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Chitosan and Phthaloylated Chitosan in Electrochemical Devices

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<http://dx.doi.org/10.5772/65656>

Abstract

Chitin and chitosan are widely found in nature. Chitin can be obtained from fungi and in the lower animals. Chitosan can be derived from chitin. The process of chitosan derivation from chitin is called deacetylation. Chitosan is non-toxic, odourless, biocompatible in animal tissues and enzymatically biodegradable. It has found many applications in the fields of cosmetics, wound healing, dietetics and waste-water treatment. Chitosan holds many promising potentials, but its inability to dissolve in many of the common solvents has restricted its application. Hence, chitosan has been modified, and there are now many derivatives of chitosan. In the current chapter, we discuss chitosan and only the phthaloyl chitosan derivative. Their applications in several electrochemical devices are also discussed.

Keywords: chitosan, phthaloyl chitosan, conductivity, batteries, solar cells, supercapacitors, fuel cells

1. General characteristics

Nature contains many types of polysaccharides. One of the important polysaccharides is chitin. Chitin can be obtained from crabs, shrimps and other sea creatures. Chitin can also be derived from insects and algae. Chitosan is the product that can dissolve in dilute acids after chitin has been deacetylated for a sufficient amount of time [1, 2]. Chitosan is a linear polysaccharide.

In nature, chitosan can also be found in some fungi, diatoms, sponges, worms and molluscs [3]. Both chitin and chitosan are versatile and promising biomaterials.

The dilute acids that can dissolve chitosan include dilute acetic, hydrochloric, formic and butyric acids [4]. Chitosan is biodegradable, biocompatible, odourless and non-toxic. The

linear polysaccharide also has the ability to form thin films, is resistant to chemical attack, has electrolytic properties, easy to cross-link or modify and has antibacterial property [5–7].

Chitosan has found uses in waste-water processing [8, 9], medicine for wound healing and dietetics [10, 11], agriculture [12], reverse osmosis, food industry [13–15] and also in cosmetics [16–18]. In this article, emphasis is on chitosan and chitosan-derived materials as hosts for ionic conduction.

The utilization of chitosan in energy devices depends on its chemical and mechanical properties. Chitosan films are good liquid absorbers. Thus, chitosan can achieve good ionic conductivity when immersed in liquid electrolytes. This is important for energy storage devices. However, when swollen, chitosan becomes less stable.

A chitin monomer has an amide functional group, HNC(O)CH_3 , the infrared (IR) transmission peak is located at 1650 cm^{-1} . This has been partially replaced by the amine functional group, when chitin was deacetylated. The IR peak for the $-\text{NH}_2$ group is located at 1590 cm^{-1} in the chitosan spectrum. There is only one $-\text{NH}_2$ functional group in the chitosan monomer. The nitrogen atom in the amine group is an electron donor. So is the oxygen atom in the hydroxyl ($-\text{OH}$) functional group. There are two $-\text{OH}$ groups in each monomer [19]. The free amine and hydroxyl functional groups allow chitosan to be altered chemically for specific applications. The $-\text{NH}_2$ group provides attachment for coordination or chelation of cations from organic/inorganic salts. Coordination of, for example, LiCF_3SO_3 [20] with N atom of the reactive functional group enables the formation of complexes that can function as an electrolyte material. Chitosan has a carboxyl group at 1650 cm^{-1} and NH_3^+ peak at 1514 cm^{-1} . According to Ritthidej [21], the NH_3^+ peak can disappear from the spectrum on storage of the film.

Chitosan has good film or membrane-forming ability. This is an advantage since most of the polymer electrolytes are prepared in film form via the solution cast technique [20, 22]. In forming a polymer electrolyte film, the cation of the salt must coordinate electrostatically with the electron donor atom of the polymer. The chitosan-based electrolyte films are homogeneous and have high mechanical strength [23, 24].

According to Sakurai and co-workers [24, 25], chitosan is not a totally amorphous polymer. From wide angle X-ray diffraction (WAXD), it is observed to be partially crystalline. These authors, however, did not investigate the effect of adding salt or plasticizer to chitosan. Alves et al. [26] reported that pure chitosan has a broad band centred at $2\theta \approx 20.6^\circ$ and X-ray diffraction (XRD) patterns change with salt addition. This band implies the amorphous structure of the chitosan-based electrolytes indicating that the polymer chains are essentially disordered. The XRD patterns also exhibited changes depending on the salt concentration. According to Kurita et al. [27], a fully deacetylated chitosan is even more amorphous than that deacetylated up to 95%.

Muzzarelli has reported that chitosan decomposes in air at elevated temperatures [28]. The glass transition temperature, T_g , of the chitosan biopolymer was successfully observed by Sakurai and co-workers [25]. Using differential scanning calorimetry (DSC), they reported T_g at 203°C . According to Dong et al. [29], chitosan has a T_g between 140 and 150°C . The re-

searchers also found that the number of alkali treatments or the degree of deacetylation of chitosan does not influence the T_g .

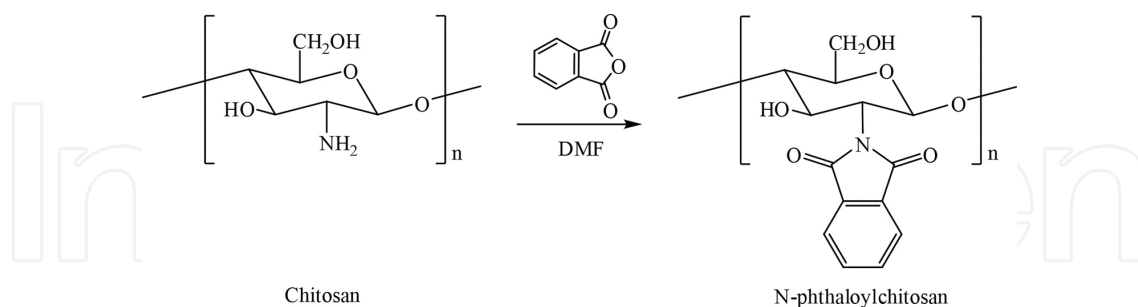


Figure 1. Reaction of N-phthaloylation.

