mobility and trapping of the gel in the metal oxide pores [53–56]. The next proposed alternative is solid polymer electrolytes in which polyether's and biopolymer-salt complexes are playing the dominant role [76–88,105–109]. In addition to their high conductivity and good thermal stability, biodegradable thin/thick film formation abilities make them suitable electrolyte candidates for DSSCs.

It is well accepted that rechargeable batteries are the most dominant energy storage devices especially in automotive industry and portable electronic devices [1–3]. It is also identified that Li-ion batteries (LIBs) are the preferred system for electric vehicles, grid energies and flexible electronic devices due to their high energy and power density [4]. Particularly, flexible and wearable electronics are expected to increase an exceptional importance in the future as energy storage devices. The important parts in rechargeable batteries are anode, cathode and electrolytes. The electrolytes commonly used are traditional liquid based electrolytes containing organic solvents, which are volatile and flammable. This requires alternative electrolyte material which prevents the leakage of the liquid electrolyte as well as internal short circuit in LIBs due to lithium dendrite growth on the anodes. As a result, safety issues are the major concerns in the applications of batteries. In such a situation, the development of solid-state electrolytes is a major challenge to be faced by scientific research [1–5].

Nowadays, researchers focus on light, safe, environmentally friendly and sustainable devices for conversion and storage of energy, preferentially at low cost. Although there is almost no concerns on the added value of biopolymers in weight, safety and environmental issues, one may question the sustainability of biopolymers and may claim that utilization of them in energy sector may raise the price of food products and even lead to food crises. However, if one also considers that energy heads the top ten problems of today's world and each and every attempt on minimizing it has the potential to minimize the influence of the others, i.e. water, food, environment, poverty, terrorism, disease, education, democracy, population [12], we think that not utilization of biopolymers in energy applications but, ignoring the energy problems will absolutely lead to food crises. Additionally, being one of the most widely known biopolymers cellulose, is the most abundant polymer in the world, recycling process of it is very well known and represents one of the most studied BPE component.

In this review, after the introduction of general experimental process followed in the fabrication of DSSCs and batteries and ion transport mechanism in biopolymer electrolytes, we summarized the literature on utilization of BPEs in electrochemical devices of DSSCs and batteries and presented our recent laboratory studies.

2. General experimental process followed in the fabrication of DSSCs and batteries

2.1. Fabrication of a DSSC

A DSSC comprises a sandwiched structure of two electrodes (anode, cathode) and electrolyte. The anode is prepared by the use of mesoporous metal oxides, e.g. TiO_2 , ZnO and the cathode is obtained by platinum coating on transparent conductive oxide. The TiO_2 electrode is immersed in dye solution overnight and the space between the sandwiched electrodes is filled with an electrolyte. Under illumination, the cell produces current through an external load connected to the electrodes. The absorption of light in the DSSC occurs due to the dye molecules and charge separation by electron injection from the dye to the TiO_2 at the semiconductor electrolyte interface (Fig. 1). The color of the device can be easily varied by the choice of dye [67–75]. The chemical and physical composition and structure of electrolyte mainly effects on the stability and solar energy conversion efficiency of the DSSC [49–55].

2.2. Fabrication of a battery

Batteries are composed of a cathode and an anode as the electrodes, a metal salt solution (or solid polymer electrolyte) as the

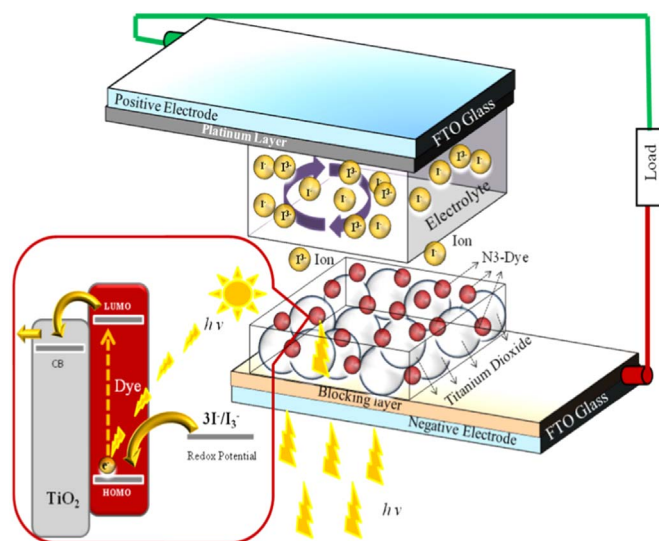


Fig. 1. Schematic diagram presenting working principle of dye sensitized solar cells (DSSC).

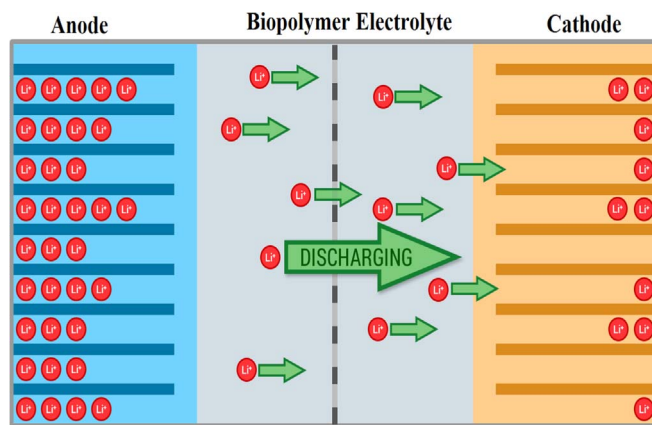


Fig. 2. Schematic diagram of Li-ion battery discharge.

electrolyte, a separator and functional additives which converts chemical into electrical energy. Copper and Aluminum foils are used as substrates for coating anode and cathode materials in rechargeable battery. The chemical reactions in the battery cause a buildup of electrons at the anode. This results in an electrical difference between the anode and the cathode. The electrolyte keeps the electrons from going straight from the anode to the cathode within the battery. When the circuit is closed (a wire connects the cathode and the anode) the electrons will be able to get to the cathode (Fig. 2). The common anode materials used in batteries are titanium oxides, graphite, porous carbons, alloys (Si, Ge, Al, Sn, Sb etc.), metal oxides and oxysalts, pure metal foils etc. The cathode materials used in batteries are vanadium oxide, molybdenum sulfide, molybdenum oxide, manganese oxide, silicates, LiCoO_2 , LiFePO_4 , LiMn_2O_4 etc. [1–5]. The different types of electrolyte materials based on biopolymer are studied briefly in this review.

2.3. Preparation of biopolymer electrolyte

BPE films reported in this review are prepared by the standard solution cast technique. In a common procedure, biopolymers and the desired amount of salts are weighed separately and dissolved in distilled methanol or any other suitable solvents. The mixture is stirred for a long time to obtain clear solution and then poured in

polypropylene/teflon molds under controlled environmental conditions (temperature, relative humidity). The solvent is evaporated slowly at room temperature and a free standing BPE film is obtained. In some instances, biopolymer films are soaked in an electrolyte solution to allow diffusion of ions. The BPE film matrix obtained is characterized by using various techniques [101,136,137,166]. The basic organic chemistry and physics that lie behind preparation and working principle of a BPE is summarized in the following section.

3. Solid biopolymer electrolyte used in electrochemical devices

3.1. Development of solid biopolymer electrolytes for electrochemical devices

Polysaccharides represent the dominant class of biopolymers used in developing efficient electrochemical devices [1–4,27–89,101–291]. Some of the widely used polysaccharides are briefly introduced below.

3.1.1. Agarose/Agar

Agarose is a linear polymer consisting of alternating beta-D-galactose and 1, 4-linked 3, 6-anhydro-alpha-L-galactose units [10]. It has very few sulfate groups. The gelling temperature ranges from 32–45 °C, and the melting temperature range is normally 80–95 °C. Methylation, alkylation and hydroxyalkylation of the polymer chain can change the melting and gelling temperatures [11]. Generally agarose/agar are insoluble in cold water, but it swells considerably. However, it can easily dissolve in hot water (H₂O) other solvents at temperatures between 95° and 100 °C such as DMF (Dimethylformamide), DMSO (Dimethyl sulfoxide), dimethylacetamide (DMAc), Glycol, orthophosphoric acid, (NMP) N-Methyl-2-pyrrolidone etc. Mechanically strong gel with a small amount of agarose can be produced, while maintaining the ionic conductivity of the liquid electrolyte. Agarose shows good ionic conductivity in the order of 10^{−2}–10^{−4} S/cm. Complex impedance spectroscopy analysis revealed that doping of KI provide additional charge carriers (cations/anions) and enhance the overall conductivity. The maximum conductivity reported in literature is around 10^{−2} S/cm [1,7].

3.1.2. Carrageenan

Carrageenan is obtained from the red seaweeds of the class rhodophyceae. It is a group of linear galactan with ester sulfate content of 15–40% (w/w) and containing alternating (1→3)-α-D and (1→4)-β-Dgalactopyranosyl (or 3,6-anhydro-α-D-galactopyranosyl) linkages. Three types of commercially available carrageenans are κ, ι, and λ. Anionic polysaccharides with molecular weight: 100,000–1,000,000, form gels with potassium or calcium ions [6,10,12]. Carrageenan can also easily dissolve in hot water (H₂O) even at room temperature. The solubility temperature is between 40° and 70 °C in solvents such as DMSO but it is insoluble in ethanol, acetone and some other organic solvents [11]. Ionic conductivity of carrageenan was found in the range of 10^{−7} to 10^{−3} S/cm in water and DMSO. The highest conductivity achieved for κ-carrageenan-AN/MOZ-TBP-I₂/LiI-Pr₄NI+I^{3−} is 2.98 × 10^{−3} S/cm at room temperature.

3.1.3. Alginate

Alginate is obtained from the brown seaweeds of the class Phaeophyceae, as a structural material. Linear polysaccharide composed of β-D-mannuronopyranosyl and α-L-guluronopyranosyl units. The units occur in M blocks (containing solely mannuronopyranose residues), G blocks (containing solely guluronopyranose residues), or MG blocks. Ratio of G-, M-, and MG-blocks affects the gel strength, calcium reactivity, and other

properties [10]. Alginate form gels with calcium ions. Alginate with high G-blocks results in greater gel strength. Alginate with high M-blocks is more calcium tolerant and less likely to have problem with syneresis. It dissolves slowly in water, forming a viscous solution, but is insoluble in ethanol and ether [12]. Gel polymer electrolytes (GPEs) based on sodium alginate plasticized with glycerol containing either CH₃COOH or LiClO₄. The membranes showed ionic conductivity results of 3.1 × 10^{−4} S/cm for the samples with LiClO₄ and 8.7 × 10^{−5} S/cm for the samples with CH₃COOH at room temperature. Results obtained indicate that alginate-based GPEs can be used as electrolytes in electrochemical devices.

3.1.4. Pectin

Pectin is found in all land-based plants as a structural material. Commercial pectin is extracted from citrus peel, apple pomace, sugar beet, or sunflower heads. A linear chain of galacturonic acid units has molecular weight about 110,000–150,000. Pectins are soluble in pure water. Monovalent cation (alkali metal) salts of pectinic and pectic acids are usually soluble in water; di- and trivalent cations salts are weakly soluble or insoluble [12]. The plasticized pectin and LiClO₄-based gel electrolytes were prepared and analyzed by spectroscopic, thermal, structural, and microscopic analyses. The best ionic conductivity values of 2.536 × 10^{−2} S/cm were obtained at room temperature for the composition based on diethanolamine modified pectin (DAP) and glutaraldehyde (GA) dissolved in pectin based biopolymer electrolyte [133].

3.1.5. Cellulose

Cellulose is the most abundant polymer available worldwide. Cellulose is composed of polymer chains consisting of unbranched β (1→4) linked D-glucopyranosyl units (anhydroglucose unit). Nowadays, there are various procedures for extraction of cellulose microfibrils like pulping methods, acid hydrolysis, steam explosion, etc. [11–14]. The samples of HEC (hydroxyethylcellulose) plasticized with glycerol and addition of lithium trifluoromethane sulfonate (LiCF₃SO₃) salt. The ionic conductivity obtained in the range of 10^{−4}–10^{−5} S/cm. The best ionic conductivity obtained is 4.68 × 10^{−2} S/cm at room temperature by using lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) doped biopolymer cellulose acetate (CA) matrix in 1-allyl-3-methylimidazolium chloride ([Amim] Cl) [128].

3.1.6. Plant seeds, plant tuber & root, cereal starch

The principal crops used for Starch production include potatoes, corn and rice. In all of these plants, starch is produced in the form of granules, which vary in size and somewhat in composition from plant to plant [6]. The starch granule is essentially composed of two main polysaccharides, amylose and amylopectin with some minor components such as lipids and proteins. Amylose is a linear molecule of (1→4)-linked α-D-glucopyranosyl units and molecular weights ranging from 10⁵ to 10⁶ g mol^{−1} [12] (Fig. 2). Amylopectin is a highly branched molecule composed of chains of α-D-glucopyranosyl residues linked together mainly by (1→4)-linkages but with (1→6) linkages at the branch points and having molecular weights ranging from 10⁶ to 10⁸ g mol^{−1}. Amylose is water soluble but Amylopectin is insoluble in cold water and swells in it thereby giving rise to a thick paste upon boiling with water. It is a biopolymer contains about 23% starch (20–25% amylose and 75–80% amylopectin). It is clear that adding KI in Arrowroot matrix enhances the ionic conductivity and conductivity maxima were obtained by doping NaI and KI concentration where conductivity value approaches at 6.7 × 10^{−4} and 1.04 × 10^{−4} S/cm, respectively [166,167]. Adding (Glycerol + LiCl) and KI in Sago Palm matrix enhances the ionic conductivity and conductivity maxima was obtained by adding LiCl where conductivity value approached to 10^{−3} S/cm with LiCl [38] and 3.4 × 10^{−4} S/cm for KI [136,137]. Potato starch with NH₄I based biopolymer electrolyte

prepared by solution casting technique gives best ionic conductivity of $\sim 2.4 \times 10^{-4}$ S/cm [163].

Corn starch-based biopolymer electrolytes have been prepared by solution casting technique. Lithium hexafluorophosphate (LiPF₆) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BmImTf) were used as lithium salt and ionic liquid, respectively [142]. In another study ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (BmImPF₆) was doped into the corn based biopolymer matrix and maximum ionic conductivity of 1.47×10^{-4} S/cm was reported for this system. Biopolymer blend electrolytes based on corn starch and chitosan doped with ammonium iodide (NH₄I) was also prepared. A polymer blend at 80 wt% starch and 20 wt% chitosan was found to be the most amorphous blend. The highest ionic conductivity achieved at room temperature is 3.04×10^{-4} S/cm with NH₄I [139]. The overall best ionic conductivity $\sim 10^{-5}$ S/cm is reported by using N, N-dimethylacetamide (DMAc) along with lithium chloride (LiCl) doped corn based biopolymer [151].

Rice starch doped with LiI was prepared using solution casting method, at room temperature the highest ionic conductivity achieved was around 4.7×10^{-5} S/cm [158]. Tapioca is a polymer containing heteroatoms in their structure. Hence, they can interact with protons or lithium ions leading to ionic conduction. Among different natural polymers, starch-based bio polymer electrolyte present good opto-electrochemical characteristics and can be applied to electrochemical devices. The ionic conductivity results obtained for these bio polymer electrolytes varied from 10^{-6} S/cm to 10^{-4} S/cm at room temperature, Conductivity reaches to 8.1×10^{-3} S/cm for cassava doped with lithium perchlorate. The amount of Acetic acid and NH₄NO₃ was found to influence the proton conduction. Wheat can easily dissolve in Acetic acid and room temperature conductivity was found in the order of 10^{-5} S/cm to 10^{-4} S/cm. The common starch based biopolymer electrolytes used in electrochemical devices are shown in Table 1.

3.1.7. Chitin and chitosan

Chitosan is a linear polysaccharide consisting of β (1–4) linked D-glucosamine with randomly located N-acetylglucosamine groups depending upon the degree of deacetylation of the polymer. Chitin basically found in the shells of crabs, lobsters, shrimps and insects. Chitosan is the deacetylated derivative of chitin. Chitin is insoluble in its native form but chitosan, is water soluble. Chitosan is soluble in weakly acidic solutions resulting in the formation of a cationic polymer with a high charge density and can therefore form polyelectrolyte complexes with wide range of anionic polymers. Chemical modification of chitosan can significantly affect its solubility and degradation rate [10–14].

The electrical properties of polymer electrolytes based on chitosan complexed with lithium and ammonium salts have been reported [177–179,196,197,200]. Conductivities of the order of 10^{-6} S/cm at room temperature were reported for chitosan with poly (ethylene oxide) PEO blends and doped with LiTFSI salt [101] and also for the complex formed by chitosan, poly (aminopropylsiloxane) (pAPS) and LiClO₄ [105]. Conductivity ranges from

10^{-5} and 10^{-4} S/cm were reported for proton-conducting polymer electrolytes, based on chitosan and ammonium salts (NH₄NO₃ and NH₄CF₃SO₃) [183,188] and this value is in the range of 10^{-6} – 10^{-4} S/cm for chitosan and κ -carrageenan containing ammonium nitrate-based film [18,19]. LiMn₂O₄ doped biopolymer based chitosan with carbon has reported biopolymer-in-salt based electrolyte achieves the best ionic conductivity; 3.9×10^{-3} S/cm at room temperature [210].

3.1.8. Gum Arabic

A gummy exudate obtained from Acacia trees with molecular weight about 250,000 is highly soluble with low viscosity even at 40% concentration. Gum Arabic, e.g. Acacia arabica, Acacia babul, exhibits a conductivity of approximately 1.5×10^{-6} S/cm after drying. Gum Arabic produces salt complexes with inorganic materials like FeSO₄, [K₂SO₄, Al₂(SO₄)₃, 24H₂O], LiClO₄, iodine etc. and functions as a proton conductor through hydronium ions H₃O⁺ [69].

3.1.9. Gum Tragacanth

Gum Tragacanth is an exudate of Astragalus, a perennial short brush in Asia. It is slightly acidic and found as Ca, Mg, or Na salts. It contains neutral highly branched arabinogalactan and tragacanthic acid (linear (1→4)-linked α -D-galacturonopyranosyl units, with some substitutions). It is highly viscous with some emulsification properties. Highest conductivity reported for NaOH based biopolymer is 88.8×10^{-3} S/cm at room temperature [170].

