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Review

Chitosan biopolymer for fuel cell applications

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ABSTRACT

Fuel cell is an electrochemical device which converts chemical energy stored in a fuel into electrical energy. Fuel cells have been receiving attention due to its potential applicability as a good alternative power source. Recently, cost-effective and eco-friendly biopolymer chitosan has been extensively studied as a material for membrane electrolytes and electrodes in low to intermediate temperature hydrogen polymer electrolyte fuel cell, direct methanol fuel cell, alkaline fuel cell, and biofuel cell. This paper reviews structure and property of chitosan with respect to its applications in fuel cells. Recent achievements and prospect of its applications have also been included.

Contents

1. Introduction

Polymer-based electrolyte is an important component in many electrochemical devices. In recent years, there has been extensive research on the development of high performance electrochemical devices which can generate and store energy at low cost. Cost-effective and eco-friendly polymer electrolytes from renewable sources can become a promising substitute for synthetic polymers for use in electrochemical devices involving energy generation and storage. Among natural polymers, polysaccharides are among the best candidates due to their abundance in environment. Chitosan (CS), a polysaccharide bio resource, has been attracting considerable interest for a broad range of applications, such as medical or pharmaceutical use, water engineering, and separation

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technologies. In the past few years, CS has been extensively investigated as solid polymer electrolyte in low and intermediate temperature polymer electrolyte-based fuel cells, such as hydrogen-polymer electrolyte fuel cell (PEFC), direct methanol fuel cell (DMFC), and alkaline fuel cells. Solid polymer electrolytes are generally divided into two classes: ion-solvating polymer composites, and polyelectrolytes. CS can serve as both polyelectrolyte membrane, and as matrix material for ion-solvating polymer composite membranes. In addition, CS has promising application in electrodes of polymer electrolyte-based fuel cells and also in biofuel cells. The advantages of chitosan for use as polymer electrolyte membrane include: (1) chitosan is low-cost and eco-friendly; (2) the hydrophilicity of chitosan is a desirable property for use in high temperature and low relative humidity environment; (3) chitosan has low methanol permeability; (4) the backbone of chitosan has certain functional groups which allow chemical modification to tailor its properties. This review is focused on chitosan and its applications in fuel cells.

2. An overview of chitosan

2.1. General remarks

Chitosan is the N-deacetylated derivative of chitin with a typical degree of acetylation of less than 0.35 (Pillai, Paul, & Sharma, 2009). Chitin is the second most abundant natural polysaccharide, generally found in crustacean shells, insects, molluscan organs, and fungi. Chitin is poly (β-(1–4)-N-acetyl-D-glucosamine), and thus CS is a copolymer of glucosamine and N-acetylglucosamine. The chemical structures of chitin and chitosan are shown in Fig. 1. Characteristics of CS are influenced by a number of parameters such as its molecular weight (from approximately 10,000–1 million Da) and degree of acetylation (representing the ratio of 2-acetamido-2-deoxy-D-glucopyranose to 2-amino-2-deoxy-D-glucopyranose structural units) (Pillai et al., 2009). CS is insoluble in water, and in most organic and alkali solvents. It is however soluble in dilute organic acids, such as acetic, formic, and lactic acids. CS contains three different polar functional groups, namely, hydroxyl (—OH), primary amine (—NH_2), and ether (C—O—C) groups, and due to the presence of these functional groups, CS has high water attracting capacity.

2.2. Chemical modification

The —OH and —NH_2 functional groups in CS enable various chemical modification of CS to tailor it for specific applications. Many books and journal articles have reviewed and summarized the possible chemical modification reactions (Harish Prashanth & Tharanathan, 2007; Jayakumar, Prabaharan, Reis, & Mano, 2005; Sashiwa & Aiba, 2004; Yao, Li, & Yao, 2011, chap. 2). In this paper, chemical modifications are discussed from the viewpoint of fuel cell applications. Special emphasis is placed on chemical cross-linking reaction to improve mechanical and chemical stability, and chemical modification to possibly generate ion exchange sites and improve ionic conductivity.

2.2.1. Sulfonation

Sulfonate groups can be chemically attached to CS using various methods (Jayakumar, Nwe, Tokura, & Tamura, 2007). Both N-sulfonated CS (where sulfonate group is attached to the —NH_2 sites) and O-sulfonated CS (where sulfonate group is attached to the —OH sites) are prepared by using sulfating reagents in various reaction conditions. By adjusting reaction time, temperature, and reactant concentration, a certain density of sulfonate groups can be attached to CS backbone. N-sulfonated CS with various sulfonation degrees can be prepared by using propane sultone (Tsai, Wang, Lin, & Lien, 2010). The sulfonated CS has a pendant alkyl sulfonic group attached to the side chain. One way of preparing O-sulfonated CS is described in a patent by Hayashi (1993) as shown in Fig. 2. Proper pretreatment conditions and solvent systems enable sulfonation to occur selectively on C3/C6-position (—OH sites). SO_3 or chlorosulfonic acid with dimethylformamide complex was used as sulfonating reagent.