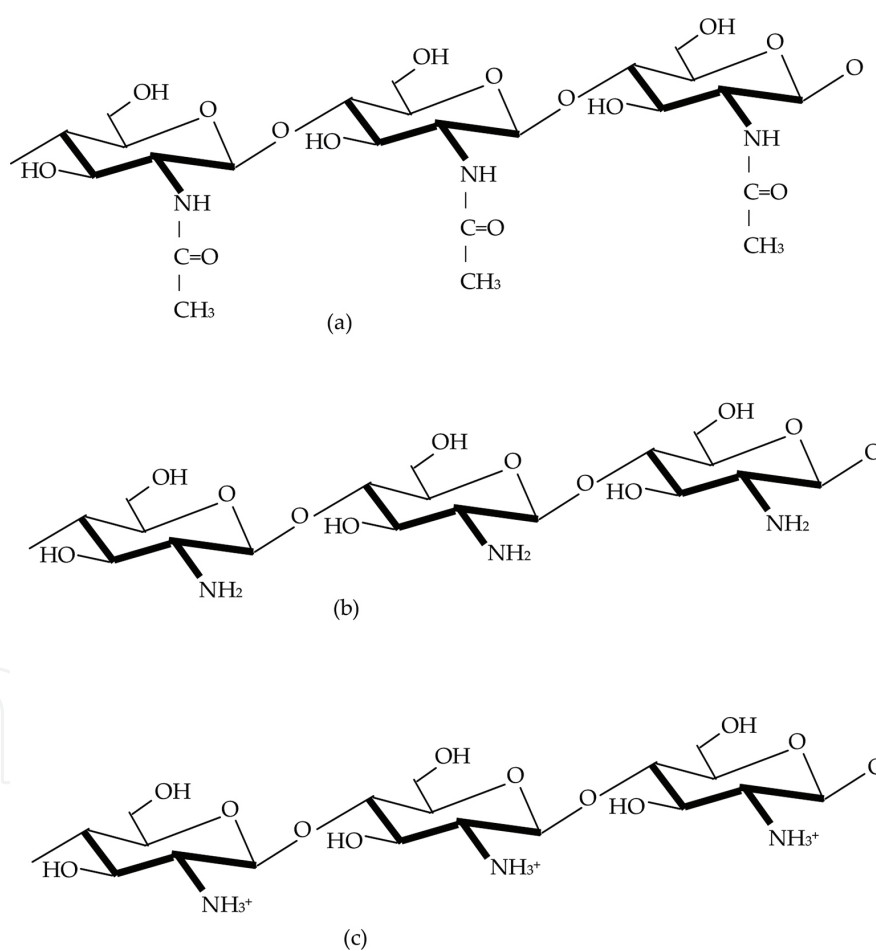


Figure 2. Chemical structure of (a) chitin, (b) chitosan and (c) phthaloyl chitosan.

As mentioned above, in swollen form, chitosan loses its mechanical strength. To overcome this, chitosan has been blended, cast in multilayers or added with inorganic/organic supports. Even then, its utilization is still restricted because of its poor solubility in many of the common

solvents such as alkali, organic solvents and water. Hence, to make chitosan soluble in other solvents, it needs to be modified. This can be done by several processes such as acylation and phthaloylation. Phthaloylation is discussed here. Phthaloyl chitosan dissolves in dimethylsulfoxide (DMSO), dimethylacetamide (DMAc), dimethylformamide (DMF) and pyridine [30].

Unlike chitosan, the IR spectrum of phthaloyl chitosan exhibits characteristic peaks at 719, 1708 and 1772 cm^{-1} . Proton NMR (Nuclear Magnetic Resonance) exhibits peaks at 3.0 and 7.5 ppm [30]. Aziz et al. [31] reported that the diffractogram of phthaloyl chitosan showed only one broad peak at around $2\theta = 18^\circ$. Phthaloyl chitosan can be considered as chitosan stripped off its hydrogen atoms, except for the hydrogen in hydroxyl group. It is therefore less rigid than chitosan since inter- and intra-hydrogen bonding have been removed. In the synthesis of phthaloyl chitosan, chitosan and phthalic anhydride were refluxed for 6 h between 100 and 120°C in dimethylformamide (DMF) and nitrogen environment. The temperature was then reduced to 60°C, and the mixture was left overnight. To precipitate out the product, the solution was poured into iced water. The product, N-phthaloyl chitosan (PhCh), was then washed with ethanol and dried in vacuum at 60°C. The synthesis process is shown in **Figure 1**. The chemical structures of chitin, chitosan and phthaloyl chitosan are shown in **Figure 2**.

2. Ionic conductivity

An important characteristic that any electrolyte should have is high ionic conductivity especially at room temperature. In polymer electrolytes, ionic conductivity is attributed to the motion of cations and anions of the doping salt. However, in polymers, both crystalline and amorphous phases exist and ionic conductivity can only occur in the amorphous phase. Hence, if the electrolyte is more amorphous, then more ions can be conducted through the enlarged amorphous region and the conductivity enhanced. The increased amorphousness of the electrolyte can be achieved through several ways. One such way is through doping the polymer with salt. Depending on the salt concentration, some portion of the crystalline phase of the polymer can be disrupted. Increasing the salt concentration can increase amorphousness, but to a certain extent. It has been observed that beyond a particular salt content and for a fixed polymer mass, the salt cannot be totally dissolved in the polymer, and the X-ray diffractogram showed peaks due to the salt [32].

The amorphousness of the electrolyte can also be increased by adding additives such as plasticizers and inert fillers. The plasticizers should have a high dielectric constant and low viscosity. The high dielectric constant helps to dissociate the salt into ions and probably also to dissociate contact ions. The low viscosity is required to promote ion mobility, which will be reduced if the viscosity of the plasticizer is high. The two additives also provide additional pathways for ionic conduction and this is manifested in the smaller activation energy or pseudo-activation energy of the chitosan (Ch) and PhCh ionic conduction hosts. **Table 1** lists representative of the conductivity value of some plasticized Ch- and PhCh-based electrolytes.