3.1.10. Xanthan gum

Xanthan gum is prepared through culturing Xanthomonas campestris, a single-cell organism producing gum as protective coating. A trisaccharide side chain is attached to alternate D-glucosyl units at the O-3 position. The side chain consists of a D-glucuronosyl unit between two D-mannosyl units. Molecular weight is about 2,000,000–3,000,000. Its viscosity is stable at a wide temperature and pH range. Among the systems studied, i.e. Gum Xanthan + PVP, Gum tragacanth + PVP and Gum Acacia + PVP, Gum Acacia + PVP presents better compatibility as it has stronger intermolecular interaction. In the same manner, among Gum Xanthan + PEG, Gum Acacia + PEG and Gum tragacanth + PEG systems, Gum Tragacanth + PEG has better compatibility [171].

3.1.11. Gellan gum

Gellan gum is prepared by culturing Pseudomonas elodea and composed of a four-sugar repeating sequence containing one D-glucuronopyranosyl, two D-glucopyranosyl, and one L-rhamnopyranosyl unit. Its molecular weight is about 1,000,000–2,000,000. It requires either monovalent or divalent cations to form a gel [10–14]. The ionic conductivity measurements revealed that the ionic conductivity of the Gellan gum doped with 40 wt% of (lithium trifluoromethanesulfonate) LiCF₃SO₃ electrolyte varies with the salt concentration reaching the highest conductivity value of 5.4×10^{-4} S/cm at room temperature [173]. When doped

Table 1
Conductivity values of some of the starch based biopolymer electrolytes reported in literature.

Starch	Amylose (%)	Starch (%)	Type	Gelatinization temperature range [°C]	Dispersoids	Conductivity (S/cm)	Ref.
Arrowroot	20.5	84	Root	70–75	KI	1.04×10^{-4}	[136,137]
Corn	28	31–50	Cereal	62–72	LiI	1.83×10^{-4}	[146]
Pea	27	40	Legume	60–75	–	–	–
Potato	20	65	Tuber	59–68	NaI	1.3×10^{-4}	[161,162]
Rice	18.5	87	Grain	–	LiI	4.68×10^{-5}	[158,159]
Sago	25.8	84	Root	70–72	KI	3.4×10^{-4}	[166]
Tapioca/ Cassava	16.7	84	Root	58–70	Li salt	10^{-6} to 10^{-4} , 8.1×10^{-3}	–
Wheat	26	25	Cereal	58–64	CH ₃ COOH	10^{-5} to 10^{-4}	–

with LiI, it exhibit ionic conductivity of 3.8×10^{-4} S/cm at room temperature [174]. To achieve good ionic conductivity, plasticizers such as, glycerol, ethylene glycol, ethylene carbonate, propylene carbonate are used, and adding lithium salts of LiClO_4 , LiBF_4 , LiCF_3SO_3 , LiI/I_2 or acetic acid promoted the proton conduction [173–175].

3.1.12. Carboxymethyl cellulose (CMC)

Carboxymethyl cellulose (CMC) is prepared by soaking cellulose in aqueous sodium hydroxide and reacting with monochloroacetic acid [10,11]. Carboxymethyl cellulose doped with Lithium perchlorate and plasticizer polycarboxylate based transparent solution of CMC/ LiClO_4 /PC is reported and ionic conductivity of the biopolymer electrolyte is found to be 2×10^{-4} S/cm. In another system, oleic acid based biopolymer electrolyte and NH_4Br based electrolyte achieved ionic conductivity values of 2.11×10^{-5} and 1.12×10^{-4} S/cm, respectively [213,218]. CMC is doped with different concentration of DTAB/EC via solution casting technique. The highest ionic conductivity, σ , was found to be 2.37×10^{-3} S/cm at room temperature [216].

3.2. Gelatinization and ion transport mechanism in biopolymer electrolytes

3.2.1. Gelatinization

Polysaccharides can also be classified according to their ionic character (neutral, anionic, cationic). As a result of which they bring different properties and chemical functionalities to the biocomposites. The polysaccharides indicated in Table 2 derive from natural sources, hence presenting advantages in terms of biodegradability, low-toxicity and low cost. Polysaccharide is an emerging branch of polymer which acts as a novel electrolyte in electrochemical devices [11,15]. Polysaccharides have been used as composite matrices due to several characteristics of relevance for biological and electrochemical

device applications. Variety of structures in biopolymers imparts different properties in them. The biopolymers which are most commonly used in developing electrochemical devices are summarized in Table 2. In biopolymers the hydroxyl groups of sugar rings allow the structure to substitute easily with other functional groups. Differences in the sugar composition and functional group substitution, effect on the three-dimensional packing of the polysaccharides and their interactions with other polymers or salts. Polysaccharides having extensive hydrogen bonding appear to be more conductive than that of the ones with a few hydrogen bonds and ion mobility of the electroactive material depends on the crystallinity of the polymer. When a dopant salt is introduced in to the matrix, the dominant energetic barrier experienced by the cation in conduction, is given by the dissociation of the alkali itself. The material can be both ionically and electronically conducting. However, in most biopolymers (polysaccharides) conduction is mainly due to the movement of single ionic specie. The ion conduction mechanism could be clearly understood in a common biopolymer electrolyte *i.e.* starch. Biopolymer starch is the plasticized starch that has been processed (typically using heat and pressure) to destroy the crystalline structure and to form an amorphous thermoplastic starch. Thermoplastic starch processing typically involves an irreversible molecular organization termed gelatinization and affected by starch-water interactions [7,12]. Fig. 3 summarizes the gelatinization process. Pure biopolymer starch presents a compact nature (Fig. 3a) made up of amylose (linear) and amylopectin (branched) molecules. In aqueous media, the crystallinity is affected and helices are disturbed (Fig. 3b) [7] and upon heating, swelling of the granules is accelerated that allows the amylose diffusion out of the granule (Fig. 3c).

3.2.2. Ion transport mechanism

The common ion transport in a biopolymer-salt complex can be understood using agarose biopolymer: KI polymer electrolyte in which both cation (K^+) and anion (I^-) play dominant roles.

Table 2

Source, dominant functional group and physical structure of some biopolymers commonly used in electrochemical devices.

Source	Biopolymer	Functional groups	Film type	Structure	Ref.
Marine red Algae	Agarose/ Agars	OH	Gel	Linear	[18]
Red seaweeds	Carrageenans	OH, OSO_3^-	Gel	Linear	[19]
Brown algae	Alginate	OH, COO^-	Gel	Linear	[20]
Plant cell wall	Cellulose	OH	Gel	Linear	[21]
	Pectin	OH, COO^-	Gel	Linear	[21]
Derived	Carboxymethyl Cellulose	OH, COO^-	Thickening/viscosity agents	Linear	[21]
	Methylcellulose (MC)	OH, COO^-	Gel/ Thickening/viscosity agents	Linear	[21]
Plant seeds/cereal starch	Sago Starch	OH	Thickening/viscosity agents	Linear/Branch-on-branch	[22]
	Corn Starch	OH	Thickening/viscosity agents	Linear/Branch-on-branch	[22]
	Pea Starch	OH	Thickening/viscosity agents	Linear/Branch-on-branch	[22]
	Rice Starch	OH	Thickening/viscosity agents	Linear/Branch-on-branch	[22]
	Wheat Starch	OH	Thickening/viscosity agents	Linear/Branch-on-branch	[22]
	Oats Starch	OH	Thickening/viscosity agents	Linear/Branch-on-branch	[22]
Plant tuber & root	Potato Starch	OH	Thickening/viscosity agents	Linear/Branch-on-branch	[22]
	Tapioca/Arrowroot Starch	OH	Thickening/viscosity agents	Linear/Branch-on-branch	[22]
Plant exudates/Acacia trees	Gum Arabic	OH, COO^-	Thickening/viscosity agents	Branch-on-branch	[23]
Plant exudates	Gum Tragacanth	OH, COO^-	Thickening/viscosity agents	Short branched	
Microorganism	Xanthan Gum	OH, COO^-	Gel	Short branched	
	Gellan Gum	OH, COO^-	Gel	Linear	
Shellfish & fungi cell wall/ Insects	Chitin	OH, NH_3^+	Gel	Liner	[24]
	Chitosan	OH, NH_3^+	Gel	Liner	[24]

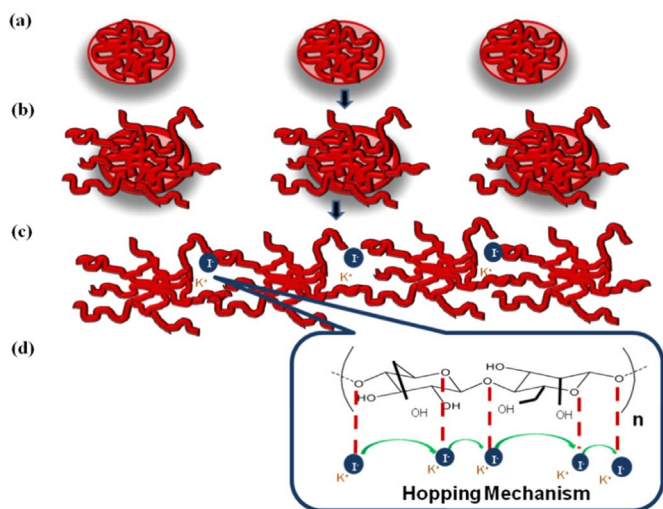


Fig. 3. Common gelatinization process occur in biopolymers (polysaccharides a, b, and c) while common ion transport mechanism in starch-KI biopolymer-salt complex (d).

Adding dispersoids (KI) in biopolymer matrix may enhance amorphous region. The etheric oxygen can easily associate with K⁺ as similar to the other systems reported on PEO based polymer electrolytes [1,2]. This weak interaction can be dissociated under the influence of an electric field and together with I⁻, K⁺ ions can hop consistently at the coordinating side of the biopolymer structure. Increasing the K⁺ and I⁻ concentration in the media will increase the number of charge carriers and hence the conductivity. The ionic hopping mechanism is demonstrated in Fig. 3d and maybe applied in biopolymer matrix with different alkali salts [1–4].

3.3. Dye sensitized solar cell using solid biopolymer electrolyte

The primary aim of development of solid polymer electrolyte is to avoid the disadvantages caused by liquid electrolyte. Biopolymer electrolytes are free from leakage, corrosion and more stable. The moderate conductivity and other advantageous properties make them suitable candidates for DSSCs. The photovoltaic parameters of polysaccharides with various salts (like NaI, KI and NH₄I etc) are reported in literature and tabulated in Table 3. As expected, the most efficient biopolymer electrolyte based DSSCs contain I⁻/I³⁻ redox couple [101–117,136,137,160,166,178–181].

3.4. Batteries using biopolymer electrolytes

As already mentioned earlier an efficient battery needs electrolytes with high ionic conductivity [1,29,30,33,226]. Solid polymer electrolytes (SPEs) have been widely examined to substitute conventional liquid electrolytes because of their attractive properties, such as ability to eliminate problems of corrosive solvent leakage, wide electrochemical stability range, light weight, ease of processability and excellent thermal stability as well as low volatility [225,226]. The most commonly studied polymer electrolytes for batteries are high molecular weight polyethylene oxide (PEO) complexed with Li salts [2]. PEO qualifies as a host polymer for electrolytes because of its high solvating power for lithium salts and compatibility with lithium electrode [227]. However, one of the major drawbacks of PEO-based solid polymer electrolytes is their low ionic conductivity (10^{-7} – 10^{-8} S/cm) at ambient temperature, which limits their practical applications [228–230].

Most of SPEs are based on hydroxethyl cellulose [231], starch [232], chitosan [233–235], agar-agar [236], pectin [237], and

gelatin [238] etc., wherein the ionic conductivity has been reported in the order of 10^{-4} S/cm at room temperature.

Cellulose constitutes are the most abundant, renewable polymer source available worldwide today. It is principally used as construction material, in the form of wood or as textile fiber, such as cotton, or in the form of paper and board [239]. Cellulose exists in many forms from micrometric cellulose fibers to nanocellulose. Over the last decade, nanocellulose has attracted an ever increasing attention for the production of cellulose based nanocomposite materials, due to their high strength and stiffness combined with low weight, biodegradability and renewability [240]. Recently, cellulose and its derivatives have been successfully applied in rechargeable batteries for the production of electrodes, separators or as reinforcing agents in solid polymer electrolytes [241]. Samsudin et al. [242] investigated the use of CMC based biopolymer electrolyte complexed with NH₄Br for the application of rechargeable proton battery. The highest ionic conductivity of the CMC-NH₄Br BPE obtained at room temperature is 1.12×10^{-4} S cm⁻¹ and ionic transference number was reported to be ~ 0.98 for this system. Linear sweep voltammetry results revealed that this BPE is electrochemically stable up to 1.42 ± 0.01 V and suitable for proton battery application. The cell potential of proton battery is 1.52 V and showed good rechargeability.

The biopolymer CMC complexed with CH₃COONH₄ electrolyte has been reported the best conductivity value of 5.77×10^{-4} S cm⁻¹ for the system containing 20 wt% of CH₃COONH₄ at ambient temperature. The electrochemical stability of this system is achieved up to ~ 2.5 V and suitable for electrochemical device applications [243]. Ramesh et al. [244] has been studied the effect 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) on cellulose acetate (CA) complexed with LiTFSI biopolymer electrolyte. The sample composition of CA:LiTFSI:[AMIM]Cl (14 wt%:6 wt%:80 wt%) exhibits the highest ionic conductivity of 1.75×10^{-3} S cm⁻¹ at room temperature. The collective data of batteries using BPE are tabulated in Tables 4 and 5.

The crops used for starch production include tapioca, wheat, potatoes, corn and rice. Starch is extracted in the form of granules, which vary in composition of amylase and amylopectin from plant to plant [6]. Starch attracts scientists because of its rich variety and abundance in nature. A solid BPE based on amylopectin-rich starch is plasticized with glycerol and contain LiClO₄. The highest ionic conductivity reported from this medium is 1.1×10^{-4} S/cm at 30 °C. The ionic conductivity as a function of time for amylopectin-rich starch plasticized with 30 wt% of glycerol and containing [O]/[Li]=10 showed conduction stability over 6 months ($\sigma \sim 3.01 \times 10^{-5}$ S cm⁻¹). These results show that it has the potential to meet all the conditions required by optical and electronic devices which use an electrolyte layer [265]. Lopes et al. investigated the NMR and conductivity results of solid electrolyte systems based on amylopectin rich starch plasticized with glycerol and containing LiClO₄. The samples were prepared with salt concentration [O]/[Li]=6 and 8 and plasticized with 30% of glycerol, having ionic conductivities of about 5×10^{-5} S cm⁻¹ at room temperature. The cation–proton interaction in this system is smaller than that of the grafted systems. The low temperature corresponding to the ⁷Li spin-lattice relaxation rate maximum indicated that the lithium has a relatively high mobility in the plasticized electrolytes, whereas the starch acts as a polymer matrix for the electrolyte. The results of the BPE based on amylopectin rich starch, plasticized with glycerol and containing lithium salt can be potentially useful for SPE applications [266].

Recently, Navaratnam et al. [267] studied the transport mechanism of chitosan based biopolymer electrolytes. They studied the chitosan-ethylene carbonate/propylene carbonate (chitosan-EC/PC) system with lithium acetate (LiCH₃COO) and lithium triflate (LiCF₃SO₃) as salts. The room temperature conductivity of the sample were found to be 6.1×10^{-7} S/cm for chitosan system containing lithium acetate salt and 5.0×10^{-6} S/cm for chitosan

Table 3

Status of dye sensitized solar cell (DSSC), battery and other electrochemical devices using solid biopolymer electrolyte.