2.2.2. Phosphorylation

Preparative methods of phosphorylated CS have been reviewed by Jayakumar, Selvamurugan, Nair, Tokura, and Tamura (2008). Phosphorylated CS can be prepared by heating CS with orthophosphoric acid and urea in N,N-dimethylformamide (Jayakumar et al., 2008), or by reaction of CS with phosphorous pentoxide in methanesulfonic acid (Yao et al., 2011, chap. 2). An N-methylene phosphonic CS can be prepared by using CS, phosphorous acid and formaldehyde (Ramos, Rodríguez, Aguló, Rodríguez, & Heras, 2002). The phosphonic acid is introduced in the CS via the Moedritzer and Irani (1966) reaction method. The reaction scheme is shown in Fig. 3. An O-ethyl phosphonate CS can be prepared by using KOH/methanol and 2-chloroethyl phosphonic acid (Palma, Casals, & Cardenas, 2005).

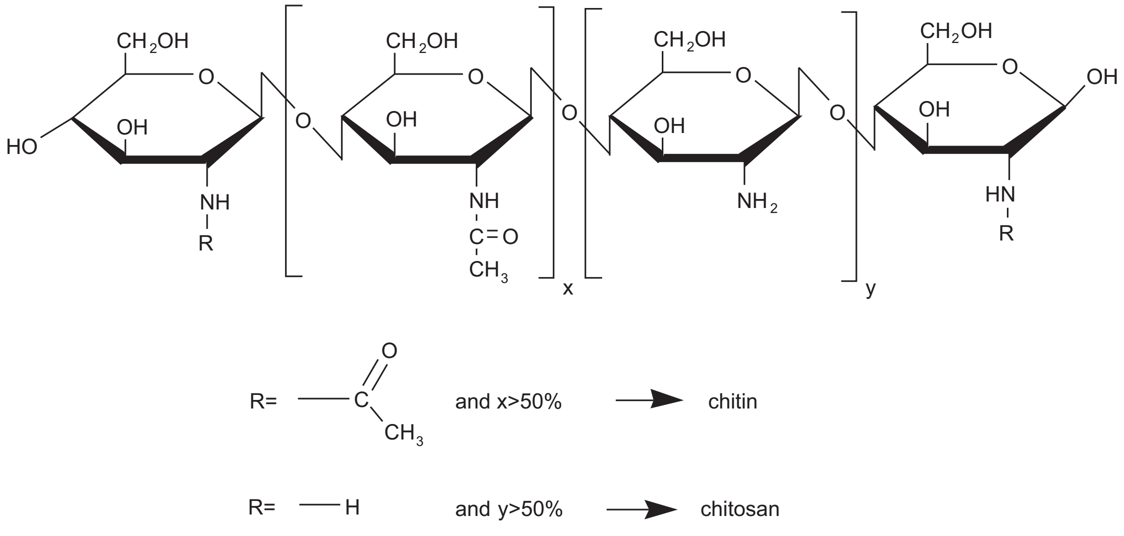


Fig. 1. Structures of chitin and chitosan.

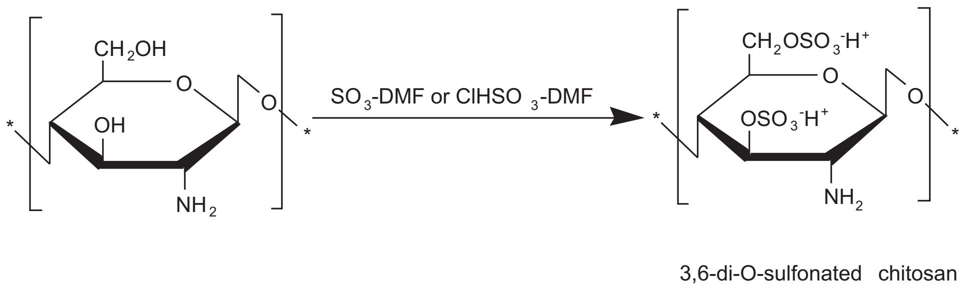


Fig. 2. Synthesis of O-sulfonated CS.

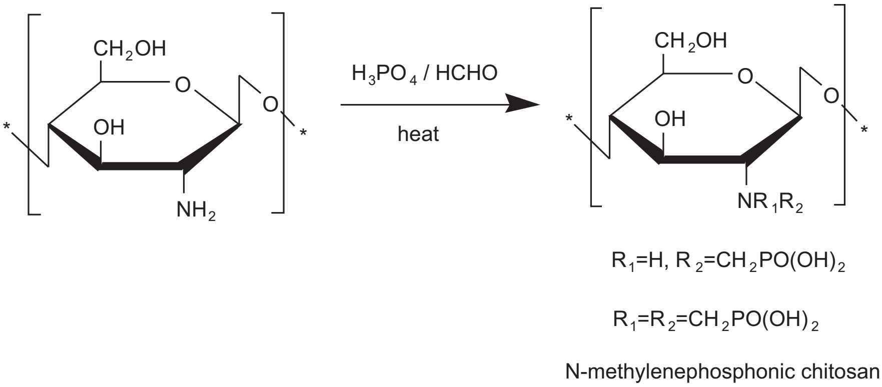


Fig. 3. Synthesis of N-methylenephosphonic CS.