According to Croce et al. [34], plasticization can ensure conductivity of polymer electrolytes to achieve appreciable values at ambient temperature. However, plasticization deteriorates the

mechanical strength of the ion-conducting medium. Plasticization can also increase the electrolyte's reactivity towards lithium metal anode. The authors have also shown that inert metal oxides such as Al_2O_3 , SiO_2 and TiO_2 can act as solid plasticizers or fillers to enhance ionic conductivity without sacrificing dimensionality of the electrolyte. The fillers must be inert to the contents of the polymer electrolyte. Xiao et al. [35] have investigated the influence of multiwall carbon nanotubes (MWCNTs) on chitosan/cellulose. Conductivity was enhanced on addition of MWCNT. To our knowledge, works concerning filler addition to Ch- and PhCh-salt complexes are scarce. Thus, this could be another area of research that could be carried out to complement work on electrolytes based on Ch and PhCh.

Sample	$\sigma_{\text{RT}}/\text{S m}^{-1}$	ϵ	$\eta/\text{mPa s}$	References
Ch- LiCF_3SO_3	1.70×10^{-3}	–	–	[32]
Ch-LiTFSI	2.00×10^{-3}	–	–	[33]
Ch-EC- LiCF_3SO_3	4.00×10^{-3}	89 (EC)	1.90 (EC)	[22]
Ch-SN-LiTFSI	6.00×10^{-2}	55 (SN)	1.69 (SN)	[33]
PhCh-TPAI-LiI	0.61	–	–	[30]
PhCh- NH_4SCN	2.42×10^{-3}	–	–	[31]
PhCh-EC-DMF-TPAI- I_2	0.55	37 (DMF)	0.80 (DMF)	[30]

EC = ethylene carbonate, DMF = dimethylformamide, SN = succinonitrile, LiCF_3SO_3 = lithium triflate, LiTFSI = lithium bis (trifluoromethylsulfonyl) imide, TPAI = tetrapropylammonium iodide.

Table 1. Room temperature conductivity (σ_{RT}) of Ch- and PhCh-based electrolytes, dielectric constant (ϵ) and viscosity (η) of the plasticizers.

Aziz et al. have prepared proton-conducting electrolytes based on phthaloylated chitosan that was incorporated with NH_4SCN as the doping salt [31]. The highest room temperature conductivity was $2.42 \times 10^{-3} \text{ S m}^{-1}$ for the 30 wt.% salt-containing sample.

Muthumeenal et al. have measured the conductivity of polyethersulfone/phthaloyl chitosan blend electrolyte dissolved in concentrated sulphuric acid. The highest room temperature conductivity achieved was $92 \times 10^{-2} \text{ S m}^{-1}$ [36]. The high H^+ conductivity can be attributed to the sulfonic acid groups and the presence of the polar groups in PhCh.

Azzahari et al. determined the conductivity of PhCh-iodide-mixed salt (LiI, CsI and BMII) gel polymer electrolyte systems using the method of electrochemical impedance spectroscopy [37]. They have also predicted the conductivity of the systems using response surface methodology and artificial neural network. The authors showed that artificial neural network gave a better prediction than response surface methodology.

Ionic transport in polymer electrolytes can be explained using the Lewis acid-base reaction theory [38]. In this theory, bases donate electron pairs and acids accept them. The oxide and hydroxide groups on the filler provide additional sites (apart from the heteroatoms in the polymer chain) for interaction with the cations of the salt and indirectly form conduction paths

for the transport of ions via Lewis acid-base interactions between the O/OH groups on the surface of the filler and the ionic species. Dissanayake et al. [39] and Jayathilaka et al. [40] have demonstrated this concept through the conductivity enhancement of the electrolytes with the addition of fillers.

3. Transference number measurement (TNM)

Transference number is a parameter indicating as to how much an ionic species contribute to the overall conductivity of the electrolyte. Knowing the transference number, one can tell whether the major contributor towards the conductivity is the cation or anion. It can be expected and proven that chitosan-based polymer electrolytes are ionic conductors. Osman et al. [22] reported that the conductivity of a chitosan electrolyte comprising LiCF_3SO_3 as the ion source and ethylene carbonate (EC) as the plasticizer was in the order of 10^{-3} S m^{-1} . The ionic transference number obtained was 0.9. Aziz et al. [31] also measured the TN of $\text{PhCh-NH}_4\text{SCN}$.

Although these electrolytes are ionic conductors, it is vital to know, for some applications, whether the major contributor to the overall conductivity is the cation or anion. Work on this aspect for Ch- and PhCh-based electrolytes is scarce although there are some reports on the subject [41]. For battery application, it is appreciated that these electrolytes be major cationic conductors and for dye-sensitized solar cells (DSCCs) with I^-/I_3^- redox mediators, I^- transport is more important than the cation transport.

4. Application in electrochemical devices

Ch and PhCh have been used to host ionic conductivity in batteries, supercapacitors, dye-sensitized photovoltaics and fuel cells. Critical review on Ch as integrative biomaterial for microdevices has been done by Koev et al. [42]. Here, we discuss application of the Ch and PhCh materials in the electrochemical devices.

4.1. Chitosan in batteries

Some battery characteristics fabricated with Ch-based electrolytes are listed in **Table 2**.

Jia et al. [46] developed a Ch electrolyte that was incorporated with a biocompatible choline nitrate $[\text{Ch}][\text{NO}_3]$ ionic liquid that possessed negligible vapour pressure, low viscosity and flammability as well as high ionic conductivity and electrochemical stability. They have demonstrated a compact bio-battery system with the use of this thin-film gel chitosan-choline nitrate electrolyte. A magnesium alloy anode and a polypyrrole-para(toluene sulfonic acid) cathode were used. Some characteristics of the cell are listed in **Table 3**. It was reported that the gel electrolyte was also mechanically robust.

Electrolyte	σ (S m ⁻¹)	V_{oc} (V)	Q	P	References
Ch:NH ₄ NO ₃ :EC* 18:12:70 (wt.%)	0.99	1.56	17 mA h	8.70 mW cm ⁻²	[43]
PVA:Ch:NH ₄ NO ₃ :EC* 10.8:7.2:12:70 (wt.%)	0.16	1.64	38 mA h	9.47 mW cm ⁻²	[44]
Ch:choline nitrate [†]	10 ⁻² to 1 depends on choline nitrate content	1.80	1.76 mA h	3.9 mW cm ⁻³	[45]
Ch-SN-LiTSFI	6.00 × 10 ⁻²	4.2	142 m Ah g ⁻¹	468 mWhg ⁻¹	[33]

*Zn+ZnSO₄·7H₂O//MnO₂

[†]Mg//Ppy: cell area assumed 1.1 cm².