Biopolymer	Additive	σ (S/cm)	Unit	Device	References
Agarose/Agars	KI	9.02×10^{-3}	0.54%	DSSC	[101]
	LiI	3.98×10^{-3}	–	DSSC	[102]
	NH ₄ I	4.89×10^{-3}	0.008%	DSSC	[103]
	NaI	12.41×10^{-4}	–	–	[104]
	1-allyl-3-ethylimidazolium iodide	–	5.89%	DSSC	[105]
	1-allyl-3-ethylimidazolium iodide	–	7.43%	DSSC	[106]
	DMSO/PC-(MPII)	14.2×10^{-3}	1.97%	DSSC	[107]
	DMSO/4EG-(MPII)	4.4×10^{-3}	1.38%	DSSC	[107]
	DMSO/3EG-(MPII)	4.6×10^{-3}	1.39%	DSSC	[107]
	DMSO/PG-(MPII)	6.2×10^{-3}	1.06%	DSSC	[107]
	Pure DMSO-(MPII)	5.0×10^{-3}	1.15%	DSSC	[107]
	Polysorbate80/Fe ₃ O ₄ nanoparticles	2.98×10^{-3}	1.83%	DSSC	[108]
	PEG 200/Fe ₃ O ₄ nanoparticles	2.88×10^{-3}	–	DSSC	[109]
	TiO ₂ -modified	2.66×10^{-3}	1.71%	DSSC	[110]
	Co ₃ O ₄ -modified	4.37×10^{-3}	2.11%	DSSC	[110]
	NiO-modified	3.33×10^{-3}	2.02%	DSSC	[110]
	NMP/LiI	3.94×10^{-4}	4.14%	DSSC	[111,112]
	NMP/LiI/nanoparticle TiO ₂	4.4×10^{-4}	4.74%	DSSC	[112]
	1-alkyl-3-methyl-imidazolium salts	–	2.93%	DSSC	[113]
	Acetic acid/glycerol	1.1×10^{-4}	–	–	[114]
	1-ethyl-3-methylimidazolium acetate	2.35×10^{-5}	–	–	[115]
Carrageenans	3-methyl-2-oxazolidinone	–	6.87%	DSSC	[116]
	AN/MOZ- TBP- I ₂ /Li-Pr ₄ NI + I ³⁻	2.92×10^{-3}	6.87%	DSSC	[117]
	Chitosan + carrageenan	1.38×10^{-6}	–	–	[118]
	Chitosan + carrageenan + NH ₄ NO ₃	2.39×10^{-4}	13to18.5 F g ⁻¹	EDLCs	[118]
	Chitosan + carrageenan + H ₃ PO ₄ + PEG	6.29×10^{-4}	35 F g ⁻¹	EDLCs	[119]
	NH ₄ NO ₃	2.1×10^{-6}	–	–	[120]
Cellulose	NH ₄ NO ₃ PEG	–	31.52mA cm ⁻²	Fuel cells	[121]
	Cellulose acetate (CA) + LiBOB + GBL	5.36×10^{-3}	4.7 Voc	Battery	[122]
	Cellulose acetate + TiO ₂	1.37×10^{-2}	54.1 mA h	Battery	[123]
	Cellulose acetate + NH ₄ CF ₃ SO ₃ + EC	$\sim 10^{-4}$	1.4 Voc	Battery	[124]
	Cellulose acetate electrolyte	–	22.41 mA h	Battery	[125]
	PEO-HPC + LiTFSI	2.5×10^{-4}	3.65 Voc	Battery	[126]
	LiCF ₃ SO ₃	5.3×10^{-7}	–	–	[127]
	CA-LiTFSI-[Amim] Cl	4.68×10^{-2}	–	–	[128]
	CA-NH ₄ BF ₄	2.18×10^{-7}	–	–	[129]
	CA-NH ₄ BF ₄ + PEG600	1.41×10^{-5}	–	–	[129]
	CA-LiTFSI-DES	2.61×10^{-3}	–	–	[130]
	BC-TEA	1.89×10^{-5}	–	–	[131]
Pectin	Amidated pectin + Glutaraldehyde (GA)	1.098×10^{-3}	–	–	[132]
	DAP + glutaraldehyde (GA)	2.536×10^{-2}	–	–	[133]
	LiClO ₄	4.7×10^{-4}	–	–	[134]
	KCl	1.45×10^{-3}	–	–	[135]
Sago Starch	KI	3.4×10^{-4}	0.57%	DSSC	[136,137]
	Glycerol + LiCl	10^{-3}	–	–	[138]
Corn Starch	Starch – chitosan-NH ₄ I	3.04×10^{-4}	–	–	[139]
	NH ₄ Br	5.57×10^{-5}	–	–	[140]
	NH ₄ Br + Glycerol	1.80×10^{-3}	–	–	[141]
	LiPF ₆ + BmImTf	3.21×10^{-4}	–	–	[142]
	LiOAc	2.07×10^{-5}	33.31 F g ⁻¹	EDLC	[143]
	Glycerol- LiOAc	1.04×10^{-3}	–	–	[143]
	LiPF ₆ -BmImTf at 80 °C	6.00×10^{-4}	–	–	[144]
	LiClO ₄	1.28×10^{-4}	–	–	[145]
	LiTFSI-DES(Choline chloride & urea)	1.04×10^{-3}	–	–	[146]
	LiI	1.83×10^{-4}	–	–	[147]
	LiI- Glycerol	9.56×10^{-4}	–	–	[147]
	LiTFSI-[Amim] Cl	4.18×10^{-2}	–	–	[148]
	LiTFSI-[Amim] Cl	5.68×10^{-2}	–	–	[149]
	LiPF ₆ -BmImPF ₆	1.47×10^{-4}	–	–	[149]
	LiClO ₄ -SiO ₂	1.23×10^{-4}	–	–	[150]
	[Amim]Cl	$10^{-1.6}$	–	–	[151,152]
	DMAc - LiCl	$10^{-0.5}$	–	–	[151,153]
	Glycerol	10^{-8}	–	–	[151,154]
	Glycerol - Carbon black	7.08	–	–	[151,154]
	[BMIM]Cl	$10^{-4.6}$	–	–	[155]
Pea Starch	Starch-Chitosan blend-NH ₄ I-Glycerol	1.28×10^{-3}	1.8- 4.0 F g ⁻¹	EDLC	[156]
	KI	2.28×10^{-4}	–	–	[157]
Rice Starch	LiI	4.68×10^{-5}	–	–	[158,159]
	LiI-TiO	2.27×10^{-4}	–	–	[160]
	LiI-MPII-TiO ₂	3.63×10^{-4}	0.17%	DSSC	[160]
Wheat Starch	CH ₃ COOH (Acetic acid)	10^{-5} to 10^{-4}	–	–	–
	NaI	1.3×10^{-4}	–	–	[161,162]
Potato Starch	NaClO ₄	7.19×10^{-6}	–	–	[161]
	NaSCN	1.12×10^{-4}	–	–	[161]
	NH ₄ I	2.4×10^{-4}	–	–	[163]

Table 3 (continued)

Biopolymer	Additive	σ (S/cm)	Unit	Device	References
Arrowroot Starch	Methanol-GA	2.50×10^{-6}	–	–	[164]
	Methanol-GA-NaI	8.40×10^{-6}	–	–	[164]
	Methanol-GA -PEG300-NaI	1.80×10^{-4}	–	–	[164]
	Acetone- GA	8.80×10^{-6}	–	–	[164]
	Acetone- GA- NaI	3.22×10^{-5}	–	–	[164]
	Acetone -GA- PEG300-NaI	4.30×10^{-5}	–	–	[164]
	–	–	335 F g^{-1}	EDLC	[165]
	KI	5.68×10^{-4}	0.63%	DSSC	[166]
	NaI	6.7×10^{-4}	–	–	[167]
	Chitosan blend - NH_4NO_3	3.89×10^{-5}	–	–	[168]
Gum Arabic	–	1.5×10^{-6}	–	–	[169]
Gum Tragacanth	NaOH	88.8×10^{-3}	–	–	[170]
Xanthan Gum	Water-based thixotropic	–	4.78%	DSSC	[171]
Gellan Gum	LiCF_3SO_3	5.4×10^{-4}	–	–	[172]
Chitin/Chitosan	LiI	1.5×10^{-3}	–	–	[173]
	Polypyrrole-Gellan gum	–	–0.8to +0.4 V	EDLC	[174]
	NaI	–	0.13%	DSSC	[175]
	EMImSCN-NaI	2.60×10^{-4}	0.73%	DSSC	[175]
	$\text{NH}_4\text{SCN-Al}_2\text{TiO}_5$	2.10×10^{-4}	–	–	[176]
	$\text{LiNO}_3 \text{ NH}_4\text{I}$	2.7×10^{-4}	1.113V	Battery	[177]
	$\text{NH}_4\text{I-EC}$	3.73×10^{-7}	0.29%	DSSC	[178]
	$\text{NH}_4\text{I-BMII}$	7.34×10^{-6}	0.51%	DSSC	[178]
	Tartaric- $\text{NH}_4\text{I-BMII}$	8.47×10^{-4}	1.24%	DSSC	[178]
	Tartaric-PEO- $\text{NH}_4\text{I- BMII}$	3.02×10^{-4}	0.38%	DSSC	[179]
	Tartaric-Phthaloyl chitosan- $\text{NH}_4\text{I-BMII}$	5.52×10^{-4}	0.39%	DSSC	[179]
	Tartaric-Phthaloyl chitosan-PEO- $\text{NH}_4\text{I-BMII}$	5.86×10^{-4}	0.43%	DSSC	[179]
	PEO blend- NH_4I	6.24×10^{-4}	0.46%	DSSC	[179]
	PEO blend- NH_4I (Dye-Sumac/Rhus)	–	–	–	–
	$\text{NH}_4\text{CF}_3\text{SO}_3$	4.32×10^{-6}	0.46%	DSSC	[180]
	Methylcellulose blend - $\text{H}_4\text{CF}_3\text{SO}_3$	1.18×10^{-5}	1.5%-	DSSC	[181]
	EC-LiOAc	8.91×10^{-7}	–	–	[183]
	NaI	4.99×10^{-6}	–	–	[183]
	EMImSCN-NaI	7.6×10^{-6}	0.13%	–	[184]
	chitosan-LiOAc-oleic acid	10^{-5}	–	–	[185]
	chitosan, palmitic acid (PA)-LiOAc	5.5×10^{-6}	–	–	[186]
	Corn starch - $\text{NH}_4\text{Cl-Glycerol}$	5.11×10^{-4}	–	–	[187]
	NH_4NO_3	2.53×10^{-5}	–	–	[188]
	NH_4NO_3 -Acetic acid	1.46×10^{-1}	27.90 mA h^{-1}	Battery	[189]
	–	–	3.67 mW cm^{-2}	–	–
	NH_4NO_3 -EC- Acetic acid	9.93×10^{-3}	8.70 mW cm^{-2}	Battery	[190]
	–	–	17.0 mA h	–	–
	Polyethylene oxide - NH_4NO_3	1.02×10^{-4}	–	–	[191]
	LiCF_3SO_3	2.75×10^{-5}	–	–	[192]
	CMC-Chitosan-DTAB	1.85×10^{-6}	–	–	[193]
	PVA-Chitosan- NH_4NO_3	2.07×10^{-5}	1.6 and 1.7 V	Battery	[194]
	PVA-chitosan- NH_4NO_3 -EC	1.60×10^{-3}	27.1 F g^{-1}	EDLC	[195]
	PVA- NH_4I	1.77×10^{-6}	–	–	[196]
	NH_4I	3.73×10^{-7}	0.22%	DSSC	[196,197]
	$\text{NH}_4\text{I-EC}$	7.34×10^{-6}	0.18FF	DSSC DSSC	[197]
	$\text{NH}_4\text{I-BMII}$	3.43×10^{-5}	0.22 FF	–	[197]
	LiCF_3SO_3 -DEC-EC	4.26×10^{-5}	–	Fuel cell	[198]
	H_3PO_4	5.36×10^{-5}	–	Fuel cell	[199]
	$\text{H}_3\text{PO}_4\text{-Al}_2\text{SiO}_5$	1.12×10^{-4}	–	Fuel cell	[199]
	$\text{H}_3\text{PO}_4\text{-NH}_4\text{NO}_3$	1.16×10^{-4}	–	Fuel cell	[199]
	$\text{H}_3\text{PO}_4\text{-NH}_4\text{NO}_3\text{-Al}_2\text{SiO}_5$	1.82×10^{-4}	–	–	[199]
	PEO- LiTFSI	1.40×10^{-6}	–	Battery	[200]
	LiCF_3SO_3 -DEC-EC	4.26×10^{-5}	–	Battery	[201]
	LiCF_3SO_3 - PC/EC	1.09×10^{-4}	–	–	[201]
	LiOAc	2.20×10^{-7}	–	–	[202]
	NH_4SCN	1.81×10^{-4}	–	–	[203]
	$\text{NH}_4\text{SCN-Glycerol}$	1.51×10^{-3}	7.68×10^{-4}	–	[203]
	PVA - NH_4Br	3.0×10^{-6}	–	–	[204]
	PVA- LiClO_4	1.47×10^{-4}	–	Battery	[205]
	$\text{NH}_4 \text{CH}_3\text{COO-EC}$	1.47×10^{-4}	1.83 mW cm^{-2}	Battery	[206]
	$\text{NH}_4 \text{CH}_3\text{COO-EC}$	4.38×10^{-7}	1.36 mW cm^{-2}	–	[206]
	Chitosan- NH_4Br	2.15×10^{-4}	–	–	[207]
	Chitosan- $\text{NH}_4\text{Br-glycerol}$	9.72×10^{-5}	1.44×10^{-3}	–	[207]
	Starch blend- NH_4Br	3.9×10^{-3}	–	EDLC	[208,209]
	Starch blend- $\text{NH}_4\text{Br+EC}$	4.0×10^{-5}	$0.1400 \text{ mA h g}^{-1}$	Battery	[208,209]
	LiCF_3SO_3 -EC-DMC	4.6×10^{-5}	1.5 V	–	[210]
	EC- LiCF_3SO_3	10^{-5}	–	Battery	[211]
	Acetic acid- NaClO_4	5.5×10^{-6}	1.114V	–	[212]
	NH_4Br	1.12×10^{-4}	–	Battery	[213]
	NH_4F	2.68×10^{-7}	–	–	[214]
Carboxymethyl Cellulose	Salicylic acid	9.50×10^{-8}	–	–	[215]
	DTAB	7.72×10^{-4}	–	–	[216]

Table 3 (continued)

Biopolymer	Additive	σ (S/cm)	Unit	Device	References
Methylcellulose (MC)	DTAB-EC	2.37×10^{-3}	–	–	[216]
	CH ₃ COONH ₄	5.77×10^{-4}	–	–	[217]
	Oleic acid	2.11×10^{-5}	–	–	[218]
	–	3.08×10^{-11}	–	–	[219]
	NH ₄ NO ₃	2.10×10^{-6}	–	–	[219]
	NH ₄ F	6.40×10^{-7}	–	–	[220]
	Glycolic acid	7.16×10^{-10}	–	–	[221]
	MC-NH ₄ NO ₃	1.17×10^{-4}	–	–	[222]
	MC-NH ₄ NO ₃ -PC	4.91×10^{-3}	–	–	[222]
	MC-NH ₄ NO ₃ -EC	1.74×10^{-2}	–	–	[222]
	PVDF-MC/PVDF-LiFePO ₄	1.5×10^{-3}	34 mA g ⁻¹	Battery	[223]
	NH ₄ NO ₃ -PEG	1.14×10^{-4}	31.52 mA cm ⁻²	Fuel cell	[224]

Table 4

Morphology, treatment conditions and matrix of some of the cellulosic biopolymer materials used as electrolytes in Li-ion batteries [245].

Cellulose form	Treatment/modification before introduction into the matrix	Polymeric matrix	Ref.
<i>Cellulose used as a reinforcement of polymeric matrices</i>			
Sheet	None	Photocured acrylic matrices	[246,247]
Fibers	Grafting with acrylic acid	PVA	[248]
NCC	None	PEO or crosslinked PEO	[249–251]
NCC	None	Ethyleneoxide-epi-chlorohydrin Copolymers	[252]
MFC	None	PEO	[253]
MFC	None	Photocured acrylic matrices	[254]

Table 5

Some of the cellulosic biopolymer materials used as electrolytes in Li-ion batteries [246].

Cellulose Derivative	Treatment/modification	Ref.
<i>Cellulose derivatives used as SPEs or GPEs</i>		
Hydroxypropylcellulose	Grafting with PEO	[255]
Cellulose triacetate	Plasticization with ionic liquids	[256]
Ethylcellulose	Plasticization with glycerol	[257]
Ethylcellulose	Grafting with methylmethacrylate	[258]
Cellulose acetate	Plasticization with ionic liquid or eutectic solvents	[259]
Cellulose phthalate	None	[260]
Cyanoethylated cellulose	None	[261]
Cyanoethylated cellulose	Blended with PVDF	[262]
Cellulose esters	Esterification with PEO monocarboxylic acid	[263]
Hydroxyethylcellulose	Grafted with oligoetherisocyanate	[264]

system containing lithium triflate salt. The room temperature conductivity of LiCF₃SO₃ electrolyte was higher than that of the LiCH₃COO electrolyte. The difference in conductivity is associated with the nature of the lithium salt and it is supposed that LiCF₃SO₃ salt dissociated more LiCH₃COO anion. Triflate anion is larger than acetate anion and therefore lithium triflate salt will have lower lattice energy than lithium acetate salt.

Alias et al. [268] reported the porous chitosan-SiO₂ membranes prepared by ultrasonic mixing solution-cast and porogen removal method at different SiO₂ weight ratios. They soaked these membranes in NH₄CH₃COO electrolyte solution for two days and obtained a conductivity value of 3.6×10^{-3} S/cm. The proton battery displayed an open circuit potential of 1.5 V for 7 days, maximum power density (6.7 mW cm⁻²) and small current resistance (0.03 Ω). The specific discharge capacities obtained from discharge profile of 39.7 mA h g⁻¹ (0.5 mA) and 43.8 mA h g⁻¹ (1.0 mA)

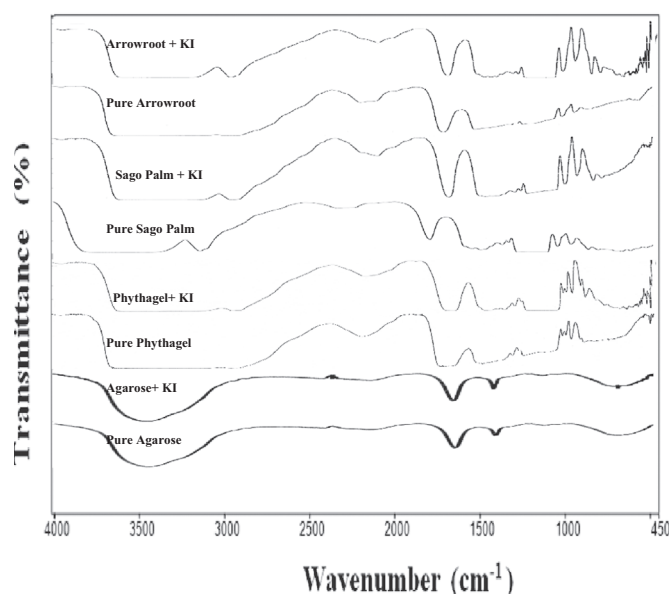


Fig. 4. Infrared spectroscopy of pure biopolymers and biopolymers-KI samples.

increased as the discharge currents were increased. These results indicated that porous chitosan-SiO₂ membrane is a suitable membrane for the proton batteries.

Solid polymer electrolytes consisting of chitosan, lithiumbis (trifluoromethylsulfonyl) imide (LiTFSI) as a salt and succinonitrile as a plastic crystal are reported by Taib and Idris [269]. The highest room temperature ionic conductivity observed for the sample Chitosan-LiTFSI containing 50 wt% succinonitrile exhibited a conductivity of 4×10^{-4} S/cm, a high lithium ion transference number (0.598) and wide electrochemical window (4.7 V). This system with LiFePO₄ as a cathode, displays a stable discharge capacity of 160 mA h g⁻¹ for up to 50 cycles at a current density of 17 mA g⁻¹. The results demonstrate that this system is potential electrolyte material for lithium rechargeable batteries.