2.2.3. Quaternization

Quaternized CS can be synthesized using methyl iodide by a method reported in Uragami, Aketa, Gobodani, and Sugihara (1986) and shown in Fig. 4. Glycidyltrimethylammonium chloride is also used as a quarternizing agent because it has a quaternary ammonium group itself. A primary amino group at C2 position of CS reacts with glycidyltrimethylammonium chloride according to the reaction shown in Fig. 5 (Loubaki, Ourevitch, & Sicsic, 1991). The anion exchange conductor of quaternized CS is thus obtained by replacing hydroxide ions with chloride ions.

2.2.4. Chemical cross-linking

Cross-linking is a common chemical modification to ensure good mechanical and chemical stability of CS. Structure and

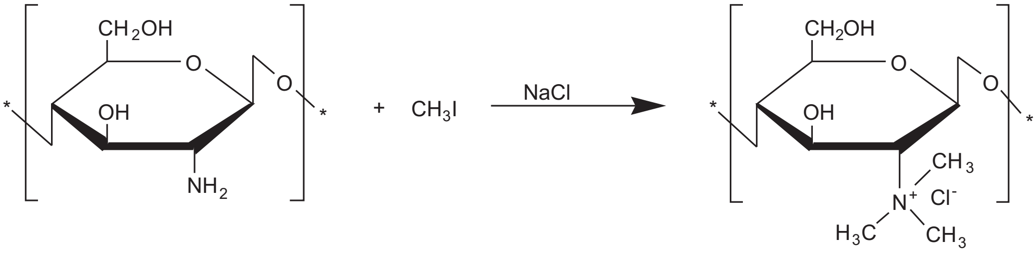


Fig. 4. Synthesis of quaternized CS.

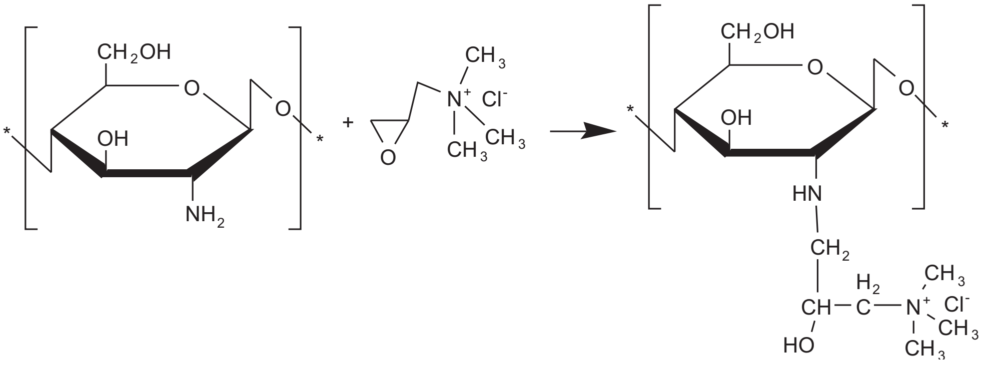


Fig. 5. Reaction of CS with glycidyltrimethylammonium chloride.

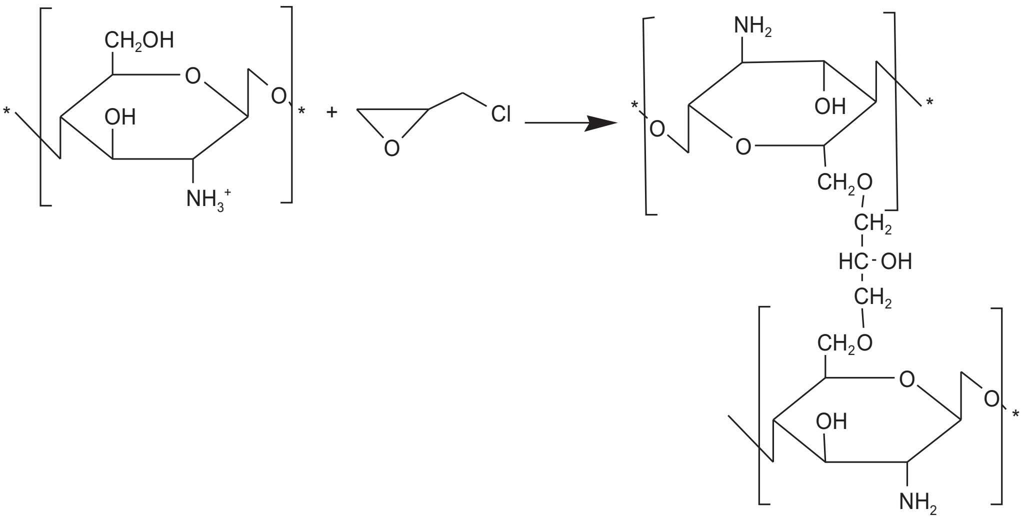


Fig. 6. Cross-linking process of CS treated with epichlorohydrin.