Table 2. Battery characteristics, electrolyte conductivity, open circuit voltage (V_{oc}), capacity (Q) and power density (P).

Material	Conductivity (S m ⁻¹)	Selectivity index (S s m ⁻³)	Methanol permeability (m ² s ⁻¹)	References
PCh	2	1.25 × 10 ¹⁰	1.62 × 10 ⁻¹¹	[57]
Ch/Cs ₂ -PTA-5 wt.%	0.6	1.1 × 10 ¹⁰	5.6 × 10 ⁻¹¹	[49]
Ch flakes	–	–	3.1 × 10 ⁻¹⁰ (20°C)	[58]
Ch/15 wt.% mordenite/30 wt.% sorbitol/60	–	–	4.9 × 10 ⁻¹¹	[59]
Ch-40 wt.% HO ₃ SY	2.07	2.3 × 10 ¹⁰	9.04 × 10 ⁻¹¹	[60]
Ch-zeolite	1.75		1 × 10 ⁻¹⁰	[61]
Ch/PMA	1.5	5.6 × 10 ¹⁰	2.7 × 10 ⁻¹¹	[62]
GS-Ch/PVP	2.4		7.3 × 10 ⁻¹²	[63]
CGS-12/Nafion 112	7.5	~2 × 10 ¹¹ (25°C)	~4 × 10 ⁻¹¹	[64]
Ch/SHNT	1.88 (25°C)	2 × 10 ¹⁰	9.2 × 10 ⁻¹¹	[65]
Ch/sodium alginate (3:1)	4.2	–	4.6 × 10 ⁻¹²	[66]

Table 3. Material characteristics for DMFC.

Apart for application as host for ionic conductors, chitosan was also used as a binder material for battery cathodes. Prasanna et al. [47] have investigated the potential of Ch as a binder material for the fabrication of cathode in lithium ion batteries. The cathode-active material was LiFePO₄. The cathode fabricated with chitosan binder showed a high ionic conductivity compared to the LiFePO₄ cathode with poly(vinylidene difluoride) binder. The lithium ion cell fabricated with the cathode using chitosan binder also exhibited a discharge capacity higher than the cell with poly(vinylidene difluoride) binder by ~32 mAh g⁻¹. The capacity retention after 30 cycles for the cell with chitosan binder was ~98.4% and that of the cell with PVDF binder was ~85%.

4.2. Chitosan in electrical double-layer capacitors (EDLCs)

Arof et al. [48] have prepared an electrolyte for electrical double-layer capacitor (EDLC) study. The electrolyte comprised a chitosan/iota (i)-carrageenan-blended polymer with H_3PO_4 as the proton source and plasticized with poly(ethylene glycol) (PEG). The highest conducting sample has conductivity of $6.29 \times 10^{-2} \text{ S m}^{-1}$ at room temperature. This electrolyte contained equal amounts of chitosan and i-carrageenan (37.5% by weight), 18.75 wt.% H_3PO_4 and 6.25 wt.% PEG. This electrolyte was used as separator cum electrolyte in an EDLC. The discharge showed stability for 30 cycles.

Apart from being used to host ionic conduction, chitosan has been used to produce activated carbon (AC) [49]. The AC has high specific surface area of $\approx 3500 \text{ m}^2 \text{ g}^{-1}$. This is higher than the surface area of AC derived from durian shell [45]. The EDLC fabricated with the chitosan-based AC exhibited a capacitance of 338 F g^{-1} at 2 mV s^{-1} scan rate. The charge-discharge curves showed an inverted 'V' shape indicating excellent EDLC performance.

Izabela Stepniak et al. [7] have prepared a Ch/chitin-based membrane for use in an EDLC. To enable the membrane to host Li^+ ion conduction, the membrane was soaked in lithium acetate (LiOAc) solution. The researchers also fabricated an EDLC with Ch-LiOAc electrolyte for comparison. The specific discharge capacitances of the EDLCs with films of Ch/chitin and Ch were 96 and 87 F g^{-1} , respectively. On comparing the first and 10,000th charge/discharge characteristics for the EDLC with the Ch/chitin membrane, it was observed that the device showed excellent capacity retention. The inverted 'V' shape of the charge/discharge curves and the almost 'rectangular' shape of the cyclic voltammogram of the EDLC with Ch/chitin membrane confirm the excellent symbiotic nature among the materials in the cell. From this work, it can be inferred that Ch has potential for use as a host material in EDLC electrolyte. Its performance can be improved by blending with chitin extracted from *Ianthella basta* sponge.

4.3. Chitosan in polymer electrolyte fuel cells (PEFCs)

Application of chitosan electrolyte in fuel cells is a demanding task. Chitosan is receiving a lot of attention as materials for bioelectrolytes and electrodes [45]. Membrane is the core component of polymer electrolyte fuel cells (PEFCs). The search for low-cost, efficient and stable polymer electrolyte has led researchers to study the chitosan biopolymer electrolyte as alternative candidate for possible production of cheaper fuel cells. Vaghari et al. [51] have written an informative review on the use of chitosan-based electrolytes for fuel cells.

Glutaraldehyde cross-linked N-[(2-hydroxy-3-trimethyl-ammonium) propyl] chitosan chloride was blended with crosslinked quaternized PVA [18]. Quaternized PVA has a low mechanical strength and blending with the chitosan derivative improved their performance.

Majid and Arof [52] have applied chitosan-based electrolytes in PEFCs. The electrolyte systems comprise Ch, H_3PO_4 and Al_2SiO_5 . The open-circuit voltage of the PEFCs was 0.9 V and the room temperature current density was greater than 200 A m^{-2} . This again showed that chitosan can be used to host ionic conductivity for fuel cell application.

Wan et al. [53] studied the ionic conductivity of chitosan electrolytes with different molecular weights and degree of deacetylation. They have proposed that chitosan can be used as electrolyte material for alkaline fuel cells.

Wang et al. [54] have incorporated quaternized chitosan with polystyrene. Tensile strength improved and the composite also showed better tolerance to bases. However, ionic conductivity decreased with polystyrene content.