The biopolymer electrolyte based agar complexed with magnesium triflate (Mg(CF₃SO₃)₂) has been investigated by Alves et al. [270]. The sample that exhibited the highest conductivity is Agar_{32.30%}Mg(CF₃SO₃)₂, and the maximum conductivity values are 1.0×10^{-6} and 3.8×10^{-5} S cm⁻¹ at 30 °C and 70 °C, respectively. Agar doped with different ionic liquids has been reported [271,272]. The best conductivity value of 2.35×10^{-5} S cm⁻¹ was observed for the agar based on 1-ethyl-3-methylimidazolium acetate composition at ambient temperature. At 100 °C, this electrolyte exhibits a conductivity of about 1.58×10^{-3} S cm⁻¹. The highest ionic conductivity value of agar-NiO system is 5.19×10^{-5} S/cm at room temperature for the sample with 0.25 g of NiO. It was also stated

Table 6

Infrared spectra data of pure biopolymer and KI doped bio-polymer electrolyte system.

Wavelength in cm^{-1}								Freq. ranges	Groups (bonds)	Functional groups
Pure Arrowroot	Arrow root + KI	Pure Sago Palm	Sago Palm + KI	Pure Agarose	Agarose + KI	Pure Phythagel	Phythagel + KI			
3584	3372	3313	3252	3445.86	3434.15	3358	3626	3500–3200 (s,b) 3640–3610(s,sh)	O–H stretch, free hydroxyl, H-bonded	alcohols, phenols
–	2929	2929	2931	–	–	2926	2921	3000–2850 (m)	C–H (stretch)	Alkane
2149	–	2149	–	2124.66	2105.69	2126	2142	2260–2100 (w)	–CC– stretch	Alkynes
1645	–	1642	–	–	–	–	1667,1663,1660,1651	1680–1640 (m)	–C=C– stretch	Alkenes
–	1626	–	1633	1636.32	1637.57	1619	1644,1614	1650–1580 (m)	N–H bend	1° amines
1462	1408	1412	1454,1416	1400.34	1400.22	1409	1445,1427,1416	1500–1400 (m)	C–C stretch (in-ring)	Aromatics
–	–	1364	1372	–	–	–	–	1370–1350 (m)	C–H rock	alkanes
1169	1234, 1203, 1075	1241,1204,1052,1151	1239, 1203, 1165,1047	1121.00	1109.07	1337,1297, 1235,1194	1237,1196, 1171	1300–1150 (m) 1300–1150 (m)	C–O stretch C–H wag (–CH ₂ X)	alcohols, carboxylic acids, esters, ether s alkyl halides
936	935	932	935	–	–	942,924	943,923	950–910 (m)	O–H bend	Carboxylic acid
863, 787	860, 762, 709	859, 762,708	860, 762, 715	687.28	–	890,836,812,749,699	891,836,815,755	900–675 (s)	C–H “oop”	Aromatics
482	607, 588	–	–	666.77	666.72, 545.30	666,644,608,565, 546,539	666,462,421,407	690–515 (m)	C–I stretch	Alkyl halides

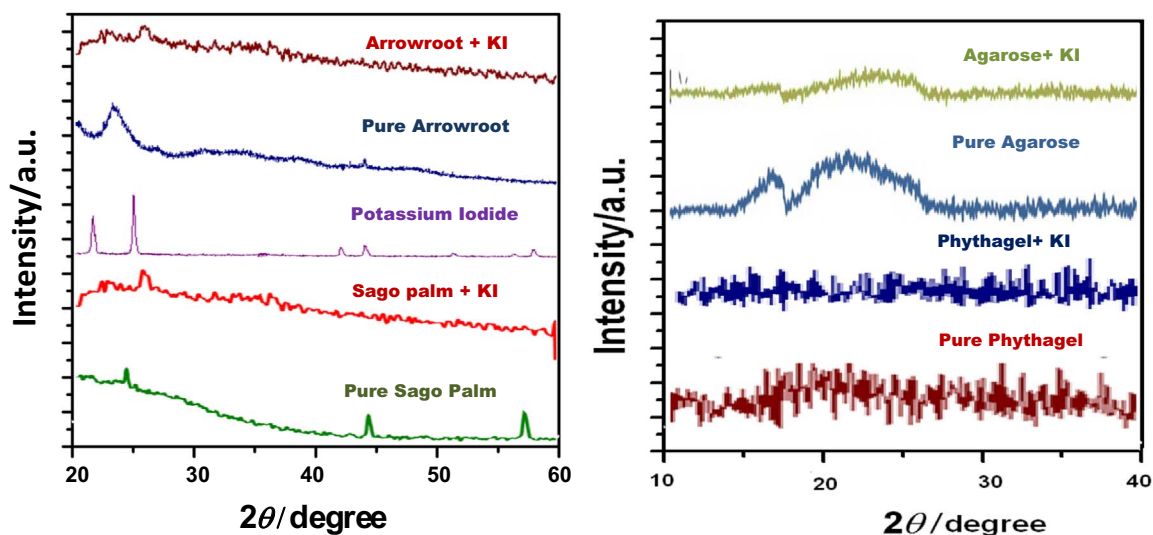


Fig. 5. The XRD pattern of pure biopolymers and KI doped biopolymers systems.

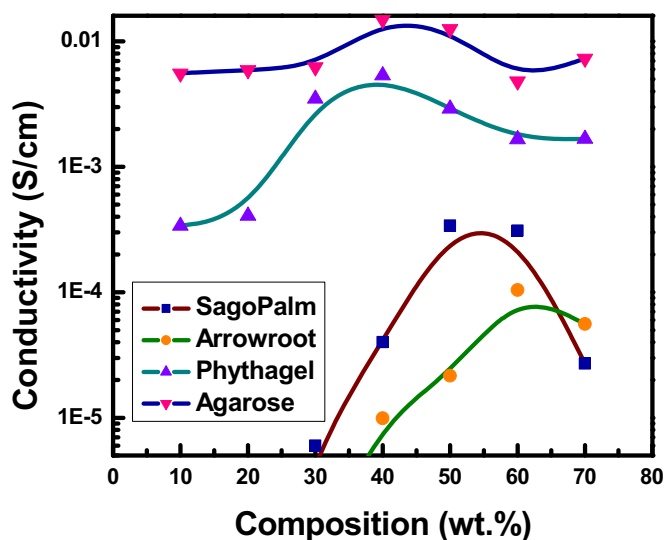


Fig. 6. Ionic conductivity vs composition plot in biopolymers:KI polymer electrolyte system.

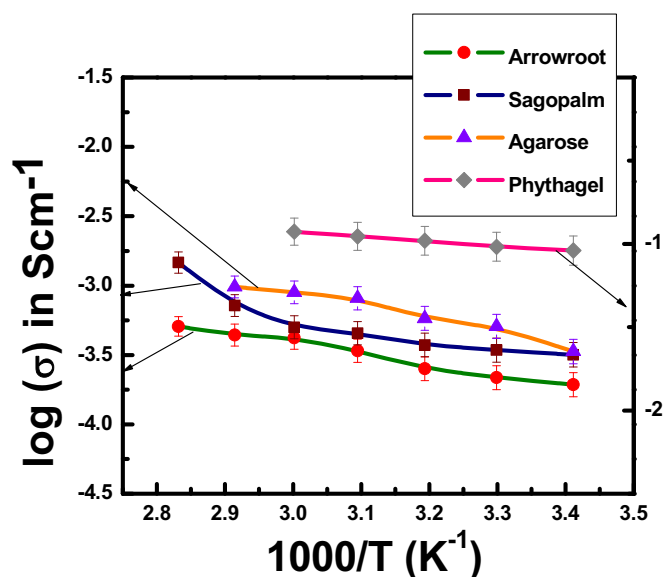


Fig. 8. Variation of conductivity with temperature plot in biopolymers: KI systems.

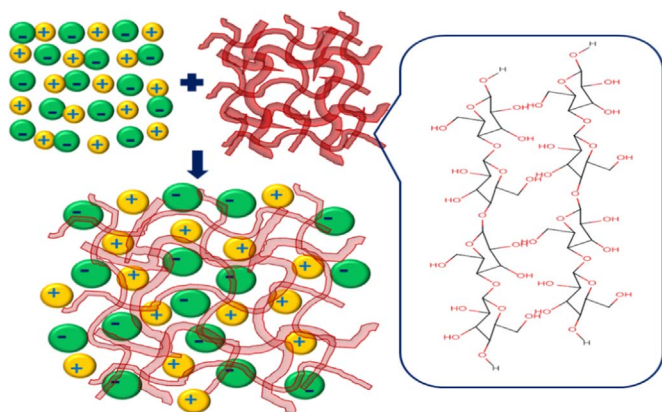


Fig. 7. Schematic diagram showing ion dissociation in biopolymer salt matrix.

that the increase in temperature up to 80 °C promoted an increase in the ionic conductivity to $3.32 \times 10^{-4} \text{ S cm}^{-1}$ [273].

Pectin-based membranes with different salts such as LiClO_4 , KCl , $\text{LiClO}_4\text{-Ir(III)}$ and KCl-Ir(III) contents are prepared and studied

by Leones et al. [274]. The most conductive sample of Pectin and KCl exhibits the ionic conductivity of $1.45 \times 10^{-3} \text{ S cm}^{-1}$ and $6.31 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C and 90 °C, respectively. The overall redox stability of 7.0 V suggests that this material has an acceptable stability window for an application in solid state electrochemical devices. Such a high ionic conductivity, thermal stability and reproducibility affirm the suitability of biopolymers as electrolyte in electrochemical devices.

4. Recent works by authors

In our laboratory we have tested a series of biopolymers (like Agarose/ Agars, Sago Starch, Arrowroot Starch, Phythage) doped with different alkali metal salts and carried out detailed electrical and structural investigations specific for the application area of DSSCs [101,136,137,166]. The experimental observations and discussions are described below.

4.1. Structural measurements

4.1.1. FTIR studies

Fourier Transform Infrared Spectroscopy (FTIR) spectra of pure biopolymer and biopolymers doped with KI were recorded using Perkin Elmer 883 IR spectrophotometer between 4000 and 450 cm^{-1} [276–280] (Fig. 4). The different bands assigned to various functional groups are listed in Table 6. Major differences observed in the stretching peaks of the biopolymers with the addition of KI are at the frequency ranges of –OH and –C–O functional groups. This indicates complex formation between the biopolymer and KI [1,2,4,26].

4.1.2. XRD studies

Fig. 5 shows the X-ray diffraction patterns (XRD) of biopolymer-KI electrolytes obtained by using Rigaku D/max-2500 with a scan rate of $2^\circ/\text{min}$. It is evident that all salts are well dissolved in biopolymer matrix which is affirmed by the disappearance of the crystallinity of biopolymer with the addition of KI. Doping of salt broadens the peak which is clear indication of increase in the amorphous behavior of biopolymer-KI. The decrease in crystallinity (or the increase in amorphicity) by salt doping has the potential of enhancing the overall ionic conductivity of the system.

4.2. Electrical measurements

4.2.1. Electrical conductivity measurements

The ionic conductivity measurements of the biopolymer-KI based electrolyte films were carried out using a CH instrument workstation (model CHI604D, USA) over frequency range of 100 Hz to 1 MHz. Free standing biopolymer electrolyte films were sandwiched between two steel electrodes and the electrical conductivity were evaluated using the below formula

$$\sigma = \frac{1}{R_b} \left(\frac{l}{A} \right) \quad (1)$$

where, σ is the ionic conductivity, R_b is the bulk resistance, l is the thickness of sample and A is the area of given sample.

The calculated σ values of the biopolymer-xwt%KI based electrolytes are shown in Fig. 6. It was found that presence of KI in biopolymer matrix enhances the ionic conductivity up to a certain doping ratio. The increase in the ionic conductivity with increasing KI concentration is generally correlated with the increase in the number of mobile charge carriers while the reduction observed in this value after reaching a maximum can be attributed to

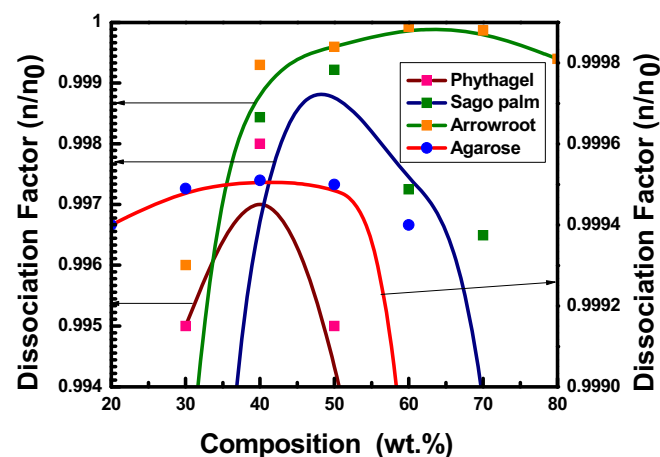


Fig. 9. Change in relative number of charge carriers with increasing amount of KI in biopolymers:KI polymer electrolyte matrix.

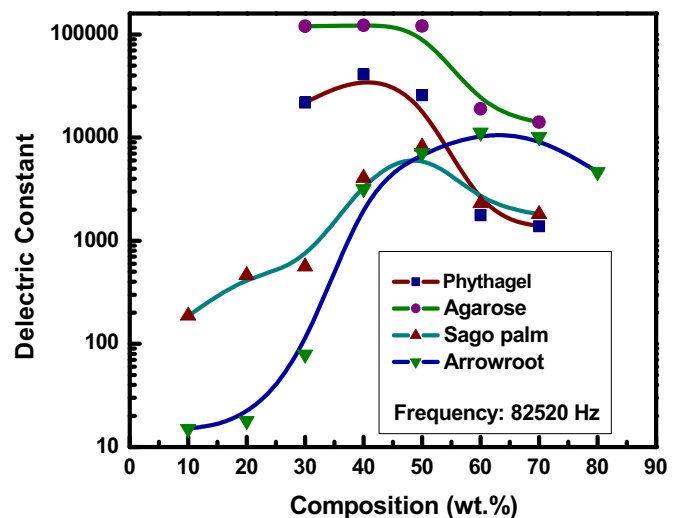


Fig. 10. Dielectric constant vs composition plot of biopolymers:KI polymer electrolyte system.

the formation of ion multiples [136,163,166]. The effect of salt concentration in biopolymer electrolyte matrix is demonstrated through dissociated ions model in Fig. 7. The impedance measurement data clearly explains the role of charge carriers in the biopolymer electrolyte matrix. It can be seen that both mobile concentration factor and dissociated charge fraction, which are both related with mobile ion concentration data, are following the conductivity trend. Hence, ion pair formation and re-dissociation theory is applicable in biopolymer-salt complex systems. Minimum conductivity is due to the decreased dissociation. Increased ion association, i.e. decreased dissociation or triplet ion formation, both contribute to the decrement in mobility [101,136,163].

The ionic conductivity (σ) in case of ion conducting electrolyte system is given as

$$\sigma = n \cdot q \cdot \mu \quad (2)$$

where n is the charge carrier density, q is the charge of the carrier and μ is the mobility of the carriers. Therefore any increase in either of the parameters n or q will certainly affect the value of ionic conductivity.

Here the concentration of free charge carrier's density can be given by:

$$n = \left[\frac{\sigma_{DC}}{\left(\sqrt{\frac{\epsilon'_s}{\epsilon'_s - 1}} \right) \epsilon_0 \epsilon'_s \omega_x} \right]^4 \epsilon_0 \epsilon'_s \frac{kT}{e^2 d^2} \quad (3)$$

σ_{DC} is the conductivity at high frequency, ϵ_0 is vacuum permittivity, k is Boltzmann constant, ϵ'_s and ϵ'_ω are the real permittivity at high frequency and at the frequency of ω , respectively and d is the thickness of the sample. Here, ϵ'_s is the real part of the dielectric permittivity in the high frequency region and ω_x is the angular frequency for which $\epsilon'(\omega_x) = 10\epsilon'_s$. Adding KI in biopolymer matrix provides additional mobile charge species, i.e. in present case K^+ cation and I^- anion, and hence ionic conductivity enhances. Variation in number of charge carriers and mobility with KI concentration can be easily understood using Eq. (2). In most of the systems we have observed that the number of charge carriers remains almost same. Beyond certain fixed wt% of dispersoid, the increase in mobility dominates by the decrease in the carrier concentration. This is due to the fact that as the salt concentration increases the amorphicity of the biopolymer matrix increases, thereby allowing more paths to the ions to migrate. As a result the conductivity increases with the addition of the salt

Table 7

The recorded photovoltaic parameters of DSSC observed in biopolymers-salt matrix.