chemical interactions in covalently and ionically cross-linked CS are reviewed by Berger et al. (2004). In cross-linked CS, polymer chains are interconnected by cross-linkers to form three dimensional networks. Main interactions forming the network are covalent or ionic bonds. Covalently cross-linked CS can be divided into three types in terms of their structure: CS cross-linked with itself; hybrid polymer networks in which cross-linking reaction occurs between a structural unit of a CS chain and a structural unit of a polymeric chain of another type; and semi- or full-interpenetrating polymer networks in which a polymer of another kind is entrapped in self-cross-linked CS network. In addition to the ionic or covalent bonds as main interaction that form the networks, some secondary interactions, such as hydrogen bridges and hydrophobic interactions, also occur in CS networks. CS dissolved in weak organic acid solution becomes a polycation which can form ionic cross-links with a number of cross-linking reagents, such as acids of sulfate ions, phosphate ions, and sulfosuccinic ions and their salts. Various dialdehydes, such as glyoxal and glutaraldehyde (Pauliukaite, Ghica, Fatibello-Filho, & Brett, 2010), are used to perform the covalent cross-linking on —NH_2 sites, forming stable imine bonds between amine groups of CS polymer and aldehyde groups. Besides dialdehydes, diethylene glycol diglycidyl ether is also used and it is able to cross-link CS molecules by anchoring two epoxy groups, respectively, on two amino groups in different CS chains (Uragami, Takuno, & Miyata, 2002). Genipin (methyl (1R,2R,6S)-2-hydroxy-9-(hydroxymethyl)-3-oxabicyclo[4.3.0] nona-4,8-diene-5-carboxylate) is a natural cross-linker for CS cross-linking. It is much less toxic than glutaraldehyde and many other commonly used synthetic cross-linking reagents (Mi, Shyu, & Peng, 2005). Epichlorohydrin is another cross-linker which reacts with —OH groups under weak basic conditions according to Fig. 6 (Zeng & Ruckenstein, 1996).

3. Chitosan membrane for polymer electrolyte membrane fuel cell

The interior part of a PEFC is polymer electrolyte or proton exchange membrane which separates anode from cathode. As electron nonconductive materials, proton exchange membranes transfer newly formed protons from anode to cathode side of the cell. For such an application, an ideal proton exchange membrane should fulfill a number of requirements including high proton conductivity, long-term chemical and mechanical durability under heated and humidified conditions. A primary goal is to find stable polymer-based materials with ionic conductivities within the range of mS cm^{-1} at temperatures up to 100 °C (López-Chávez et al., 2005). To a lot of polymer membranes, ionic conductivity increases with water content, and thus hydration is of significance to achieve a high conductivity, especially at high temperatures. Perfluorinatedionomers such as Nafion, with fluoroalkyl ether side chains and sulfonic acid end groups on polytetrafluoroethylene backbones, have been the most commonly used polymer electrolyte membrane so far. Nafion material is also used as electrode binder which facilitates ionic conduction, provides mechanical support for catalyst particles, and enhances dispersion of catalyst particles in the catalyst layer. Nafion possesses many desirable properties as a polymer electrolyte, and yet it is very expensive and loses ionic conductivity if not sufficiently hydrated. As a low-cost and eco-friendly biopolymer, CS-based membrane electrolyte is being studied as alternative candidate for PEFC application to possibly produce economical fuel cells.

For application in a direct methanol fuel cell, PEM also needs to have a low methanol crossover. The commonly used Nafion membrane has relatively high methanol permeability. To alleviate the problem of methanol crossover, methanol is usually feed to the anode chamber as a dilute solution, which results in low energy density, and a relatively thick Nafion membrane is used, which increases cell resistance. CS is able to significant reduce methanol permeability, which makes CS attractive for use in DMFCs. Table 1 summarizes chitosan-based membranes examined in polymer electrolyte membrane-based fuel cells and their conductivity and methanol crossover properties.

3.1. Self-cross-linked and salt-complexed chitosan

In its dry state, CS has a very low electrical conductivity. However, CS can be used as a polymer matrix for ionic conduction. When solvated with lithium salt (Soontarapa & Intra, 2006) or proton donor salts such as ammonium salts (Du, Bai, Chu, & Qiao, 2010a; Du, Bai, Chu, & Qiao, 2010b; Majid & Arof, 2005, 2009), ionic conductivity of CS membrane is enhanced. The addition of salts leads to the formation of complexation between salts and CS matrix, and also enhancement of amorphous nature (Du et al., 2010b). The conductivity of salt-complexed CS membrane is dependent on the number of mobile ions and mobility (Majid & Arof, 2005), and coulombic interaction between salts and functional groups of CS (Du et al., 2010b).

The ionic conduction of polymer electrolytes is dominated by amorphous phase rather than crystalline phase (Du et al., 2010b).

Table 1
Summary of properties of chitosan-based membranes.