A good direct methanol fuel cell (DMFC) should be fabricated with a polymer electrolyte membrane that only allows a low methanol permeability. Nafion membrane allows a high methanol crossover. Chitosan with desirable proton conductivity has been used in DMFCs [55]. The chitosan electrolyte was added with salt and plasticized for conductivity enhancement [56]. However, excessive water uptake can make the membranes fragile and less robust for fuel cell application. **Table 3** lists some materials based on chitosan for DMFC.

In **Table 3**, PCh-G1h is a blend of poly(vinyl alcohol) and chitosan with PVA/Ch weight ratio of 90/10 cross-linked in glutaraldehyde for 1 h [57]. Cs2-PTA is Cs2HPW12O40. Ch/Cs2-PTA-5 wt.% is chitosan doped with 5 wt.% caesium phototungstate salt [49]. Ch flakes [58] were prepared from chitin. The power density of the DMFC with the chitosan flakes is 27.78 W m^{-2} . The Ch/15 wt.% mordenite/30 wt.% sorbitol/60 was prepared at 60°C [59]. The hybrid membrane in [60] consisted of Ch and $-\text{SO}_3\text{H}$ -modified zeolite. Data shown are for 2.0 mol L^{-1} methanol concentration. Methanol permeability was observed to increase with the decrease in zeolite size for the zeolite-filled chitosan membranes as reported in [61]. Ch/PMA [62] was prepared by adding phosphomolybdic acid chitosan, both in solution form. The methanol permeability is about one order of magnitude less than that of Nafion 117. Ch was blended in poly(vinyl pyrrolidone) or PVP (Ch:PVP of 4:1). The polymer blend was cross-linked with glutaraldehyde and sulphuric acid to form GS-Ch/PVP [63]. ChGS-12 is a structurally modified chitosan membrane that was developed by the authors [64]. In ChGS-12/Nafion 112 membrane, two layers of ChGS-12 were coated on Nafion 112 in order to synergize the low methanol permeability of ChGS-12 with the higher proton conductivity of Nafion 112. ChGS-12 is chitosan cross-linked with glutaraldehyde and sulfosuccinic acid. The maximum output power density of the DMFC was 662.5 W m^{-2} . SHNT [65] are halloysite nanotubes bearing sulphonate polyelectrolyte brushes. SHNT was incorporated in Ch matrix. The proton conductivity of CS/SHNT increases with SHNT content.

4.4. Chitosan in dye-sensitized solar cells (DSSCs)

Some examples of dye-sensitized solar cells using chitosan-based electrolytes are listed in **Table 4**.

EMImSCN is 1-ethyl 3-methylimidazolium thiocyanate ionic liquid. It has low viscosity. DSSC with 1-butyl-3-methylimidazolium iodide (BMII) used anthocyanin dye as the sensitizer.

As in studies on lithium ion batteries, chitosan was also used as a binder in TiO_2 photoelectrode of the DSSCs. The chitosan-based TiO_2 paste was prepared by mixing nano- TiO_2 particles in a chitosan colloidal solution [71]. The dye used was N719 or $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ and the concentration was 0.5 mmol L^{-1} ethanol. The electrolyte comprised 1,2-dimethyl-3-propylimidazoli-

um iodide with the I⁻/I³⁻ redox mediator. The DSSC also contained 2.0% by weight of chitosan in the photoanode and exhibited the highest photon conversion efficiency of 4.16%. The Voc, Jsc and FF were 0.69 V, 10.15 mA cm⁻² and 0.59, respectively. The amount of chitosan in the photoanode influences the efficiency.

Electrolyte	Dye	J _{sc} (mA cm ⁻²)	V _{oc} (V)	η (%)	References
chitosan:NaI/I ₂	–	1.05	0.35	0.13	[67]
chitosan:NaI/I ₂ +150 wt.% EMImSCN	–	2.62	0.53	0.73	[67]
11 wt.% chitosan-9 wt.% NH ₄ I-80 wt.% BMII	ABR	0.90	0.36	0.15	[68]
11 wt.% chitosan-9 wt.% NH ₄ I-80 wt.% BMII	ARC ^{*1}	1.59	0.45	0.29	[68]
11 wt.% chitosan-9 wt.% NH ₄ I-80 wt.% BMII	ARC ^{*2}	2.09	0.62	0.38	[68]
11 wt.% (chitosan:PEO, wt. ratio 30:70)-9 wt.% NH ₄ I-80 wt. % BMII	ARC ^{*2}	2.52	0.40	0.39	[68]
11 wt.% phthaloyl chitosan-9 wt.% NH ₄ I-80 wt.% BMII	ARC ^{*2}	3.47	0.36	0.43	[68]
11 wt.% (phthaloyl chitosan:PEO, wt. ratio 30:70)-9 wt.% NH ₄ I-80 wt. % BMII	ARC ^{*2}	3.50	0.34	0.46	[68]
12.02 wt.% phthaloyl chitosan-36.06 wt.% EC-36.06 wt.% DMF-14.42 wt.% TPAI-1.44 wt.% I ₂	N3	12.72	0.60	5.00	[30]
PhCh:EC:PC:TPAI:LiI:I ₂ 15.82:31.65:31.65: 18.99:0.00:1.90	N719	7.38	0.72	3.50	[69]
PhCh:EC:PC:TPAI:LiI:I ₂ 15.82:31.65:31.65:15.82:3.16:1.90	N719	6.33	0.80	3.61	[69]
PhCh:EC:PC:TPAI:LiI:I ₂ 15.82:31.65:31.65:12.66:6.33:1.90	N719	7.25	0.77	3.71	[69]
PhCh:EC:PC:TPAI:LiI:I ₂ 15.82:31.65:31.65:9.49:9.49:1.90	N719	3.64	0.75	2.04	[69]
PhCh:EC:PC:TPAI:LiI:I ₂ 15.82:31.65:31.65:6.33:12.66:1.90	N719	3.64	0.70	1.77	[69]
disulphide/thiolate	MP	4.72	0.57	1.47	[70]
disulphide/thiolate	MP	3.88	0.58	0.60	[70]
disulphide/thiolate	MP	8.70	0.60	2.63	[70]
I ₂ /NaI	MP	5.40	0.62	1.75	[70]
I ₂ /NaI	MP	4.33	0.58	0.88	[70]

ABR: anthocyanin from black rice; ARC: anthocyanin from red cabbage; MP: mangosteen peel.
*1: in hydrochloric acid
*2: in tartaric acid

Table 4. Some characteristics of DSSCs with chitosan-based electrolytes.