Composition for Agarose/Agar based Biopolymer	Dye	Working Electrode	σ (S cm ⁻¹)	J _{sc} mA cm ⁻²	V _{oc} (V)	FF (%)	Area (cm ²)	η (%)	Intensity mW cm ⁻²	Ref.
KI-I ₂	N719	FTO-TiO ₂	9.02×10^{-3}	3.27	0.670	0.24	0.6	0.54	100	[101]
NH ₄ I-I ₂ -Glycerol	N719	ITO-ZnO	4.89×10^{-3}	0.007	0.29	–	1	–	100	[103]
MPII-PC/DMSO-GuSCN-NMBI-I ₂	N719	FTO-TiO ₂	–	11.73	0.70	0.64	0.283	5.25	100	[105]
AEII-PC/DMSO-GuSCN-NMBI-I ₂	N719	FTO-TiO ₂	–	11.71	0.72	0.65	0.283	5.45	100	[105]
APII-PC/DMSO-GuSCN-NMBI-I ₂	N719	FTO-TiO ₂	–	11.53	0.70	0.62	0.283	4.97	100	[105]
DAII-PC/DMSO-GuSCN-NMBI-I ₂	N719	FTO-TiO ₂	–	11.84	0.70	0.60	0.283	4.96	100	[105]
DMSO/PC- MPII- GuSCN-NMBI-I ₂	N719	ITO/TiO ₂	14.2×10^{-3}	4.65	0.73	0.58	0.25	1.97	100	[107]
DMSO/4EG-MPII- GuSCN-NMBI-I ₂	N719	ITO/TiO ₂	4.4×10^{-3}	3.69	0.65	0.57	0.25	1.38	100	[107]
DMSO/3EG-MPII- GuSCN-NMBI-I ₂	N719	ITO/TiO ₂	4.6×10^{-3}	4.01	0.61	0.57	0.25	1.39	100	[107]
DMSO/PG- MPII- GuSCN-NMBI-I ₂	N719	ITO/TiO ₂	6.2×10^{-3}	3.21	0.58	0.57	0.25	1.06	100	[107]
DMSO- MPII- GuSCN-NMBI-I ₂	N719	ITO/TiO ₂	5.0×10^{-3}	3.69	0.58	0.54	0.25	1.15	100	[107]
TiO ₂ -NMP- Lil/I ₂	N719	FTO-TiO ₂	2.66×10^{-3}	5.28	0.605	0.55	0.25	1.71	100	[110]
Co ₃ O ₄ -NMP- Lil/I ₂	N719	FTO-TiO ₂	4.37×10^{-3}	7.24	0.635	0.46	0.25	2.11	100	[110]
NiO-NMP- Lil/I ₂	N719	FTO-TiO ₂	3.33×10^{-3}	6.20	0.625	0.52	0.25	2.02	100	[110]
Lil/I ₂ -NMP	–	TiO ₂	3.94×10^{-4}	8.24	0.597	0.62	0.25	4.14	73	[111,112]
Lil/I ₂ -NMP-nanoparticle TiO ₂	–	TiO ₂	4.4×10^{-4}	10.96	0.545	0.57	0.25	4.74	73	[112]
AN/MOZ- TBP- I ₂ /Lil - Pr ₄ Ni + I ³⁻	N3	FTO/ITO/TiO ₂	4.36×10^{-3}	14.00	0.76	0.66	0.20	7.06	100	[117]
1-alkyl-3-methylimidazoliumiodides- Lil/I ₂ -NMP	N719	FTO/TiO ₂	–	6.77	0.650	0.66	0.25	2.93	100	[113]
Lil/I ₂ -NMP- Fe ₃ O ₄ - polysorbate 80	N719	FTO/TiO ₂	2.98×10^{-3}	5.00	0.7	0.53	–	1.83	100	[108]
Lil/I ₂ -NMP- Fe ₃ O ₄ - PEG200	N719	FTO/TiO ₂	–	3.70	0.67	0.61	–	1.50	100	[108]
Lil/I ₂ -NMP- Fe ₃ O ₄ - PVP	N719	FTO/TiO ₂	–	3.00	0.67	0.59	–	1.19	100	[108]
Lil/I ₂ -NMP- Fe ₃ O ₄ - SDS	N719	FTO/TiO ₂	–	3.18	0.66	0.62	–	1.29	100	[108]
Composition	Dye	Working electrode	σ (S cm ⁻¹)	J _{sc} mA cm ⁻²	V _{oc} (V)	FF (%)	Area (cm ²)	η (%)	Intensity mW cm ⁻²	Ref.
Carrageenan- AN/MOZ- TBP-I ₂ /Lil-Pr ₄ Ni + I ³⁻	N3	FTO/ITO/TiO ₂	2.92×10^{-3}	14.67	0.73	0.67	0.20	6.87	100	[117]
Carrageenan-AN/MOZ-TBP-I ₂ /Lil - I ³⁻	N3	FTO/ITO/TiO ₂	–	14.67	0.73	0.67	0.20	6.87	100	[117]
Carrageenan-AN/MOZ-(Pr) ₄ Ni-I ₂ - Lil -TBP	N3	PEN/ITO/TiO ₂	–	2.68	0.80	0.72	0.25	1.54	100	[116]
Carrageenan- AN/MOZ-(Pr) ₄ Ni-I ₂ - Lil -TBP	N3	FTO-TiO ₂	–	8.67	0.75	0.65	0.25	4.23	100	[116]
Gellan gum + KI	N719	FTO-TiO ₂	0.00534	0.0666	0.57	0.57	0.45	0.56	100	–
Sago Starch + KI	N719	FTO-TiO ₂	3.4×10^{-4}	0.0291	0.582	0.60	0.45	0.578	100	[136]
Amylopectin-DMSO-I ₂ -Lil-DMHIm-(4-tertbutylpyridine)	N719	FTO-TiO ₂	–	6.83	0.74	0.66	0.16	3.34	100	[148]
Arrowroot starch + KI	N719	FTO-TiO ₂	1.04×10^{-4}	0.0568	0.56	–	0.45	0.63	100	[165]
Rice-Lil:MPII:TiO ₂	N3	ITO/TiO ₂	3.63×10^{-4}	0.49	0.45	0.75	0.25	0.17	100	[159]
Chitosan-Nal-I ₂	–	FTO-TiO ₂	–	1.05	0.349	0.34	0.16	0.13	100	[175]
Chitosan-Nal-I ₂ -EMImSCN	–	FTO-TiO ₂	2.60×10^{-4}	2.62	0.53	0.52	0.16	0.73	100	[175]
Chitosan- NH ₄ I- I ₂	–	ITO-TiO ₂	3.73×10^{-7}	0.0049	0.15	0.22	0.09	0.29	56.4	[178]
Chitosan- NH ₄ I- I ₂ -EC	–	ITO-TiO ₂	7.34×10^{-6}	0.0072	0.22	0.18	0.09	0.51	56.4	[178]
Chitosan- NH ₄ I- I ₂ -BMII	–	ITO-TiO ₂	8.47×10^{-4}	0.0192	0.26	0.14	0.09	1.24	56.4	[178]
Chitosan-NH ₄ I-BMII	Black rice anthocyanin	ITO/TiO ₂	3.02×10^{-4}	0.9	3.65	0.45	0.16	0.15	100	[179]
Chitosan-PEO-NH ₄ I-I ₂ -BMII	Black rice anthocyanin	ITO-TiO ₂	5.52×10^{-4}	1.213	4.00	0.47	0.16	0.23	100	[179]
Tartaric-Phthaloyl Chitosan-NH ₄ I-BMII	Red cabbage anthocyanin	ITO-TiO ₂	5.86×10^{-4}	3.472	3.65	0.34	0.16	0.43	100	[179]
Tartaric-Phthaloyl Chitosan-PEO-NH ₄ I -BMII	Red cabbage anthocyanin	ITO-TiO ₂	6.24×10^{-4}	3.503	3.40	0.39	0.16	0.46	100	[179]
Chitosan-PEO-NH ₄ I-I ₂	Lawsonia inermis	ITO/TiO ₂	1.18×10^{-5}	0.38	336	0.57	0.05	0.7	100	[181]
Chitosan-PEO-NH ₄ I-I ₂	Sumac/Rhus	ITO/TiO ₂	1.18×10^{-5}	0.93	394	0.41	0.05	1.5	100	[181]
Chitosan-PEO-NH ₄ I-I ₂	Curcuma longa	ITO/TiO ₂	1.18×10^{-5}	0.20	280	0.65	0.05	0.36	100	[181]

concentration and attains a maximum. This means that the conductivity is not affected by the value of n, and depends on the movement and distribution of charge carriers. At high salt concentrations, ions move in the sample within very short distances and mobility does not affect the conductivity.

4.2.2. Temperature dependent conductivity measurement

Temperature dependent ionic conductivity of solid biopolymer electrolytes are shown in Fig. 8. It is clear that with increasing temperature, the ionic conductivity values increases and follow Arrhenius type behavior. Linear relations are observed in all biopolymer electrolytes, which mean that there is no phase transition in the biopolymer matrix or no domain formed by the addition of

KI. These experiments are restricted by the T_g (glass transition) temperature where bio polymers start phase transition. Variation of conductivity is given with the equation below by considering Arrhenius type behavior

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (4)$$

where, σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann constant. From this relationship, the E_a of biopolymer electrolytes with maximum conductivity values are calculated. The values obtained are 0.33, 0.40, 0.39 and 0.24 eV for the biopolymer electrolytes Sago Palm, Arrowroot, Agarose and Phytagel systems respectively.

4.2.3. Ion dissociation factor

To further clarify the role of charge carriers in biopolymer electrolyte matrix we have evaluated the room temperature dissociation factor (n/n_0) for all studied biopolymers-salt samples. The change in the relative number of charge carriers (n/n_0) with increasing wt% KI are shown in Fig. 9. It is observed that at the maximum doping limit, the n/n_0 values reach a maximum as well and then presents a decreasing trend; follows the same trend observed in conductivity and dielectric measurements. Therefore, the conductivity, in biopolymers:KI matrix is predominantly governed by the number of charge carriers as suggested by Barker [275] (electrolyte dissociation theory) using the equation

$$n = n_0 \exp \left\{ - \frac{U}{2\epsilon kT} \right\} \quad (5)$$

where, U is the dissociation energy of the salt, k is Boltzmann constant, ϵ is the dielectric constant of the system, and T is the temperature of the sample.

4.2.4. Dielectric studies

The information about different molecular motion and relaxation processes, are well correlated with the dielectric studies. Dielectric measurements are extremely sensitive to small changes in material properties (molecular relaxation of the order of only a few nanometer involves dipole changes that can be observed by dielectric study). In order to justify the overall contribution of the number of free charge carriers in the total conductivity, the dielectric constant (ϵ) of the biopolymer electrolyte films are calculated. Fig. 10 shows the change in dielectric constant with increasing amount of KI in the biopolymer electrolyte at one typical frequency i.e. at 82520 Hz. It is clear that conductivity data are well matched with the dielectric data. The addition of KI in the biopolymers causes changes in the dielectric constant of the matrix, which effects the number of free charge carriers and thereby the conductivity.

4.2.5. Ionic transference number measurement using DC polarization method

Using this simple method, we have evaluated the percentage of ionic or electronic nature in biopolymer:KI electrolyte films. Fixed DC potential of 0.25 V is applied for ~6 h to the steel plate/biopolymer electrolyte/steel plate system. The DC current is monitored with respect to time using Keithley 2400 source meter. After applying a DC potential, due to the ionic movement (ions start moving towards the other donor site) current is increased initially and after attaining the peak current it is saturated and decreasing trend is appeared (Fig. not shown here). By monitoring initial current and final current and using Eq. (6), the ionic transference numbers of biopolymer electrolytes are calculated as 0.94, 0.93, 0.82, 0.92 for Sago Palm, Arrowroot, Agarose and Phythage systems respectively, which confirms the ionic nature of the biopolymers electrolyte system.

$$t_{\text{ion}} = \frac{I_{\text{initial}} - I_{\text{final}}}{I_{\text{initial}}} \quad (6)$$

4.3. Dye sensitized solar cell performance (I - V curve)

The photovoltaic performance (I - V curve) of the DSSCs are measured with Keithley 2400 source meter under 1 sun light condition (Fig. not shown). For developing redox couple in biopolymer-KI electrolyte system, addition of iodine in the polymer matrix is needed. DSSCs are fabricated by using the highest ionic conductivity composition of the electrolytes. The different photovoltaic parameters such as J_{sc} (A cm^{-2}), V_{oc} (V), FF (%), Area (cm^2) and light intensity in biopolymers: salt matrix developed in our

laboratory [101,136,137,166] as well as exist in literature are listed in Table 7 [101–181].

5. Conclusions

This review article provides a thorough overview of the structure, occurrence, and properties- chemical, physical, electrical with technical applications of the most biopolymers generated by different sources. We have successfully presented collective data on the additives used by the researchers to enhance the ionic conductivity of biopolymer based electrolytes for device performance particularly on DSSC and battery. It was observed that the biopolymer electrolytes in general followed Arrhenius type of behavior and its ionic conductivity is predominantly governed by the ionic charge carriers. Structural studies revealed that the complexation of biopolymer with dispersoids (salts) decreases the crystallinity of biopolymer matrix and consequently enhances the amorphous region and hence conductivity increases drastically. These biopolymer-salt complexed systems possess high conductivity values (10^{-3} to 10^{-4} S/cm) which further affirm that biopolymer electrolyte could be a novel alternative in developing highly efficient DSSC and battery and help the scientific community to keep the environment clean and ecofriendly.

Acknowledgments

The authors are thankful to the Scientists/researchers on sabbatical leave, 2221 support program of the Scientific and Technological Research Council of Turkey, TUBITAK, Department of Science & Technology project (DST/TSG/PT/2012/51-C) government of India and National Research Foundation under the Ministry of Science, ICT & Future Planning, Korea (2011-0031570).

References

- [1] MacCallum JR, Vincent CA. Polymer Electrolyte Reviews. Elsevier: London; 1987 and 1989. 1 and 2.
- [2] Gray FM, editor. Solid Polymer Electrolytes: Fundamentals and Technological Applications. New York: VCH Publishers; 1991.
- [3] Kato Y, Hori S, Saito T, Suzuki K, Hirayama M, Mitsui A, Yonemura M, Iba H, Kanno R. High-power all-solid-state batteries using sulfide superionic conductors. Nat Energy 2016;1:16030.
- [4] Xue Z, He D, Xie X. Poly(ethylene oxide)-based electrolytes for lithium-ion batteries. J Mater. Chem. A 2015;3:19218.
- [5] Steinbuchel A. Biopolymers, general aspects and special applications. Weinheim: Wiley-VCH; 2003. p. 10.
- [6] Chandra R, Rustgi R. Biodegradable polymers. Prog Polym Sci 1998;23(7):1273–335.
- [7] Özdemir C, Güner A. Solubility profiles of poly (ethylene glycol)/solvent systems, I: Qualitative comparison of solubility parameter approaches. Eur Polym J 2007;43(7):3068–93.
- [8] Amelia RPD, Tomic JC, Nirode WF. The determination of the solubility parameter (δ) and the Mark-Houwink constants (K & α) of food grade Polyvinyl Acetate (PVAc). J Polym Biopolym Phys Chem 2014;2(4):67–72.
- [9] Lenz RW. Biodegradable polymer. Adv Polym Sci 1993;107:1–40.
- [10] Stephen AM, Phillips GO, Williams PA. Food Polysaccharides and their Applications. Second Edition. Taylor & Francis Group LLC; 2006.
- [11] Finkenstadt VL. Natural polysaccharides as electroactive polymers. Appl Microbiol Biotechnol 2005;67:735–45.
- [12] Smalley RE. Future global energy prosperity: the terawatt challenge. MRS Bull 2005;30:412–7.
- [13] Dumitriu S. Polysaccharides: structural diversity and functional versatility ed. New York City: Marcel Dekker, Inc.; 1998.
- [14] Rees DA. Polysaccharide shapes, outline studies in biology. Netherlands: Springer; 1977.
- [15] Habibi Y, Lucia LA. Polysaccharide building blocks: a sustainable approach to the development of renewable biomaterials. United States: John Wiley and Sons Ltd; 2012. p. 430.
- [16] Finkenstadt VL, Willett JL. Preparation and characterization of electroactive biopolymers. Macromol. Symp 2005;227(1):367–72.