Membrane	Ionic conductivity, S cm^{-1}	Methanol permeability, cm^2 s^{-1}	References
CS–H_2SO_4–$LiNO_3$	6.64×10^{-2}, 100% R.H., H_2, RT		Soontarapa and Intra (2006)
CS–H_3PO_4–Al_2SiO_5–NH_4NO_3	1.82×10^{-4}, RT		Majid and Arof (2009)
CS–H_2SO_4	2×10^{-2}, hydrated, 60 °C	8.0×10^{-7}, 12 mol L^{-1} MeOH, 20 °C	Mukoma et al. (2004a, 2004b)
CS–glutaraldehyde–sulfosuccinic acid	4.52×10^{-2}, hydrated, 25 °C	9.6×10^{-7}, 25 °C	Dashtimoghadam et al. (2010)
Sulfonated CS	3.1×10^{-2} at 80 °C	4.7×10^{-7}, 2 M MeOH	Xiang et al. (2009)
PVA/CS (glutaraldehyde)	9.9×10^{-3} at 100% R.H.	9.45×10^{-8}, 50% MeOH	Smitha et al. (2005a)
Phosphonic CS/PVA (formaldehyde, Na_2SO_4, H_2SO_4)	2.48–4.29×10^{-2}	0.49–1.03×10^{-7}, 30% MeOH	Binsu et al. (2006)
CS/PAA	3.8×10^{-2}, hydrated, RT	3.9×10^{-8}, 30 °C, 50% MeOH	Smitha et al. (2004)
CS/sodium alginate	4.2×10^{-2}, 100% R.H., 30–32 °C	4.6×10^{-8}, 30–32 °C, 50% MeOH	Smitha et al. (2005b)
CS/P(AA-AMPS) (H_2SO_4)	3.59×10^{-3}, hydrated, 30 °C	2.41×10^{-7}, 5 M MeOH	Jiang, Zheng, Wu, Wang, et al. (2008)
CS/PSSA-MA (H_2SO_4)	$>10^{-2}$, hydrated, RT		Seo et al. (2009)
CS/PVP (H_2SO_4, glutaraldehyde)	2.4×10^{-2}, hydrated, RT	7.3×10^{-8}, 30 °C, 50% MeOH	Smitha et al. (2006)
CS/silica (H_2SO_4)	1.6–2.9×10^{-2}, hydrated, 20 °C	6.31–11.4×10^{-7}, 2 M MeOH	Wang et al. (2009)
N-p-carboxybenzyl CS/silica/PVA (HCHO, H_2SO_4)	1.92–5.31×10^{-2}, hydrated, 30 °C	2.0–10.0×10^{-7}	Tripathi and Shahi (2008)
CS/phosphorylated titanate nanotube (H_2SO_4)	1.58–1.75×10^{-2}, hydrated, 20 °C	6.42–8.64×10^{-7}, 2 M MeOH	Wang, Zhao, et al. (2010)
CS/organophosphorylated titania submicrospheres (H_2SO_4)	1.14×10^{-2}, 25 °C	2.8×10^{-7}, 2 M MeOH	Wu et al. (2010)
CS/beta zeolite–SO_3H (H_2SO_4)	1.17×10^{-2} to 1.49×10^{-2} hydrated, 20 °C	5.8–9.55×10^{-7}, 2 M MeOH	Wang, Yang, et al. (2008)
CS/biomimetic mineralized hydroxyapatite	1.46–0.963×10^{-2}, hydrated	6.85–8.11×10^{-7}, 2 M MeOH	Zhao et al. (2011)
CS/$STiO_2$ (H_2SO_4)	1.14–1.86×10^{-2}, hydrated, 20 °C	5.69–7.62×10^{-7}, 2 M MeOH	Wang, Zhang, et al. (2010)
CS/phosphomolybdic acid	1.5×10^{-2}, 25 °C	2.7×10^{-7}, ambient temperature	Cui et al. (2009)
CS/hydroxyethyl cellulose/stabilized phosphotungstic acid (H_2SO_4)	5.9×10^{-3}, hydrated, 70 °C		Mohanapriya et al. (2009)
CS/PVA/organophosphorus acids	$\sim 3.5 \times 10^{-2}$, hydrated, 20 °C	$\sim 3 \times 10^{-7}$, ambient temperature, 5 M MeOH	Jiang, Zheng, Wu, and Pan (2008)
CS/sulfonated PSF (H_2SO_4)	4.6×10^{-2}, hydrated, RT		Smitha et al. (2008)
CS/SPAEK (glutaraldehyde, H_2SO_4)	3.9–4.4×10^{-2}, hydrated, 25 °C	2.81–9.79×10^{-7}, 25 °C, 1 M MeOH	Zhong et al. (2008)
CS/phosphotungstic acid/SPAEK	7.5–8.6×10^{-2}, hydrated, 25 °C	0.12–1.71×10^{-7}, 25 °C, 10 M MeOH	Zhao et al. (2009)
Nafion-implanted CS/PVA (H_2SO_4)	10^{-2}, hydrated, ambient temperature	1.0–2.2×10^{-6}, ambient temperature	Zhang et al. (2009)
CS functionalized montmorillonite/Nafion	4.5–8.3×10^{-2}, 95% R.H., 25 °C	0.57–1×10^{-7}, 25 °C	Hasani-Sadrabadi et al. (2010)
CS/Nafion triple layer (glutaraldehyde, sulfosuccinic acid)	8.8×10^{-2}, 95% R.H., 25 °C	2.52×10^{-7}, 25 °C	Hasani-Sadrabadi et al. (2012)
(CS/SPAEK) multilayer/Nafion	7.0×10^{-2}, hydrated, 25 °C	2.7×10^{-7},10 M MeOH	Lin et al. (2009)
(CS/silicotungstic acid) multilayer/Nafion	5.33×10^{-2}, 100% R.H., 95 °C		Zhang et al. (2012)
CS-adenosine triphosphate/Nafion	1.58×10^{-1}		Majedi et al. (2012)
CS/KOH/CS (glutaraldehyde)	10^{-2}, hydrated, RT		Wan et al. (2005)
Quaternized CS (glutaraldehyde)	4.8–7.5×10^{-3}, hydrated, RT		Wan et al. (2008)
Quaternized PVA/CS (glutaraldehyde)	10^{-3}–10^{-2}, hydrated, 30 °C	5.68–4.42×10^{-6}, 30 °C, 1 M MeOH	Xiong et al. (2008)
Quaternized CS/PS (glutaraldehyde)	0.7–5.5×10^{-2}, in KOH, 75 °C		Wang, He, et al. (2011)