Maiaugree et al. [70] studied DSSCs using an organic disulphide/thiolate solution as the electrolyte. The advantages of this electrolyte are its high transmittance and low corrosiveness. These authors have compared counter-electrodes of Pt, PEDOT-PSS and mangosteen peel carbon. DSSCs were also fabricated using these CEs, but liquid I₂/NaI electrolyte.

5. Summary

As a summary, chitosan and its derivatives have potential for use as electrolytes or binders or as a source for activated carbon. We have given some examples of such uses in this article. Chitosan is a material useful for green technology.

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References

- [1] Muzzarelli RAA. Natural Chelating Polymers. Pergamon Press: New York, USA; 1973.
- [2] Bolker HI. Natural and Synthetic Polymers: An Introduction. Marcel Dekker Incorporated: New York, USA; 1974.
- [3] Kurita K. Controlled functionalization of the polysaccharide chitin. *Prog Polym Sci* 2001;26:1921–71. doi:10.1016/S0079-6700(01)00007-7.
- [4] Demarger-Andre S, Domard A. Chitosan carboxylic acid salts in solution and in the solid state. *Carbohydr Polym* 1994;23:211–9. doi:10.1016/0144-8617(94)90104-X.
- [5] Peng Z, Li Z, Shen Y, Zhang F, Peng X. Fabrication of gelatin/chitosan microspheres with different morphologies and study on biological properties. *Polym Plast Technol Eng* 2012;51:739–43. doi:10.1080/03602559.2012.663037.
- [6] Liu Y, An M, Qiu HX, Wang L. The properties of chitosan-gelatin scaffolds by once or twice vacuum freeze-drying methods. *Polym Plast Technol Eng* 2013;52:1154–9. doi:10.1080/03602559.2013.798818.

- [7] Stepniak I, Galinski M, Nowacki K, Wysokowski M, Jakubowska P, Bazhenov V V., et al. A novel chitosan/sponge chitin origin material as a membrane for supercapacitors – preparation and characterization. *RSC Adv* 2016;6:4007–13. doi:10.1039/C5RA22047E.
- [8] Northcott KA, Snape I, Scales PJ, Stevens GW. Dewatering behaviour of water treatment sludges associated with contaminated site remediation in Antarctica. *Chem Eng Sci* 2005;60:6835–43. doi:10.1016/j.ces.2005.05.049.
- [9] Crini G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog Polym Sci* 2005;30:38–70. doi:10.1016/j.progpolymsci.2004.11.002.
- [10] Berger J, Reist M, Mayer JM, Felt O, Gurny R. Structure and interactions in chitosan hydrogels formed by complexation or aggregation for biomedical applications. *Eur J Pharm Biopharm* 2004;57:35–52. doi:10.1016/S0939-6411(03)00160-7.
- [11] Ng LT, Swami S. IPNs based on chitosan with NVP and NVP/HEMA synthesised through photoinitiator-free photopolymerisation technique for biomedical applications. *Carbohydr Polym* 2005;60:523–8. doi:10.1016/j.carbpol.2005.03.009.
- [12] Chung YC, Wang HL, Chen YM, Li SL. Effect of abiotic factors on the antibacterial activity of chitosan against waterborne pathogens. *Bioresour Technol* 2003;88:179–84. doi:10.1016/S0960-8524(03)00002-6.
- [13] Suntornsuk W, Pochanavanich P, Suntornsuk L. Fungal chitosan production on food processing by-products. *Process Biochem* 2002;37:727–9. doi:10.1016/S0032-9592(01)00265-5.
- [14] Ham-Pichavant F, Sèbe G, Pardon P, Coma V. Fat resistance properties of chitosan-based paper packaging for food applications. *Carbohydr Polym* 2005;61:259–65. doi:10.1016/j.carbpol.2005.01.020.
- [15] Devlieghere F, Vermeulen A, Debevere J. Chitosan: Antimicrobial activity, interactions with food components and applicability as a coating on fruit and vegetables. *Food Microbiol* 2004;21:703–14. doi:10.1016/j.fm.2004.02.008.
- [16] Sun L, Du Y, Yang J, Shi X, Li J, Wang X, et al. Conversion of crystal structure of the chitin to facilitate preparation of a 6-carboxychitin with moisture absorption-retention abilities. *Carbohydr Polym* 2006;66:168–75. doi:10.1016/j.carbpol.2006.02.036.
- [17] Rinaudo M. Chitin and chitosan: properties and applications. *Prog Polym Sci* 2006;31:603–32. doi:10.1016/j.progpolymsci.2006.06.001.
- [18] Xiong Y, Liu QL, Zhang QG, Zhu AM. Synthesis and characterization of cross-linked quaternized poly(vinyl alcohol)/chitosan composite anion exchange membranes for fuel cells. *J Power Sources* 2008;183:447–53. doi:10.1016/j.jpowsour.2008.06.004.
- [19] Agrawal P, Strijkers GJ, Nicolay K. Chitosan-based systems for molecular imaging. *Adv Drug Deliv Rev* 2010;62:42–58. doi:10.1016/j.addr.2009.09.007.