- [17] Finkenstadt VL, Willett JL. Electroactive materials composed of starch. *J Polym Environ* 2004;12(2):43–6.
- [18] Nijenhuis K. Thermoreversible networks – viscoelastic properties and structure of gels. *Adv Polym Sci* 1997;130:194–202.
- [19] Campo VI, Kawano DF, Braz da Silva Jr D, Carvalho I. Carrageenan: biological properties, chemical modifications and structural analysis – a review. *Carbohydr Polym* 2009;77:167–80.
- [20] Augst AD, Kong HJ, Mooney DJ. Alginate hydrogels as biomaterials. *Macromol Biosci* 2006;6:623–33.
- [21] Kalia S, Kaith BS, Kaur I. Cellulose fibers: bio- and nano-polymer composites. green chemistry and technology. Berlin Heidelberg: Springer; 2011.
- [22] Le CD, Bras J, Dufresne A. Starch nanoparticles: a review. *Biomacromolecules* 2010;11:1139–53.
- [23] Ali BH, Ziada A, Blunden G. Biological effects of gum arabic: a review of some recent research. *Food Chem Toxicol* 2009;47:1–8.
- [24] Rinaudo M. Chitin and chitosan: properties and applications. *Prog Polym Sci* 2006;31:603–32.
- [25] Ohno H, editor. *Electrochemical Aspects of Ionic Liquids*. New Jersey: VCH-interscience; 2005.
- [26] Sequeira C, Santos D. *Polymer electrolytes fundamentals and applications*. Cambridge: Woodhead Publishing Limited; 2010.
- [27] Zhang C, Gamble S, Ainsworth D, Slawin AMZ, Andreev YG, Bruce PG. Alkali metal crystalline polymer electrolytes. *Nat Mater* 2009;8:580–4.
- [28] Wang Y, Chen KS, Mishler J, Cho SC, Adroher XC. A review of polymer electrolyte membrane fuel cells: technology, applications, and needs on fundamental research. *Appl Energy* 2011;88(4):981–1007.
- [29] Stephan AM. Review on gel polymer electrolytes for lithium batteries. *Eur Polym J* 2006;42(1):21–42.
- [30] Fonseca CP, Rosa DS, Gaborardi FA, Neves S. Development of a biodegradable polymer electrolyte for rechargeable batteries. *J Power Sources* 2006;155:381–4.
- [31] Tarascon JM, Armand M. Issues and challenges facing rechargeable lithium batteries. *Nature* 2001;414:359–67.
- [32] Ozer S, Javorniczky J, Angell CA. Polymer electrolyte photoelectrochemical cells with involatile plasticizers: I. The n Si / I⁻ / I₂ cell batteries and energy conversion. *J Electrochem Soc* 2002;149:A87.
- [33] Grätzel M. Dye-sensitized solar cells. *J Photochem Photobiol C: Photochem Rev* 2003;4:145.
- [34] Bhattacharya B, Upadhyaya HM, Chandra S. Photoelectrochemical studies of an ion conducting polymer (PEO)/semiconductor (Si) junction. *Solid State Commun* 1996;98:633.
- [35] Gerischer H, Gobrecht J. On the power characteristics of electrochemical solar cells. *Ber Bunsenges Phys Chem* 1976;80:327.
- [36] Skotheim TA, Inganas O. Polymer solid electrolyte photoelectrochemical cells with n-si-polypyrrole photoelectrodes. *J Electrochem Soc* 1985;132:2116.
- [37] Ellis AB, Kaiser SW, Wrighton MS. Visible light to electrical energy conversion. Stable cadmium sulfide and cadmium selenide photoelectrodes in aqueous electrolytes. *J Am Chem Soc* 1976;98:1635.
- [38] Skotheim TA. Tandem photovoltaic cell using a thinfilm polymer electrolyte. *Appl Phys Lett* 1981;38:712.
- [39] Meyer GJ. The 2010 millennium technology grand prize: dye-sensitized solar cells. *ACS Nano* 2010;4:4337–43.
- [40] Robertson N. Optimizing dyes for dye-sensitized solar cells. *Angew Chem Int Ed Engl* 2006;45:2338–45.
- [41] Yella A, Lee HW, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK, et al. Porphyrin-sensitized solar cells with cobalt (II/III)-Based redox electrolyte exceed 12% efficiency. *Science* 2011;334:629–34.
- [42] Grätzel M. Perspectives for dye-sensitized nanocrystalline solar cells. *Prog Photovolt Res Appl* 2000;8:171.
- [43] Hagfeldt A, Grätzel M. Molecular photovoltaics. *Acc Chem Res* 2000;33:269.
- [44] Toyoda T, Sano T, Nakajima J, Doi S, Fukumoto S, Ito A, et al. Outdoor performance of large scale DSC modules. *J Photochem Photobiol A: Chem* 2004;164:203.
- [45] Li B, Wang L, Kang B, Wang P, Qiu Y. Review of recent progress in solid-state dye-sensitized solar cells. *Sol Energy Mater Sol Cells* 2006;90:549.
- [46] O'Regan B, Grätzel M. A low-cost, high-efficiency solar-cell based on dye-sensitized colloidal TiO₂ films. *Nature* 1991;353:737–40.
- [47] Grätzel M. Photoelectrochemical cells. *Nature* 2001;414:338–44.
- [48] Hardin BE, Snaith HJ, McGehee MD. Renaissance of dye-sensitized solar cells. *Nat Photon* 2012;6:162.
- [49] Narsaiiah EL, Reddy MJ, Rao UVS. Study of a new polymer electrolyte (PVP+KYF₄) for solid-state electrochemical cells. *J Power Sources* 1995;55:255.
- [50] Yohannes T, Iganas O. Photoelectrochemical studies of the junction between poly[3-(4-octylphenyl)thiophene] and a redox polymer electrolyte. *Sol Energy Mater Sol Cells* 1998;51:193.
- [51] Jung YS, Sathiyaraj PAR, Lim MK, Lee SY, Kim KJ. Influence of amylopectin in dimethylsulfoxide on the improved performance of dye-sensitized solar cells. *J Photochem Photobiol A: Chem* 2010;209:174–80.
- [52] Mathew S, Yella A, Gao P, Humphry BR, Curchod BFE, Astani NA, et al. Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. *Nat Chem* 2014;6:242–7.
- [53] Bai Y, Cao Y, Zhang J, Wang M, Li R, Wang P, et al. High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts. *Nat Mater* 2008;7:626–30.
- [54] Grätzel M. Recent advances in sensitized mesoscopic solar cells. *Acc Chem Res* 2009;42:1788–98.
- [55] Longo C, De Paoli MA. Dye-sensitized solar cells: a successful combination of materials. *J Braz Chem Soc* 2003;14:889.
- [56] Kim YJ, Kim JH, Kang MS, Lee MJ, Won J, Lee JC, et al. Supramolecular electrolytes for use in highly efficient dye-sensitized solar cells. *Adv Mater* 2004;16:1753.
- [57] Kim JH, Kang MS, Kim YJ, Won J, Park NG, Kang YS. Dye-sensitized nanocrystalline solar cells based on composite polymer electrolytes containing fumed silica nanoparticles. *Chem Commun* 2004:1662–3.
- [58] Kang MS, Kim JH, Kim YJ, Won J, Park NG, Kang YS. Dye-sensitized solar cells based on composite solid polymer electrolytes. *Chem Commun* 2005:889.
- [59] Kang MS, Kim JH, Won J, Kang YS. Oligomer approaches for solid-state dye-sensitized solar cells employing polymer electrolytes. *J Phys Chem* 2007:111–5222.
- [60] Kang MS, Kim JH, Won J, Kang YS. Dye-sensitized solar cells based on crosslinked poly(ethylene glycol) electrolytes. *J Photochem Photobiol A: Chem* 2006;183:15.
- [61] Kang MS, Ahn KS, Lee JW, Kang YS. Dye-sensitized solar cells employing non-volatile electrolytes based on oligomer solvent. *J Photochem Photobiol A: Chem* 2008;195:198.
- [62] Ren Y, Zhang Z, Fang S, Yang M, Cai S. Application of PEO based gel network polymer electrolytes in dye-sensitized photoelectrochemical cells. *Sol Energy Mater Sol Cells* 2002;71:253.
- [63] Akhtar MS, Chun JM, Yang OB. Advanced composite gel electrolytes prepared with titania nanotube fillers in polyethylene glycol for the solid-state dye-sensitized solar cell. *Electrochim Commun* 2007;9:2833.
- [64] Akhtar MS, Cheralathan KK, Chun JM, Yang OB. Composite electrolyte of heteropolyacid (HPA) and polyethylene oxide (PEO) for solid-state dye-sensitized solar cell. *Electrochim Acta* 2008;53:6623.
- [65] Nogueira AF, Vante NA, De Paoli MA. Solid-state photoelectrochemical device using poly (o-methoxy aniline) as sensitizer and an ionic conductive elastomer as electrolyte. *Synth Met* 1999;105:23.
- [66] Nogueira AF, Durrant JR, De Paoli MA. Dye-sensitized nanocrystalline solar cells employing a polymer electrolyte. *Adv Mater* 2001;13:826.
- [67] Nogueira AF, De Paoli MA, Montanari I, Monkhouse R, Nelson J, Durrant JR. Electron transfer dynamics in dye sensitized nanocrystalline solar cells using a polymer electrolyte. *J Phys Chem B* 2001;105:7517.
- [68] Nogueira AF, Spinace MAS, Gazotti WA, Girotto EM, De Paoli MA. Poly (ethylene oxide-co-epichlorohydrin)/NaI: a promising polymer electrolyte for photoelectrochemical cells. *Solid State Ion* 2001;140:327.
- [69] Kim JH, Kang MS, Kim YJ, Won J, Kang YS. Poly(butyl acrylate)/NaI/I₂ electrolytes for dye-sensitized nanocrystalline TiO₂ solar cells. *Solid State Ion* 2005;176:579.
- [70] Kalaigan GP, Kang MS, Kang YS. Effects of compositions on properties of PEO-KI-I₂ salts polymer electrolytes for DSSC. *Solid State Ion* 2006;177:1091.
- [71] Katsaros G, Stergiopoulos T, Arabatzis IM, Papadokostaki KG, Falaras P. A solvent-free composite polymer/inorganic oxide electrolyte for high efficiency solid-state dye-sensitized solar cells. *J Photochem Photobiol A: Chem* 2002;149:191.
- [72] Chatzivasiloglou E, Stergiopoulos T, Spyrellis N, Falaras P. Solid-state sensitized solar cells, using [Ru(dcbpyH₂)₂Cl₂] · 2H₂O as the dye and PEO/titania/I⁻/I₂⁻ as the redox electrolyte. *J Mater Process Technol* 2005;161:234.
- [73] Stergiopoulos T, Arabatzis IM, Katsaros G, Falaras P. Binary polyethylene oxide/titania solid-state redox electrolyte for highly efficient nanocrystalline TiO₂ photoelectrochemical cells. *Nano Lett* 2002;2:1259.
- [74] Nogueira AF, Longo C, De Paoli MA. Polymers in dye sensitized solar cells: overview and perspectives. *Coord Chem Rev* 2004;248:1455.
- [75] Chen Z, Tang Y, Yang H, Xia Y, Li F, Yi T, Huang C. Nanocrystalline TiO₂ film with textural channels: exhibiting enhanced performance in quasi-solid/solid-state dye-sensitized solar cells. *J Power Sources* 2007;171:990.
- [76] Haque SA, Palomares E, Upadhyaya HM, Otlej L, Potter RJ, Holmes AB, et al. Flexible dye sensitised nanocrystalline semiconductor solar cells. *Chem Commun* 2003;3008.
- [77] Anandan S, Pitchumani S, Muthuraaman B, Maruthamuthu P. Heteropolyacid-impregnated PVDF as a solid polymer electrolyte for dye-sensitized solar cells. *Sol Energy Mater Sol Cells* 2006;90:1715.
- [78] Anandan S, Sivakumar R, Tharani P. Solid-state dye-sensitized solar cells constructed with an electrochromic impregnated elastomeric electrolyte. *Synth Metals* 2008;158:1067.
- [79] Ganesan S, Muthuraaman B, Mathew V, Madhavan J, Maruthamuthu P, Suthanthiraraj SA. Performance of a new polymer electrolyte incorporated with diphenylamine in nanocrystalline dye-sensitized solar cell. *Sol Energy Mater Sol Cells* 2008;92:1718.
- [80] Ganesan S, Muthuraaman B, Madhavan J, Mathew V, Maruthamuthu P, Suthanthiraraj SA. The use of 2,6-bis (N-pyrazolyl) pyridine as an efficient dopant in conjugation with poly(ethylene oxide) for nanocrystalline dye-sensitized solar cells. *Electrochim Acta* 2008;53:7903.
- [81] Freitas JN, Gonçalves AS, De Paoli MA, Durrant JR, Nogueira AF. The role of gel electrolyte composition in the kinetics and performance of dye-sensitized solar cells. *Electrochim Acta* 2008;53:7166.
- [82] Freitas JN, Nogueira AF, De Paoli MA. New insights into dye-sensitized solar cells with polymer electrolytes. *J Mater Chem* 2009;19:5279.
- [83] Flores IC, Freitas JN, Longo C, De Paoli MA, Winnischofer H, Nogueira AF. Dye-sensitized solar cells based on TiO₂ nanotubes and a solid-state electrolyte. *J Photochem Photobiol A: Chem* 2007;189:153.

- [84] Freitas JN, Longo C, Nogueira AF, De Paoli MA. Solar module using dye-sensitized solar cells with a polymer electrolyte. *Sol Energy Mater Sol Cells* 2008;92:1110.
- [85] Benedetti JE, De Paoli MA, Nogueira AF. Enhancement of photocurrent generation and open circuit voltage in dye-sensitized solar cells using Li⁺ trapping species in the gel electrolyte. *Chem Commun* 2008;1121.
- [86] Kang J, Li W, Wang X, Lin Y, Xiao X, Fang S. Polymer electrolytes from PEO and novel quaternary ammonium iodides for dye-sensitized solar cells. *Electrochim Acta* 2003;48:2487.
- [87] Han H, Liu W, Zhang J, Zhao XZ. A Hybrid Poly(ethylene oxide)/ Poly(vinylidene fluoride)/TiO₂ nanoparticle solid-state redox electrolyte for dye-sensitized nanocrystalline solar cells. *Adv Funct Mater* 2005;15:1940.
- [88] Zhang J, Han H, Wu S, Xu S, Yang Y, Zhou C, et al. Conductive carbon nanoparticles hybrid PEO/P(VDF-HFP)/SiO₂ nanocomposite polymer electrolyte type dye sensitized solar cells. *Solid State Ion* 2007;178:1595.
- [89] Zhang J, Han H, Wu S, Xu S, Zhou C, Yang Y, et al. Ultrasonic irradiation to modify the PEO/P(VDF-HFP)/TiO₂ nanoparticle composite polymer electrolyte for dye sensitized solar cells. *Nanotechnology* 2007;18:295606.
- [90] Ieperuma OA, Dissanayake MAK, Somasunderam S, Bandara LRAK. Photo-electrochemical solar cells with polyacrylonitrile-based and polyethylene oxide-based polymer electrolytes. *Sol Energy Mater Sol Cells* 2004;84:117.
- [91] Kumar M, Sekhon SS. Role of plasticizer's dielectric constant on conductivity modification of PEO-NH₄F polymer electrolytes. *Eur Polym J* 2002;38:1297.
- [92] Croce F, Appetecchi GB, Persi L, Scrosati B. Nanocomposite polymer electrolytes for lithium batteries. *Nature* 1998;394:456.
- [93] Preechatiwong W, Schultz JM. Electrical conductivity of poly(ethylene oxide)—alkali metal salt systems and effects of mixed salts and mixed molecular weights. *Polymer* 1996;37:5109.
- [94] Wang GX, Yang L, Wang JZ, Liu HK, Dou SX. Enhancement of ionic conductivity of PEO based polymer electrolyte by the addition of nanosize ceramic powders. *J Nanosci Nanotechnol* 2005;5:1135.
- [95] Yang Y, Zhou C, Xu S, Hu H, Chen B, Zhang J, et al. Improved stability of quasi-solid-state dye-sensitized solar cell based on poly (ethylene oxide)—poly (vinylidene fluoride) polymer-blend electrolytes. *J Power Sources* 2008;185:1492.
- [96] Gorlov M, Kloo L. Ionic liquid electrolytes for dye-sensitized solar cells. *Dalton Trans* 2008;2655.
- [97] Iwakia YO, Hernandez Escalona M, Briones JR, Pawlicka A. Sodium Alginate-Based Ionic Conducting Membranes. *Molecular Crystals and Liquid Crystals*.
- [98] Chandra S. Superionic solids: principles and applications. *Acta Cryst* 1982; A38:878.
- [99] Agrawal RC, Pandey GP. Solid polymer electrolytes: materials designing and all-solid-state battery applications: an overview. *J Phys D: Appl Phys* 2008;41:223001.
- [100] Agrawal RC, Gupta RK. Superionic solid: composite electrolyte phase—an overview. *J Mater Sci* 1999;34(6):1131–62.
- [101] Singh R, Jadhav NA, Majumder S, Bhattacharya B, Singh PK. Novel biopolymer gel electrolyte for dye-sensitized solar cell application. *Carbohydr Polym* 2013;91:682–5.
- [102] Weijia W, Xueyi G, Ying Y. Lithium iodide effect on the electrochemical behavior of agarose based polymer electrolyte for dye-sensitized solar cell. *Electrochim Acta* 2011;56:7347–51.
- [103] Siti SA, Ahmad AM. Effect of NH₄I and I₂ concentration on Agar gel polymer electrolyte properties for a Dye-Sensitized Solar Cell. *Ionics* 2013;19:1185–94.
- [104] Jeremy CHK, Zainal AA, Ahmad AM. Bacto agar-based gel polymer electrolyte. *Ionics* 2012;18(4):359–64.
- [105] Hsu HL, Tien CF, Yang YT, Leu J. Dye-sensitized solar cells based on agarose gel electrolytes using allylimidazolium iodides and environmentally benign solvents. *Electrochim Acta* 2013;91:208–13.
- [106] Hsu HL, Tien CF, Leu J. Effect of pore size/distribution in TiO₂ films on Agarose gel electrolyte-based Dye-Sensitized Solar Cells. *J Solid State Electrochem* 2014;18:1665–71.
- [107] Hsu HL, Hsu WT, Leu J. Effects of environmentally benign solvents in the Agarose gel electrolytes on Dye-Sensitized Solar Cells. *Electrochim Acta* 2011;56:5904–9.
- [108] Guo X, Yi P, Yang Y, Cui J, Xiao S, Wang W. Effects of surfactants on agarose-based magnetic polymer electrolyte for dye-sensitized solar cells. *Electrochim Acta* 2013;90:524–9.
- [109] Guo XY, Yi PF, Wang WJ, Xiao S, Yang Y. Effects of polyethylene glycol on agarose-based magnetic polymer electrolyte for dye-sensitized solar cell. *Adv Mater Res* 2013;860:652–4.
- [110] Yang Y, Cui J, Yi P, Zheng X, Guo X, Wang W. Effects of nanoparticle additives on the properties of agarose polymer electrolytes. *J Power Sources* 2014;248:988–93.
- [111] Yang Y, Guo XY, Zhao XZ. Influence of polymer concentration on Polysaccharide electrolyte for quasi-Solid-State Dye-Sensitized Solar Cell. *Mater Sci Forum* 2011;685:76–81.
- [112] Yang Y, Hu H, Zhou CH, Xu S, Sebo B, Zhao XZ. Novel agarose polymer electrolyte for quasi-solid state dye-sensitized solar cell. *J Power Sources* 2011;196:2410–5.
- [113] Suzuki K, Yamaguchi M, Kumagai M, Tanabe N, Yanagida S. Dye-sensitized solar cells with ionic gel electrolytes prepared from imidazolium salts and agarose. *Comptes Rendus Chim* 2006;9(5–6):611–6.
- [114] Raphael E, Avellaneda CO, Manzolli B, Pawlicka A. Agar-based films for application as polymer electrolytes. *Electrochim Acta* 2010;55:1455–9.
- [115] Leones R, Santanin F, Rodrigues LC, Marrucho IM, Esperança JMSS, Pawlicka A, et al. Investigation of polymer electrolytes based on agar and ionic liquids. *eXPRESS Polym Lett* 2012;6(12):1007–16.
- [116] Nemoto J, Sakata M, Hoshi T, Ueno H, Kaneko M. All plastic Dye-Sensitized Solar Cell using a Polysaccharide film containing excess redox electrolyte solution. *J Electroanal Chem* 2007;599:23–30.
- [117] Masao K, Takayuki H, Yuuki K, Hirohito U. Solid type dye-sensitized solar cell using polysaccharide containing redox electrolyte solution. *J Electroanal Chem* 2004;572:21–7.
- [118] Shuhaimi NEA, Alias NA, Majid SR, Arof AK. Electrical double layer capacitor with proton conducting K-Carrageenan–Chitosan electrolytes. *Funct Mater Lett* 2008;01(03):195–201.
- [119] Arof AK, Shuhaimi NEA, Alias NA, Kufian MZ, Majid SR. Application of chitosan/iota-carrageenan polymer electrolytes in electrical double layer capacitor (EDLC). *J Solid State Electrochem* 2010;14(12):2145–52.
- [120] Shuhaimi NEA, Teo LP, Majid SR, Arof AK. Transport studies of NH₄NO₃ doped methyl cellulose electrolyte. *Synth Metals* 2010;160(9–10):1040–4.
- [121] Shuhaimi NEA, Alias NA, Kufian MZ, Majid SR, Arof AK. Characteristics of methyl cellulose-NH₄NO₃-PEG electrolyte and application in fuel cells. *J Solid State Electrochem* 2010;14(12):2153–9.
- [122] Abidin SZZ, Ali AMM, Hassan OH, Yahya MZA. Electrochemical studies on cellulose acetate-LiBOB polymer gel electrolytes. *Int J Electrochem Sci* 2013;8:7320–6.
- [123] Johari NA, Kudin TIT, Ali AMM, Yahya MZA. Electrochemical studies of composite Cellulose Acetate-based polymer gel electrolytes for proton batteries. *Proc Natl Acad Sci Sect A: Phys Sci* 2012;82(1):49–52.
- [124] Saaid SIY, Kudin TIT, Ali AMM, Ahmad AH, Yahya MZA. Solid state proton battery using plasticised cellulose-salt complex electrolyte. *Mater Res Innov* 2009;13(3):252–4.
- [125] Johari NA, Kudin TIT, Ali AMM, Winie T, Yahya MZA. Studies on cellulose acetate-based gel polymer electrolytes for proton batteries. *Mater Res Innov* 2009;13(3):232–4.
- [126] Chelmecki M, Meyer WH, Wegner G. Effect of crosslinking on polymer electrolytes based on cellulose. *J Appl Polym Sci* 2007;105(1):25–9.
- [127] Jafirin S, Ahmadl, Ahamad A. Potential use of cellulose from keaf in polymer electrolyte based on MG49 Rubber composites. *Bioresources* 2013;8(4):5947–64.
- [128] Ramesh S, Shanti R, Morris Ezra. Employment of [Amim] Cl in the effort to upgrade the properties of cellulose acetate based polymer electrolytes. *Cellulose* 2013;20(3):1377–89.
- [129] Harun NI, Ali RM, Ali AMM, Yahya MZA. Dielectric behaviour of cellulose acetate-based polymer electrolytes. *Ionics* 2012;18(6):599–606.
- [130] Ramesh S, Shanti R, Morris Ezra. Discussion on the influence of DES content in CA-based polymer electrolytes. *J Mater Sci* 2012;47(4):1787–93.
- [131] Salvi DTBD, Barud HS, Pawlicka A, Mattos RI, Raphael E, Messaddeq Y, Ribeiro SJL. Bacterial cellulose/triethanolamine based ion-conducting membranes. *Cellulose* 2014;21:1975–85.
- [132] Mishra RK, Anis A, Mondal S, Dutt M, Banthia AK. Preparation and characterization of amidated pectin based polymer electrolyte membranes. *Chin J Polym Sci* 2009;27(5):639–46.
- [133] Mishra RK, Datt M, Banthia AK, Majeed ABA. Development of novel pectin based membranes as proton conducting material. *Int J Plast Technol* 2012;16(1):80–8.
- [134] Andrade JR, Raphael E, Pawlicka A. Plasticized pectin-based gel electrolytes. *Electrochim Acta* 2009;54(26):6479–83.
- [135] Leones R, Botelho MBS, Santanin F, Cesarino I, Pawlicka A, Camargo ASS, Silva MM. Pectin-based polymer electrolytes with Ir(III) complexes. *Mol Cryst Liq Cryst* 2014;1:604.
- [136] Singh R, Baghel J, Shukla S, Bhattacharya B, Rhee HW, Singh PK. Detailed electrical measurements on sago starch biopolymer solid electrolyte. *Phase Trans: A Multinatl J* 2014;87(12):1237–45.
- [137] Singh R, Singh PK, Tomar SK, Bhattacharya B. Synthesis, characterization and dye sensitized solar cell fabrication using solid biopolymer electrolyte membranes. *High Perform Polym* 2016;28:47–54.
- [138] Pang SC, Tay CL, Chin SF. Starch-based gel electrolyte thin films derived from native sago (Metroxylon sago) starch. *Ionics* 2014;20(10):1455–62.
- [139] Yusuf YM, Shukur MF, Illias HA, Kadir MFZ. Conductivity and electrical properties of corn starch–chitosan blend biopolymer electrolyte incorporated with ammonium iodide. *Phys Scr* 2014;89:035701.
- [140] Shukur MF, Kadir MFZ. Electrical & transport properties of NH₄Br-Doped Corn starch Based Solid Biopolymer Electrolyte. *Ionics* 2015;21:111–24.
- [141] Liew CW, Ramesh S. Studies on ionic liquid-based corn starch biopolymer electrolytes coupling with high ionic transport number. *Cellulose* 2013;20:3227–37.
- [142] Shukur MF, Ithnin R, Kadir MFZ. Electrical characterization of corn starch-LiOAc electrolytes and application in electrochemical double layer capacitor. *Electrochim Acta* 2014;136:204–16.
- [143] Liew CW, Ramesh S, Ramesh K, Arof AK. Preparation and characterization of lithium ion conducting ionic liquid-based biodegradable corn starch polymer electrolytes. *J Solid State Electrochem* 2012;16(5):1869–75.
- [144] Teoh KH, Lim CS, Ramesh S. Lithium ion conduction in corn starch based solid polymer electrolytes. *Measurement* 2014;48:87–95.
- [145] Ramesh S, Shanti R, Morris E. Studies on the plasticization efficiency of deep eutectic solvent in suppressing the crystallinity of corn starch based polymer electrolytes. *Carbohydr Polym* 2012;87(1):701–6.