Plasticization is able to increase the amorphous content, and thus improves the conductivity of a solid polymer electrolyte. It was found that the conductivity of CS acetate–NH_4NO_3 membrane was increased from 10^{-5} to 10^{-3} S cm^{-1} by adding a plasticizer (Ng & Mohamad, 2006). The most used plasticizers include ethylene carbonate, propylene carbonate, dimethyl carbonate and diethyl carbonate (Ng & Mohamad, 2006; Winie, Majid, Khiar, & Arof, 2006).

Cross-linking is proposed to reduce crystallinity of CS membrane and simultaneously enhance the ionic transport (López-Chávez, Oviedo-Roa, Contreras-Pérez, Martínez-Magadán, & Castillo-Alvarado, 2010). It was found that the ion exchange capacity of CS membranes increased from 2.50 meq g^{-1} for uncross-linked membranes to 5.15–5.66 meq g^{-1} for sulfuric acid cross-linked CS membranes (Soontarapa & Intra, 2006). An atomistic molecular modeling and simulation study suggested that ionic conductivity of glutaraldehyde cross-linked CS was lower than that of sulfuric acid cross-linked CS (López-Chávez et al., 2010). A simulation study of polymer–electrolyte system consisting of CS, H_2O molecules, H_3O^+, OH^-, $SO_4{}^{2-}$ ions, suggested that sulfates anchored in the amino groups of CS membrane led the mobility of the charge carrier ionic species, and the percent of water and sulfates might improve the ionic conductivity in CS membranes to a value of 2×10^{-2} S cm^{-1} (López-Chávez et al., 2005).

Sulfuric acid cross-linked CS membrane was examined for application in DMFCs. It was found that its methanol permeability was almost three times lower than that for Nafion 117 membrane. An increased methanol concentration resulted in decreased methanol permeability for sulfuric acid cross-linked CS compared to increased methanol permeability for Nafion 117 membrane (Mukoma, Jooste, & Vosloo, 2004a, 2004b). The degree of deacetylation of CS was found to affect the water uptake and hence the proton transfer. A passive air breathing DMFC using sulfuric acid cross-linked CS membrane delivered a peak power density of 27.4 mW cm^{-2} under atmospheric condition (Osifo & Masala, 2010, 2012). CS with a higher degree of deacetylation achieved higher power density (42.4 mW cm^{-2}), possibly due to a higher proton flux. However, this result was still much lower than that of Nafion 117 membrane (75 mW cm^{-2}).

A binary cross-linking agent, consisting of sulfosuccinic acid as ionic cross-linker and glutaraldehyde as covalent cross-linker, was used to make cross-linked CS membranes (Fig. 7). It was found that introducing sulfosuccinic acid as cross-linker in addition to glutaraldehyde improved proton conductivity, and yet also increased methanol permeability as compared to using glutaraldehyde alone. The presence of hydrophilic —SO_3 groups from sulfosuccinic acid leads to the formation of more accessible pathway for proton migration through the membrane. A peak power density of 41 mW cm^{-2} was achieved by a sulfosuccinic acid and glutaraldehyde cross-linked CS membrane, at 60 °C in a DMFC (Dashtimoghadam, Hasani-Sadrabadi, & Moaddel, 2010).