- [20] Osman Z, Arof AK. FTIR studies of chitosan acetate based polymer electrolytes. *Electrochim Acta* 2003;48:993–9. doi:10.1016/S0013-4686(02)00812-5.
- [21] Ritthidej GC, Phaechamud T, Koizumi T. Moist heat treatment on physicochemical change of chitosan salt films. *Int J Pharm* 2002;232:11–22. doi:10.1016/S0378-5173(01)00894-8.
- [22] Osman Z, Ibrahim ZA, Arof AK. Conductivity enhancement due to ion dissociation in plasticized chitosan based polymer electrolytes. *Carbohydr Polym* 2001;44:167–73. doi:10.1016/S0144-8617(00)00236-8.
- [23] Muzzarelli RAA, Ferrero A, Pizzoli M. Light-scattering, X-ray diffraction, elemental analysis and infrared spectro- photometry characterization of chitosan, a chelating polymer. *Talanta* 1972;19:1222–6. doi:[http://dx.doi.org/10.1016/0039-9140\(72\)80068-7](http://dx.doi.org/10.1016/0039-9140(72)80068-7).
- [24] Sakurai K, Maegawa T. Chitin and Chitosan. *Second Asia Pacific Symp. Bangkok, Thail., 1996*, p. 224–7.
- [25] Sakurai K, Maegawa T, Takahashi T. Glass transition temperature of chitosan and miscibility of \rchitosan/poly(N-vinyl pyrrolidone) blends. *Polymer* 2000;41:7051–6.
- [26] Alves R, Donoso JP, Magon CJ, Silva IDA, Pawlicka A , Silva MM. Solid polymer electrolytes based on chitosan and europium triflate. *J Non Cryst Solids* 2015;432:1–6. doi:10.1016/j.jnoncrysol.2015.10.024.
- [27] Kurita K, Ikeda H, Yoshida Y, Shimojoh M, Harata M. Chemoselective protection of the amino groups of chitosan by controlled phthaloylation: facile preparation of a precursor useful for chemical modifications. *Biomacromolecules* 2002;3:1–4. doi:10.1021/bm0101163.
- [28] Muzzarelli RAA. Chitin. Pergamon Press: Oxford, UK; 1977.
- [29] Dong Y, Ruan Y, Wang H, Zhao Y, Bi D. Studies on glass transition temperature of chitosan with four techniques. *J Appl Polym Sci* 2004;93:1553–8. doi:10.1002/app.20630.
- [30] Yusuf SNF, Azzahari -AD, Yahya R, Majid SR, Careem MA, Arof AK. From crab shell to solar cell: a gel polymer electrolyte based on N-phthaloylchitosan and its application in dye-sensitized solar cells. *RSC Adv* 2016;6:27714–24. doi:10.1039/C6RA04188D.
- [31] Aziz NA, Majid SR, Arof AK. Synthesis and characterizations of phthaloyl chitosan-based polymer electrolytes. *J Non Cryst Solids* 2012;358:1581–90. doi:10.1016/j.jnoncrysol.2012.04.019.
- [32] Arof AK, Osman Z, Morni N, Kamarulzaman N, Ibrahim ZA, Muhamad MR. Chitosan-based electrolyte for secondary lithium cells. *J Mater Sci* 2001;36:791–3.
- [33] Taib NU, Idris NH. Plastic crystal-solid biopolymer electrolytes for rechargeable lithium batteries. *J Memb Sci* 2014;468:149–54. doi:10.1016/j.memsci.2014.06.001.

- [34] Croce F, Appetecchi GB, Persi L, Scrosati B. Nanocomposite polymer electrolytes for lithium batteries. *Nature* 1998;394:456–8. doi:10.1038/28818.
- [35] Xiao P, Deng ZQ, Manthiram A, Henkelman G. Calculations of oxygen stability in lithium-rich layered cathodes. *J Phys Chem C* 2012;116:23201–4. doi:10.1021/jp3058788.
- [36] Muthumeenal A, Neelakandan S, Kanagaraj P, Nagendran A. Synthesis and properties of novel proton exchange membranes based on sulfonated polyethersulfone and N-phthaloyl chitosan blends for DMFC applications. *Renew Energy* 2016;86:922–9. doi:10.1016/j.renene.2015.09.018.
- [37] Azzahari A, Yusuf S, Selvanathan V, Yahya R. Artificial neural network and response surface methodology modeling in ionic conductivity predictions of phthaloylchitosan-based gel polymer electrolyte. *Polymers* 2016;8:22. doi:10.3390/polym8020022.
- [38] Karuppasamy K, Antony R, Thanikaikarasan S, Balakumar S, Shajan XS. Combined effect of nanochitosan and succinonitrile on structural, mechanical, thermal, and electrochemical properties of plasticized nanocomposite polymer electrolytes (PNCPE) for lithium batteries. *Ionics* 2013;19:747–55. doi:10.1007/s11581-012-0806-9.
- [39] Dissanayake MAK, Bandara LRA K, Bokalawala RSP, Jayathilaka PARD, Ileperuma OA, Somasundaram S. A novel gel polymer electrolyte based on polyacrylonitrile (PAN) and its application in a solar cell. *Mater Res Bull* 2002;37:867–74. doi:10.1016/S0025-5408(02)00712-2.
- [40] Jayathilaka PARD, Dissanayake MAK, Albinsson I, Mellander BE. Effect of nanoporous Al_2O_3 on thermal, dielectric and transport properties of the (PEO) $_9$ LiTFSI polymer electrolyte system. *Electrochim Acta* 2002;47:3257–68. doi:10.1016/S0013-4686(02)00243-8.
- [41] Chai MN, Isa MIN. Novel proton conducting solid bio-polymer electrolytes based on carboxymethyl cellulose doped with oleic acid and plasticized with glycerol. *Sci Rep* 2016;6:27328. doi:10.1038/srep27328.
- [42] Koev ST, Dykstra PH, Luo X, Rubloff GW, Bentley WE, Payne GF, et al. Chitosan: an integrative biomaterial for lab-on-a-chip devices. *Lab Chip* 2010;10:3026–42. doi:10.1039/c0lc00047g.
- [43] Ng LS, Mohamad AA. Protonic battery based on a plasticized chitosan- NH_4NO_3 solid polymer electrolyte. *J Power Sources* 2006;163:382–5. doi:10.1016/j.jpowsour.2006.09.042.
- [44] Kadir MFZ, Majid SR, Arof AK. Plasticized chitosan–PVA blend polymer electrolyte based proton battery. *Electrochim Acta* 2010;55:1475–82. doi:10.1016/j.electacta.2009.05.011.
- [45] Jia X, Wang C, Zhao C. Biocompatible ionic liquid-biopolymer electrolyte enabled thin an. *ACS Appl Mater Interfaces* 2013;6:21110–7.