- [146] Shukur MF, Ibrahim FM, Majid NA, Ithnin R, Kadir MFZ. Electrical analysis of amorphous corn starch-based polymer electrolyte membranes doped with LiI. *Phys Scr* 2013;88:025601.
- [147] Saxena H, Bhattacharya B, Jadhav NA, Singh VK, Shukla S, Dubey M. Multiwall carbon-nanotube doped ion conducting polymer electrolyte for electrochemical application. *J Exp Nanosci* 2014;9:444–51.
- [148] Ramesh S, Shanti R, Morris Ezra. Studies on the thermal behavior of CS: LiTFSI:[Amim] Cl polymer electrolytes exerted by different [Amim] Cl content. *Solid State Sci* 2012;14(1):182–6.
- [149] Ramesh S, Liew CW, Arof AK. Ion conducting corn starch biopolymer electrolytes doped with ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. *J Non-Cryst Solids* 2011;357(21):3654–60.
- [150] Teoh KH, Ramesh S, Arof AK. Investigation on the effect of nanosilica towards corn starch–lithium perchlorate-based polymer electrolytes. *J Solid State Electrochem* 2012;16(10):3165–70.
- [151] Ahmed J, Tiwari BK, Imam SH, Rao MA. Starch-Based Polperic Materials and Nanocomposites Chemistry, Processing, and Applications. United States: Taylor & Francis Group, CRC Press; 2012.
- [152] Ning W, Xingxiang Z, Haihui L, Benqiao H. 1-Allyl-3-methylimidazolium chloride plasticized-corn starch as solid biopolymer electrolytes. *Carbohydr Polym* 2009;76(3):482–4.
- [153] Ning W, Xingxiang Z, Haihui L, Jianping WN. N-dimethylacetamide/lithium chloride plasticized starch as solid biopolymer electrolytes. *Carbohydr Polym* 2009;77(3):607–11.
- [154] Ma X, Chang PR, Yua J, Lu P. Characterizations of glycerol plasticized-starch (GPS)/carbon black (CB) membranes prepared by melt extrusion and microwave radiation. *Carbohydr Polym* 2008;74(4):895–900.
- [155] Sankri A, Arhaliass A, Dez I, Gaumont AC, Grohens Y, Lourdin D, Pillin I, Rolland SA, Leroy E. Thermoplastic starch plasticized by an ionic liquid. *Carbohydr Polym* 2010;82(2):256–63.
- [156] Yusof YM, Majid NA, Kasmani RM, Illias HA, Kadir MFZ. The effect of plasticization on conductivity and other properties of starch/chitosan blend biopolymer electrolyte incorporated with ammonium iodide. *Mol Cryst Liq Cryst* 2014;603:73–88.
- [157] Ummartyotin Manuspriya S. An overview of feasibility and challenge of conductive cellulose for rechargeable lithium based battery. *Renew Sustain Energy Rev* 2015;50:204–13.
- [158] Khanmirzaei MH, Ramesh S. Studies on biodegradable polymer electrolyte rice starch (RS) complexed with lithium iodide. *Ionics* 2014;20:691–5.
- [159] Khanmirzaei MH, Ramesh S. Ionic transport and FTIR properties of lithium iodide doped biodegradable rice starch based polymer electrolytes. *Int J Electrochem Sci* 2013;8:9977–91.
- [160] Khanmirzaei MH, Ramesh S. Nanocomposite polymer electrolyte based on rice starch/ionic liquid/TiO₂ nanoparticles for solar cell application. *Measurement* 2014;58:68–72.
- [161] Tiwari T, Srivastava N, Srivastava PC. Ion dynamics study of potato starch + sodium salts electrolyte system. *Int J Electrochem* 2013;2013:8.
- [162] Tiwari T, Srivastava N, Srivastava PC. Electrical transport study of potato starch-based electrolyte system. *Ionics* 2011;17:353–60.
- [163] Kumar M, Tiwari T, Srivastava N. Electrical transport behaviour of bio-polymer electrolyte system: potato starch + ammonium iodide. *Carbohydr Polym* 2012;88:54–60.
- [164] Tiwari T, Kumar M, Srivastava N, Srivastava PC. Electrical transport study of potato starch-based electrolyte system-II. *Mater Sci Engg B* 2014;182:6–13.
- [165] Zhao S, Wang CY, Chen MM, Wang J, Shi ZQ. Potato starch-based activated carbon spheres as electrode material for electrochemical capacitor. *J Phys Chem Solids* 2009;70:1256–60.
- [166] Singh R, Bhattacharya B, Rhee HW, Singh PK. New biodegradable polymer electrolyte for dye sensitized solar cell. *Int J Electrochem Sci* 2014;9:2620–30.
- [167] Tiwari T, Pandey K, Srivastava N, Srivastava PC. Effect of glutaraldehyde on electrical properties of arrowroot starch + NaI electrolyte system. *J Appl Polym Sci* 2011;121(1):1–7.
- [168] Khair ASA, Arof AK. Electrical properties of starch/chitosan-NH₄NO₃ polymer electrolyte. *Int J Math, Comput, Phys, Electr Comput Eng* 2011;5(11):1662–7.
- [169] Mallick H, Sarkar A. An experimental investigation of electrical conductivities in biopolymers. *Bull Mater Sci* 2000;23(4):319–24.
- [170] Singh D, Singh PK, Jadhav NA, Bhattacharya B. Electrostatic model of semiconductor nanoparticles trapped in polymer electrolytes. *Bull Mater Sci* 2013;36:977–80.
- [171] Park SJ, Yoo K, Kim JY, Kim JY, Lee DK, Kim B, Kim H, Kim JH, Cho J, Ko MJ. Water-based thixotropic polymer gel electrolyte for dye-sensitized solar cells. *ACS Nano* 2013;7(5):4050–6.
- [172] Noor ISM, Majid SR, Arof AK, Djurado D, Claro Neto S, Pawlicka A. Characteristics of gellan gum–LiCF₃SO₃ polymer electrolytes. *Solid State Ion* 2012;225:649–53.
- [173] Halim NFA, Majid SR, Arof AK, Kajzar F, Pawlicka A. Gellan gum–lii gel polymer electrolytes. *Mol Cryst Liq Cryst* 2012;554:232–8.
- [174] Higgins TM, Moulton SE, Gilmore KJ, Wallace GG, in het Panhuis M. Gellan gum doped polypyrrole neural prosthetic electrode coatings. *Soft Matter* 2011;7(10):4690–5.
- [175] Singh PK, Bhattacharya B, Nagarale RK, Kim KW, Rhee HW. Synthesis, characterization and application of biopolymer-ionic liquid composite membranes. *Synth Metals* 2010;160:139–42.
- [176] Hassan F, Woo HJ, Aziz NA, Kufian MZ, Majid SR. Synthesis of Al₂TiO₅ and its effect on the properties of chitosan–NH₄SCN polymer electrolytes. *Ionics* 2013;19:483–9.
- [177] Mohamed NS, Subban RHY, Arof AK. Polymer batteries fabricated from lithium complexed acetylated chitosan. *J Power Sources* 1995;56:153–6.
- [178] Buraidah MH, Teo LP, Majid SR, Arof AK. Characteristics of TiO₂/solid electrolyte junction solar cells with I[−]/I^{3−} redox couple. *Opt Mater* 2010;32:723–8.
- [179] Buraidah MH, Teo LP, Yusuf SNF, Noor MM, Kufian MZ, Careem MA, Majid SR, Taha RM, Arof AK. TiO₂/chitosan–NH₄(+I₂)–BMII-based dye-sensitized solar cells with anthocyanin dyes extracted from black rice and red cabbage. *Int J Photoenergy* 2011 Article ID 273683, 11 pages.
- [180] Mohamad SA, Yahya R, Ibrahim ZA, Arof AK. Photovoltaic activity in a ZnTe/PEO–chitosan blend electrolyte junction. *Solar Energy Mater Solar Cells* 2007;91(13):1194–8.
- [181] Singh VK, Annu A, Singh U, Singh P, Pandey SP, Bhattacharya B, Singh PK. Dye sensitized solar cell based on poly (vinyl alcohol) doped with ammonium iodide solid polymer electrolyte. *J Optoelectron Adv Mater* 2013;15:927–31.
- [182] Ahmad KAS, Puteh R, Arof AK. Characterizations of chitosan–ammonium triflate (NH₄CF₃SO₃) complexes by FTIR and impedance spectroscopy. *Phys Stat Sol A* 2006;203(3):534–43.
- [183] Hamdan KZ, Khair ASA. Conductivity and Dielectric Studies of Methylcellulose/Chitosan–NH₄CF₃SO₃ Polymer Electrolyte. *Key Eng Mater* 2014;594/595:812.
- [184] Yahya MZA, Arof AK. Conductivity and X-ray photoelectron studies on lithium acetate doped chitosan films. *Carbohydr Polym* 2004;55(1):95–100.
- [185] Yahya MZA, Arof AK. Effect of oleic acid plasticizer on chitosan–lithium acetate solid polymer electrolytes. *Eur Polym J* 2003;39(5):897–902.
- [186] Yahya MZA, Arof AK. Characteristics of chitosan–lithium acetate–palmitic acid complexes. *J New Mater Electrochem Systems* 2002;5:123–8.
- [187] Shukur MF, Ithnin R, Kadir MFZ. Electrical properties of proton conducting solid biopolymer electrolytes based on starch–chitosan blend. *Ionics* 2014;20(7):977–99.
- [188] Majid SR, Arof AK. Proton-conducting polymer electrolyte films based on chitosan acetate complexed with NH₄NO₃ salt. *Phys B: Condens Matter* 2005;355(1–4):78–82.
- [189] Jamaludin A, Mohamad AA. Application of liquid gel polymer electrolyte based on chitosan–NH₄NO₃ for proton batteries. *J Appl Polym Sci* 2010;118(2):1240–3.
- [190] Ng LS, Mohamad AA. Protonic battery based on a plasticized chitosan–NH₄NO₃ solid polymer electrolyte. *J Power Sources* 2006;163(1):382–5.
- [191] Kadir MFZ, Aspanut Z, Yahya R, Arof AK. Chitosan–PEO proton conducting polymer electrolyte membrane doped with NH₄NO₃. *Mater Res Innov* 2011;15:164–7.
- [192] Winie T, Arof AK. Transport properties of hexanoyl chitosan-based gel electrolyte. *Ionics* 2006;12:149–52.
- [193] Bakar NY, Isa MIN. Potential of ionic conductivity and transport properties solid biopolymer electrolytes based carboxy methylcellulose/ chitosan polymer blend doped with dodecyltrimethyl ammonium bromide. *Res J Recent Sci* 2014;3(10):69–74.
- [194] Kadir MFZ, Majid SR, Arof AK. Plasticized chitosan–PVA blend polymer electrolyte based proton battery. *Electrochim Acta* 2010;55(4):1475–82.
- [195] Kadir MFZ, Arof AK. Application of PVA–chitosan blend polymer electrolyte membrane in electrical double layer capacitor. *Mater Res Innov* 2011;15(2):S217–20.
- [196] Buraidah MH, Arof AK. Characterization of chitosan/PVA blended electrolyte doped with NH₄I. *J Non-Cryst Solids* 2011;357(16–17):3261–6.
- [197] Buraidah MH, Teo LP, Majid SR, Yahya R, Taha RM, Arof AK. Characterizations of Chitosan-Based Polymer Electrolyte Photovoltaic Cells. *Int J Photoenergy* 2010 2010: 7 Article ID 805836.
- [198] Tan Winie, Ramesh S, Arof AK. Studies on the structure and transport properties of hexanoyl chitosan-based polymer electrolytes. *Physica B* 2009;404:4308–11.
- [199] Majid SR, Arof AK. Conductivity studies and performance of chitosan based polymer electrolytes in H₂/air fuel cell. *Polym Adv Technol* 2009;20(6):524–8.
- [200] Idris NH, Senin HB, Arof AK. Dielectric spectra of LiTFSI-doped chitosan/PEO blends. *Ionics* 2007;13(4):213–7.
- [201] Tan Winie, Arof AK. Hexanoyl chitosan-based gel electrolyte for use in lithium-ion cell. *Polym Adv Technol* 2006;17(7–8):552–5.
- [202] Yahya MZA, Ali AMM, Mohammad MF, MAKM Hanafiah, Mustafa M, Ibrahim SC, Darus ZM, Harun MK. Ionic conduction model in salted chitosan membranes plasticized with fatty acid. *J Appl Sci* 2006;6:1287–91.
- [203] Nawaz A, Sharif R, Rhee HW, Singh PK. Efficient dye sensitized solar cell and supercapacitor using 1-ethyl 3-methyl imidazolium dicyanamide incorporated PVDF–HFP polymer matrix. *J Ind Eng Chem* 2016;33:381–4.
- [204] Yusof YM, Illias HA, Kadir MFZ. Incorporation of NH₄Br in PVA–chitosan blend-based polymer electrolyte and its effect on the conductivity and other electrical properties. *Ionics* 2014;20:1235–45.
- [205] Rathod SG, Bhajantri RF, Ravindrachary V, Pujari PK, Sheela T. Ionic conductivity and dielectric studies of LiClO₄ doped poly(vinylalcohol)(PVA)/chitosan(CS) composites. *Compos J Adv Dielectr* 2014;4(4):1450033.
- [206] Singh VK, Bhattacharya B, Shukla S, Singh PK. New solid polymer electrolyte material for dye sensitized solar cells. *Mater Tehnol* 2015;49:123–7.
- [207] Ummartyotin S, Manuspiya A. Critical review on cellulose: from fundamental to an approach on sensor technology. *Renew Sustain Energy Rev* 2015;41:402–12.
- [208] Shukur MF, Ithnin R, Kadir MFZ. Protonic transport analysis of starch–chitosan blend based electrolytes and application in electrochemical device. *Mol Cryst. Liq Cryst* 2014;603:52–65.