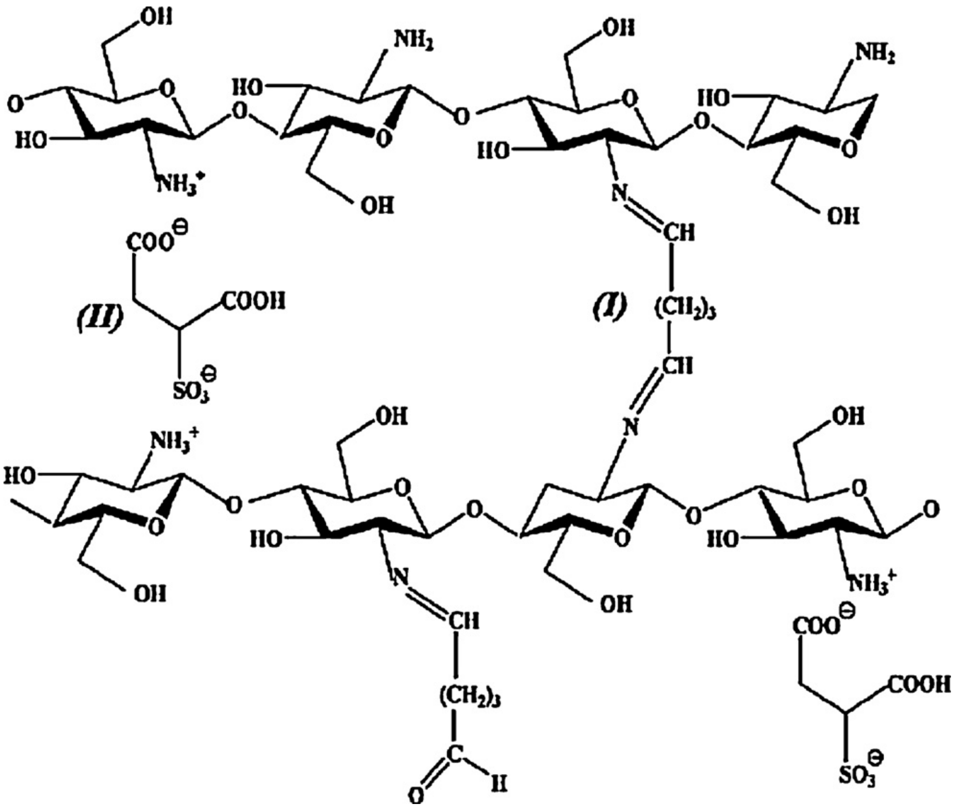


Fig. 7. Structure of cross-linked CS, I: amino and aldehyde groups reaction; II: ionic interaction of sulfosuccinic acid and CS (Dashtimoghadam et al., 2010).

3.2. Chitosan-based polymer blend

The aim of making polymer blends is generally to combine desirable properties of each component within a near-homogeneous material, while overcoming some of their weaknesses, although the latter goal is not always achieved (Chikh, Delhorbe, & Fiche, 2011). A chitosan sulfate blend membrane was prepared by first sulfonating CS to introduce sulfonic groups, and then cross-linking between the sulfonic groups in CS sulfate and the amino groups in pure CS monomers (Xiang, Yang, Guo, & Cui, 2009). CS sulfate and CS monomer have similar chemical structure, which results in good physical stability and structure compatibility of their blend. It was found that the prepared sulfonated CS membrane had enhanced proton conduction and methanol resistance as compared to pure CS membrane. This sulfonated CS blend membrane had improved tensile strength at dry state compared to pure CS membrane, and yet at wet state they were found to be comparable. Tensile strength of sulfonated CS membrane was much higher than Nafion, and yet breaking elongation of the dry membrane was not as good as Nafion.

CS and poly(vinyl alcohol) (PVA) are miscible in one another, and compatible for blending. An increase in ionic conductivity was observed after blending PVA of up to 50 wt.% into NH_4I doped CS membrane, possibly because blending CS with PVA provides more salt complexation sites e.g. the carbonyl group (Buraidah & Arof, 2011). A glutaraldehyde cross-linked PVA/CS blend membrane displayed higher tensile strength and elongation at break as compared to pure PVA membrane, although did not offer much if any advantage in terms of ionic conductivity and methanol permeability over pure PVA membrane (Smitha, Sridhar, & Khan, 2005a). The introduction of phosphonic acid group in CS matrix may serve to improve its ion exchange capacity. A blend of phosphorylated CS and PVA membrane exhibited proton conductivity of the same order of magnitude as Nafion membrane (Binsu, Nagarale, Shahi, & Ghosh, 2006). Sulfonated polyethersulfone was incorporated with a sulfosuccinic acid cross-linked CS/PVA blend membrane, which was found to enhance both ionic conductivity and mechanical properties of CS/PVA membrane (Meenakshi, Bhat, Sahu, Sridhar, et al., 2012).

CS is hydrophilic and thus has a high degree of swelling. An excessively high level of water uptake increases the fragility of the membrane, and makes it less durable in a fuel cell. To overcome the disadvantage of loss in mechanical strength in the wet state, CS is blended with tough polymer such as poly(vinyl pyrrolidone) (PVP). PVP, upon blending with CS followed by cross-linking with glutaraldehyde, forms a semi-interpenetrating network as shown in Fig. 8. Further cross-linking the polymer blend with sulfuric acid reduces methanol permeability and enhances ionic conductivity (Smitha, Sridhar, & Khan, 2006).

Mixing of negatively and positively charged polymer leads to the formation of a complex by electrostatic interaction which enforces a restriction in the polymer chain mobility and as a result an increase in the rigidity or the tensile strength and yet a decrease in the elongation at break. CS and sodium alginate form polycomplex membrane via ionic cross-linking as shown in Fig. 9 (Smitha, Sridhar, & Khan, 2005b). Alginate, a polysaccharide extracted from seaweed, is used as a membrane material for the dehydration of ethanol mixture. CS/sodium alginate blend membrane exhibited higher tensile strength, and yet lower elongation at break, than homopolymers. This blend membrane also had higher ion exchange capacity, lower methanol permeability as compared to both CS and sodium alginate alone.