- [46] Ma J, Sahai Y. Chitosan biopolymer for fuel cell applications. *Carbohydr Polym* 2013;92:955–75. doi:10.1016/j.carbpol.2012.10.015.
- [47] Prasanna K, Subburaj T, Jo YN, Lee WJ, Lee CW. Environment-friendly cathodes using biopolymer chitosan with enhanced electrochemical behavior for use in lithium ion batteries. *ACS Appl Mater Interfaces* 2015;7:7884–90. doi:10.1021/am5084094.
- [48] 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;14:2145–52. doi:10.1007/s10008-010-1050-8.
- [49] Hu Y, Wang H, Yang L, Liu X, Zhang B, Liu Y, et al. Preparation of chitosan-based activated carbon and its electrochemical performance for EDLC. *J Electrochem Soc* 2013;160:H321–6. doi:10.1149/2.062306jes.
- [50] Tey JP, Careem MA, Yarmo MA, Arof AK. Durian shell-based activated carbon electrode for EDLCs. *Ionics* 2016;1–8. doi:10.1007/s11581-016-1640-2.
- [51] Vaghari H, Jafarizadeh-Malmiri H, Berenjian A, Anarjan N. Recent advances in application of chitosan in fuel cells. *Sustain Chem Process* 2013;1:16. doi:10.1186/2043-7129-1-16.
- [52] Majid SR, Arof AK. FTIR studies of chitosan-orthophosphoric polymer electrolyte 2008;484:483–92. doi:10.1080/15421400801904286.
- [53] Wan Y, Creber KAM, Peppley B, Bui VT. Ionic conductivity of chitosan membranes. *Polymer* 2003;44:1057–65. doi:10.1016/S0032-3861(02)00881-9.
- [54] Wang J, He R, Che Q. Anion exchange membranes based on semi-interpenetrating polymer network of quaternized chitosan and polystyrene. *J Colloid Interface Sci* 2011;361:219–25. doi:10.1016/j.jcis.2011.05.039.
- [55] Ramirez-Salgado J. Study of basic biopolymer as proton membrane for fuel cell systems. *Electrochim Acta* 2007;52:3766–78. doi:10.1016/j.electacta.2006.10.051.
- [56] Mukoma P, Jooste BR, Vosloo HCM. Synthesis and characterization of cross-linked chitosan membranes for application as alternative proton exchange membrane materials in fuel cells. *J Power Sources* 2004;136:16–23. doi:10.1016/j.jpowsour.2004.05.027.
- [57] Ming Yang J, Chih Chiu H. Preparation and characterization of polyvinyl alcohol/chitosan blended membrane for alkaline direct methanol fuel cells. *J Memb Sci* 2012;419–420:65–71. doi:10.1016/j.memsci.2012.06.051.
- [58] Osifo PO, Masala A. Characterization of direct methanol fuel cell (DMFC) applications with H₂SO₄ modified chitosan membrane. *J Power Sources* 2010;195:4915–22. doi:10.1016/j.jpowsour.2009.12.093.
- [59] Yuan W, Wu H, Zheng B, Zheng X, Jiang Z, Hao X, et al. Sorbitol-plasticized chitosan/zeolite hybrid membrane for direct methanol fuel cell. *J Power Sources* 2007;172:604–12. doi:10.1016/j.jpowsour.2007.05.040.

- [60] Wu H, Zheng B, Zheng X, Wang J, Yuan W, Jiang Z. Surface-modified Y zeolite-filled chitosan membrane for direct methanol fuel cell. *J Power Sources* 2007;173:842–52. doi:10.1016/j.jpowsour.2007.08.020.
- [61] Wang J, Zheng X, Wu H, Zheng B, Jiang Z, Hao X, et al. Effect of zeolites on chitosan/zeolite hybrid membranes for direct methanol fuel cell. *J Power Sources* 2008;178:9–19. doi:10.1016/j.jpowsour.2007.12.063.
- [62] Cui Z, Xing W, Liu C, Liao J, Zhang H. Chitosan/heteropolyacid composite membranes for direct methanol fuel cell. *J Power Sources* 2009;188:24–9. doi:10.1016/j.jpowsour.2008.11.108.
- [63] Smitha B, Sridhar S, Khan AA. Chitosan-poly(vinyl pyrrolidone) blends as membranes for direct methanol fuel cell applications. *J Power Sources* 2006;159:846–54. doi:10.1016/j.jpowsour.2005.12.032.
- [64] Hasani-Sadradadi MM, Dashtimoghadam E, Majedi FS, Hojjati Emami S, Moaddel H. A high-performance chitosan-based double layer proton exchange membrane with reduced methanol crossover. *Int J Hydrogen Energy* 2011;36:6105–11. doi:10.1016/j.ijhydene.2011.01.010.
- [65] Bai H, Zhang H, He Y, Liu J, Zhang B, Wang J. Enhanced proton conduction of chitosan membrane enabled by halloysite nanotubes bearing sulfonate polyelectrolyte brushes. *J Memb Sci* 2014;454:220–32. doi:10.1016/j.memsci.2013.12.005.
- [66] Smitha B, Sridhar S, Khan AA. Chitosan-sodium alginate polyion complexes as fuel cell membranes. *Eur Polym J* 2005;41:1859–66. doi:10.1016/j.eurpolymj.2005.02.018.
- [67] Singh PK, Bhattacharya B, Nagarale RK, Kim K-W, Rhee H-W. Synthesis, characterization and application of biopolymer-ionic liquid composite membranes. *Synth Met* 2010;160:139–42. doi:10.1016/j.synthmet.2009.10.021.
- [68] Buraidah MH, Teo LP, Yusuf SNF, Noor MM, Kufian MZ, Careem MA, et al. TiO₂/chitosan-NH₄I(+I₂)-BMII-based dye-sensitized solar cells with anthocyanin dyes extracted from black rice and red cabbage. *Int J Photoenergy* 2011;2011:11 p. doi:10.1155/2011/273683.
- [69] Yusuf SNF, Aziz MF, Hassan HC, Bandara TMWJ, Mellander B, Careem MA, et al. Phthaloylchitosan-based gel polymer electrolytes for efficient dye-sensitized solar cells. *J Chem* 2014;2014:8 p.
- [70] Maiaugree W, Lowpa S, Towannang M, Rutphonsan P, Tangtrakarn A, Pimanpang S, et al. A dye sensitized solar cell using natural counter electrode and natural dye derived from mangosteen peel waste. *Sci Rep* 2015;5:15230. doi:10.1038/srep15230.
- [71] Jin EM, Park K, Park J, Lee J, Yim S, Zhao XG, et al. Preparation and characterization of chitosan binder-based TiO₂ electrode for dye-sensitized solar cells. *Int J Photoenergy* 2013;2013:1–8.