- [209] Shukur MF, Majid NA, Ithnin R, Kadir MFZ. Effect of plasticization on the conductivity and dielectric properties of starch–chitosan blend biopolymer electrolytes infused with NH_4Br . *Phys Scr* 2013;T157:014051.
- [210] Kamarulzaman N, Osman Z, Muhamad MR, Ibrahim ZA, Arof AK, Mohamed NS. Performance characteristics of LiMn_2O_4 /polymer/carbon electrochemical cells. *J Power Sources* 2001;97–98:722–5.
- [211] Osman Z, Ibrahim ZA, Arof AK. Conductivity enhancement due to ion dissociation in plasticized chitosan based polymer electrolytes. *Carbohydr Polym* 2001;44:167–73.
- [212] Subban RHY, Arof AK, Radhakrishna S. Polymer batteries with chitosan electrolyte mixed with sodium Perchlorate. *Mater Sci Eng B* 1996;38:156–60.
- [213] Samsudin AS, Isa MIN. Structural and ionic transport study on CMC doped NH_4Br : a new types of biopolymer electrolytes. *J Appl Sci* 2012;12:174–9.
- [214] Ramli MA, Isa MIN. Conductivity study of carboxyl methyl cellulose Solid biopolymer electrolytes (SBE) doped with Ammonium. *Fluoride Res J Recent Sci* 2014;3(6):59–66.
- [215] Ahmad Z, Isa MIN. Ionics conduction via correlated barrier hopping mechanism in CMC-SA solid biopolymer electrolytes. *Int J Latest Res Sci Technol* 2012;1(2):70–5.
- [216] Isa MIN, Samsudin AS. Ionic Conduction behavior of CMC based green polymer electrolytes. *Adv Mater Res* 2013;802:194.
- [217] Rani MSA, Siti Rudhiah, Azizan Ahmad, Mohamed NS. Biopolymer electrolyte based on derivatives of cellulose from kenaf bast fiber. *Polymers* 2014;6(9):2371–85.
- [218] Chai MN, Isa MIN. The oleic acid composition effect on the carboxymethyl cellulose based biopolymer electrolyte. *J Cryst Process Technol* 2013;3:1–4.
- [219] Shuhaimi NEA, Teo LP, Majid SR, Arof AK. Transport studies of NH_4NO_3 doped methyl cellulose electrolyte. *Synth Metals* 2010;160(9):1040–4.
- [220] Nik Aziz NA, Idris NK, Isa MIN. Solid Polymer electrolytes based on methyl-cellulose: FT-IR and ionic conductivity studies. *Int J Polym Anal Charact* 2010;15(5):319–27.
- [221] Samsudin AS, Kuan ECH, Isa MIN. Investigation of the potential of proton-conducting biopolymer electrolytes based methyl cellulose-glycolic acid. *Int J Polym Anal Charact* 2011;16(7):477–85.
- [222] Harun NI, Sabri NS, Rosli NHA, Taib MF, Saaid SIY, Kudin TIT, Ali AMM, Yahya MZA. Proton conductivity studies on biopolymer electrolytes. *AIP Conf Proc* 2010;1250:237.
- [223] Xiao SY, Yang YQ, Li MX, Wang FX, Chang Z, Wu YP, Liu X. A composite membrane based on a biocompatible cellulose as a host of gel polymer electrolyte for lithium ion batteries. *J Power Sources* 2014;270:53–8.
- [224] Shuhaimi NEA, Alias NA, Kufian MZ, Majid SR, Arof AK. Characteristics of methyl cellulose- NH_4NO_3 -PEG electrolyte and application in fuel cells. *J Sol State Electrochem* 2010;14(12):2153–9.
- [225] Polu AR, Kim DK, Rhee HW. Poly(ethylene oxide)-lithium difluoro(oxalato) borate new solid polymer electrolytes: ion–polymer interaction, structural, thermal, and ionic conductivity studies. *Ionics* 2015;21:2771–80.
- [226] Polu AR, Kumar R. Mg^{2+} -ion Conducting PEG- TiO_2 Composite Polymer Electrolytes for Solid-State Batteries. *Mater Express* 2014;4:79–84.
- [227] Dygas JR, Misztal-Faraj B, Florjanczyk Z, Krok F, Marzantowicz M, Zygadlo-Monikowska E. Effects of inhomogeneity on ionic conductivity and relaxations in PEO and PEO–salt complexes. *J Solid State Ion* 2003;157:249–56.
- [228] Kovac M, Gaberscek M, Gradadonik J. The effect of plasticizer on the microstructural and electrochemical properties of a $(\text{PEO})_n\text{LiAl}(\text{SO}_3\text{Cl})_4$ system. *Electrochim Acta* 1998;44:863–8.
- [229] Armand MB, Chabagno JM, Duclot MJ. In: Vashista P, Shenoy GK, editors. Fast ion transport in solids. North Holland; Elsevier; 1979. p. 131.
- [230] Berthier C, Gorecki W, Minier M, Armand MB, Chanbagnon JM, Rigaud P. Microscopic investigation of ionic conductivity in alkali metal salts-poly(ethylene oxide) adducts. *Solid State Ion* 1983;11:91–8.
- [231] Machado GO, Ferreira HCA, Pawlicka A. Influence of plasticizer contents on the properties of HEC based solid polymeric electrolytes. *Electrochim Acta* 2005;50:3827–31.
- [232] Mattos RI, Tambelli C, Donoso JP, Pawlicka A. NMR study of starch based polymer gel electrolytes: humidity effects. *Electrochim Acta* 2007;53:1461–8.
- [233] Pawlicka A, Danczuk M, Wieczorek W, Zygadlo-Monikowska E. Influence of plasticizer type on the properties of polymer electrolytes based on chitosan. *J Phys Chem A* 2008;112:8888–96.
- [234] Shuhaimi NEA, Alias NA, Majid SR, Arof AK. Electrical double layer capacitor with proton conducting k-carrageenan-chitosan-electrolytes. *Funct Mater Lett* 2008;1(3):195–201.
- [235] Idris NH, Majid SR, Khair ASA, Hassan MF, Arof AK. Conductivity studies on chitosan/PEO blends with LITFSI salt. *Ionics* 2005;11:375–7.
- [236] Fuentes S, Retuert J, Gonzalez G. Transparent conducting polymer electrolyte by addition of lithium to the molecular complex chitosane–poly(aminopropyl siloxane). *Electrochim Acta* 2003;48:2015–21.
- [237] Morni NM, Arof AK. Chitosan lithium triflate electrolyte in secondary lithium cells. *J Power Sources* 1999;77(1):42–8.
- [238] Yahya MZA, Arof AK. Effect of oleic acid plasticizer on chitosan lithium acetate solid polymer electrolytes. *Eur Polym J* 2003;39(5):897–902.
- [239] Klemm D, Heublein B, Fink H-P, Bohn A. Cellulose: fascinating biopolymer and sustainable raw material. *Angew Chem Int Ed* 2005;44:3358–93.
- [240] Klemm D, Kramer F, Moritz S, Lindström T, Ankerfors M, Gray D, Dorris A. Nanocelluloses: a new family of nature-based materials. *Angew Chem Int Ed* 2011;50:5438–66.
- [241] Jabbour L, Bongiovanni R, Chaussy D, Gerbaldi C, Beneventi D. Cellulose-based Li-ion batteries: a review. *Cellulose* 2013;20(4):1523–45.
- [242] Samsudin AS, Lai HM, Isa MIN. Biopolymer materials based carboxymethyl cellulose as a proton conducting biopolymer electrolyte for application in rechargeable proton battery. *Electrochim Acta* 2014;129:1–13.
- [243] Rani MSA, Rudhiah S, Ahmad A, Mohamed NS. Biopolymer electrolyte based on derivatives of cellulose from kenaf bast fiber. *Polymers* 2014;6:2371–85.
- [244] Ramesh S, Shanti R, Morris E. Plasticizing effect of 1-allyl-3-methylimidazolium chloride in cellulose acetate based polymer electrolytes. *Carbohydr Polym* 2012;87:2624–9.
- [245] Jabbour L. Elaboration of Li-ion batteries using cellulose fibers and paper making techniques. Docteur De L'Université De Grenoble. 2012; (<http://www.theses.fr/2012GREN1043.pdf>).
- [246] Nair JR, Gerbaldi C, Chiappone A, et al. UV-cured polymer electrolyte membranes for Li-cells: improved mechanical properties by a novel cellulose reinforcement. *Electrochim Commun* 2009;11:1796–8.
- [247] Nair JR, Chiappone A, Gerbaldi C, et al. Novel cellulose reinforcement for polymer electrolyte membranes with outstanding mechanical properties. *Electrochim Acta* 2009;57:104–11.
- [248] Wang CG, Yuan WN, Lu NQ. Studies on preparation and properties of novel gel. *Polym Electrolyte Adv Mater Res* 2010;123–125:226–30.
- [249] Azizi SMAS, Alloin F, Dufresne A. High performance nanocomposite polymer electrolytes. *Compos Interface* 2006;13:545–59.
- [250] Azizi SMAS, Alloin F, Sanchez JY, Dufresne A. Cross-linked nanocomposite polymer electrolytes reinforced with cellulose whiskers. *Macromolecules* 2004;37:4839–44.
- [251] SMAS Azizi, Chazeau L, Alloin F, et al. POE-based nanocomposite polymer electrolytes reinforced with cellulose whiskers. *Electrochim Acta* 2005;50:3897–903.
- [252] Schroers M, Kokil A, Weder C. Solid polymer electrolytes based on nanocomposites of ethylene oxide–epichlorohydrin copolymers and cellulose whiskers. *J Appl Polym Sci* 2004;93:2883–8.
- [253] Alloin F, D'Apré A, Kissi NE, et al. Nanocomposite polymer electrolyte based on whisker or microfibrils polyoxyethylene nanocomposites. *Electrochim Acta* 2010;55:5186–94.
- [254] Chiappone A. Ligno-cellulosic materials for energy storage. Politecnico di Torino; 2011. (<http://porto.polito.it/2496830>).
- [255] Chelmecki M, Meyer WH, Wegner G. Effect of crosslinking on polymer electrolytes based on cellulose. *J Appl Polym Sci* 2007;105:25–9.
- [256] Lee JM, Nguyen DQ, Lee SB, et al. Cellulose triacetatebased polymer gel electrolytes. *J Appl Polym Sci* 2010;115:32–6.
- [257] Machado GO, Ferreira HCA, Pawlicka A. Influence of plasticizer contents on the properties of HEC-based solid polymeric electrolytes. *Electrochim Acta* 2005;50:3827–31.
- [258] Paracha RN, Ray S, Eastale AJ. Grafting of LiAMPS on ethyl cellulose: a route to the fabrication of superior quality polyelectrolyte gels for rechargeable Lithium ion batteries. *J Mater Sci* 2012;47:3698–705.
- [259] Ramesh S, Shanti R, Morris E. Plasticizing effect of 1-allyl-3-methylimidazolium chloride in cellulose acetate based polymer electrolytes. *Carbohydr Polym* 2012;87:2624–9.
- [260] Ko YG, Khasabaatar AD, Choi US, Kim J-Y. Molecular interaction mechanism in solid polymer electrolyte comprising cellulose phthalate and LiClO_4 . *Solid State Ion* 2010;181:1178–82.
- [261] Sato T, Banno K, Maruo T, Nozu R. New design for a safe lithium-ion gel polymer battery. *J Power Sources* 2005;152:264–71.
- [262] Ren Z, Liu Y, Sun K, et al. A microporous gel electrolyte based on poly(vinylidene fluoride-co-hexafluoropropylene)/fully cyanoethylated cellulose derivative blend for lithiumion battery. *Electrochim Acta* 2009;54:1888–92.
- [263] Yue Z, McEwen I, Cowie JM. Novel gel polymer electrolytes based on a cellulose ester with PEO side chains. *Solid State Ion* 2003;156:155–62.
- [264] Regiani AM, de Oliveira Machado G, LeNest J-F, et al. Cellulose derivatives as solid electrolyte matrixes. *Macromol Symp* 2001;175:45–54.
- [265] RFMS Marcondes, D'Agostini PS, Ferreira J, Giotto EM, Pawlicka A, Dragunski DC. *Solid State Ion* 2010;181:586–91.
- [266] Lopes LVS, Dragunski DC, Pawlicka A, Donoso JP. Nuclear magnetic resonance and conductivity study of starch based polymer electrolytes. *Electrochim Acta* 2003;48:2021–7.
- [267] Navaratnam S, Ramesh K, Ramesh S, Sanusi A, Basirun WJ, Arof AK. Transport mechanism studies of chitosan electrolyte systems. *Electrochim Acta* 2015;175:68–73.
- [268] Alias SS, Ariff ZM, Mohamad AA. Porous membrane based on chitosan- SiO_2 for coin cell proton battery. *Ceram Int* 2015;41:5484–91.
- [269] Taib NU, Idris NH. Plastic crystal–solid biopolymer electrolytes for rechargeable lithium batteries. *J Membr Sci* 2014;468:149–54.
- [270] Alves RD, Rodrigues LC, Andrade JR, Pawlicka A, Pereira L, Martins R, Fortunato E, Silva MM. Study and characterization of a novel polymer electrolyte based on agar doped with magnesium triflate. *Mol Cryst Liq Cryst* 2013;570:1–11.
- [271] Leones R, Santanin F, Rodrigues LC, Marrucho IM, Esperança JMSS, Pawlicka A, Silva MM. Investigation of polymer electrolytes based on agar and ionic liquids. *Exp Polym Lett* 2012;6:1007–16.
- [272] Stojadinović J, Dushina A, Trócoli R, Mantia FL. Electrochemical characterization of gel electrolytes for aqueous Lithium-Ion batteries. *ChemPlusChem* 2014;79(10):1507–11.
- [273] Audeh DJSa, Alcazar JB, Barbosa CV, Carreno NLV, Avellaneda CAO. Influence of the NiO nanoparticles on the ionic conductivity of the agar-based electrolyte. *Polímeros* 2014;24:8–12.

- [274] Leones R, Botelho MBS, Sentanin F, Cesarino I, Pawlicka A, Camargo ASS, Silva MM. Pectin-based polymer electrolytes with Ir(III) complexes. *Mol Cryst Liq Cryst* 2014;604:117–25.
- [275] Barker RE, Thomas CR. Effects of moisture and high electric fields on conductivity in alkali-halide-doped cellulose acetate. *J Appl Phys* 1964;35:3203–16.
- [276] Lu DR, Xiao CM, Xu SJ. Starch-based completely biodegradable polymer materials. *Exp Polym Lett* 2009;3(6):366–75.
- [277] Elizabeth P. The polysaccharides of green, red and brown seaweeds: their basic structure, biosynthesis and function. *Br Phycol J* 1979;14:103–17.
- [278] Majda S, Pierre L. A spectroscopic investigation of the carrageenans and agar in the 1500–100 cm^{-1} spectral range. *Spectrochim Acta* 1993;49A(2):209–21.
- [279] Babak G, Hadi A. Biodegradable Polymers. (<http://Dx.Doi.Org/10.5772/56230>).
- [280] Ave RL. Biodegradable multiphase systems based on plasticized starch: a review. *J Macromol Sci Part C Polym Rev* 2004;C44(3):231–74.
- [281] Bai Y, Cao Y, Zhang J, Wang M, Li R, Wang P, Zakeeruddin SM, Grätzel M. High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts. *Nat Mater* 2008;7:626.
- [282] Kuang D, Klein C, Zhang Z, Ito S, Moser JE, Zakeeruddin SM, Grätzel M. Stable, high-efficiency ionic-liquid-based mesoscopic dye-sensitized solar cells. *Small* 2007;3:2094.
- [283] Bonhote P, Dias AP, Papageorgiou N, Kalyanasundaram K, Grätzel M. Hydrophobic, highly conductive ambient-temperature molten salts. *Inorg Chem* 1996;35:1168.
- [284] Singh PK, Kim KI, Lee JW, Rhee HW. Polymer electrolyte with ionic liquid for DSSC application. *Phys Stat Sol A* 2006;R88:203.
- [285] Surana K, Mehra RM, Bhattacharya B, Rhee HW, Polu AR, Singh PK. A comprehensive study of chalcogenide quantum dot sensitized solar cells with a new solar cell exceeding 1 V output. *Renew Sustain Energy Rev* 2015;52:1083–92.
- [286] Singh PK, Kim KW, Kim KI, Park NG, Rhee HW. Nanocrystalline porous TiO_2 electrode with ionic liquid impregnated solid polymer electrolyte for dye sensitized solar cells. *J Nanosci Nanotechnol* 2008;8:5271.
- [287] Singh PK, Kim KW, Rhee HW. Electrical, optical and photoelectrochemical studies on a PEO-polymer electrolyte doped with low viscosity ionic liquid. *Electrochem Commun* 2008;10:1769.
- [288] Singh PK, Kim KW, Park NG, Rhee HW. Mesoporous nanocrystalline TiO_2 electrode with ionic liquid based solid polymer electrolyte for dye sensitized solar cell application. *Synth Metals* 2008;158:590.
- [289] Singh PK, Kim KW, Rhee HW. Ionic liquid (1-methyl 3-propyl imidazolium iodide) with polymer electrolyte for DSSC application. *Polym Eng Sci* 2009;49:862.
- [290] Singh PK, Bhattacharya B, Nagarale RK, Pandey SP, Kim KW, Rhee HW. Ionic liquid doped poly (N-methyl 4-vinylpyridine iodide) solid polymer electrolyte for dye sensitized solar cell. *Synth Metals* 2010;160:950.