Fig. 10 shows ionically cross-linked polymer complex of cationic CS and anionic poly(acrylic acid) (PAA). The complex membrane with 50 wt.% of CS and 50 wt.% of PAA exhibited proton conductivity of 0.038 S cm^{-1} which is higher than that of a pure CS membrane (Smitha, Sridhar, & Khan, 2004). However the complex membrane with other proportions had lower conductivity as compared to pure

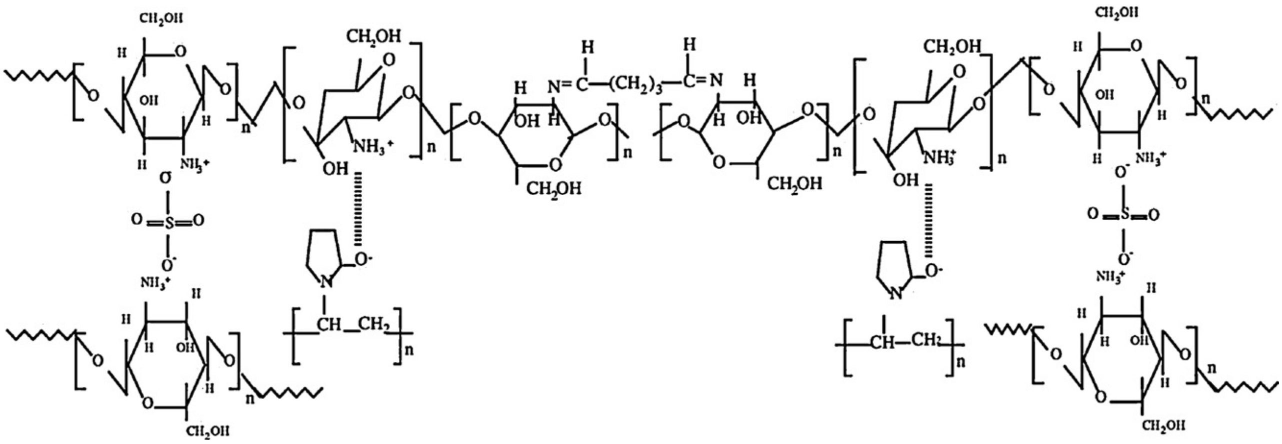


Fig. 8. Semi-interpenetrating network of CS and PVP blend with cross-linking agents (Smitha et al., 2006).

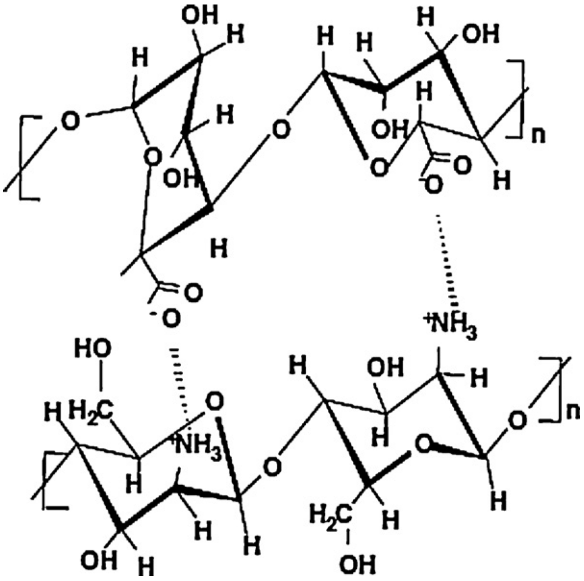


Fig. 9. Polyelectrolyte complex of CS and sodium alginate (Smitha et al., 2005b).

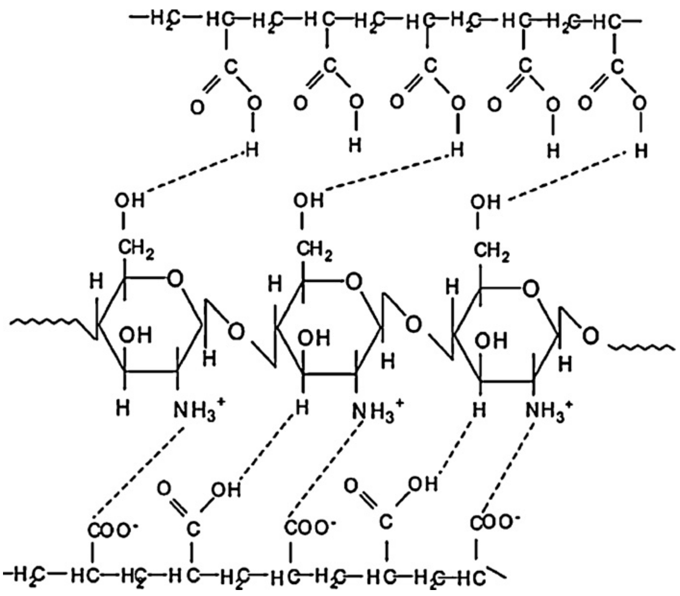


Fig. 10. Polyelectrolyte complex of CS and PAA (Smitha et al., 2004).

CS. Thus, the weight ratio of polycation and polyanion is important to achieve the optimized proton conductivity. The addition of salt (NaCl, NH_4Cl, $MgCl_2$) internally improved ionic conductivity of CS/PAA complex membrane with some sacrifice in methanol barrier property (Gümüşoğlu, Arı, & Deligöz, 2011). Treatment with sulfuric acid further increased conductivity of some of the salt complexed CS/PAA membranes and meanwhile reduced methanol permeability (Gümüşoğlu et al., 2011).

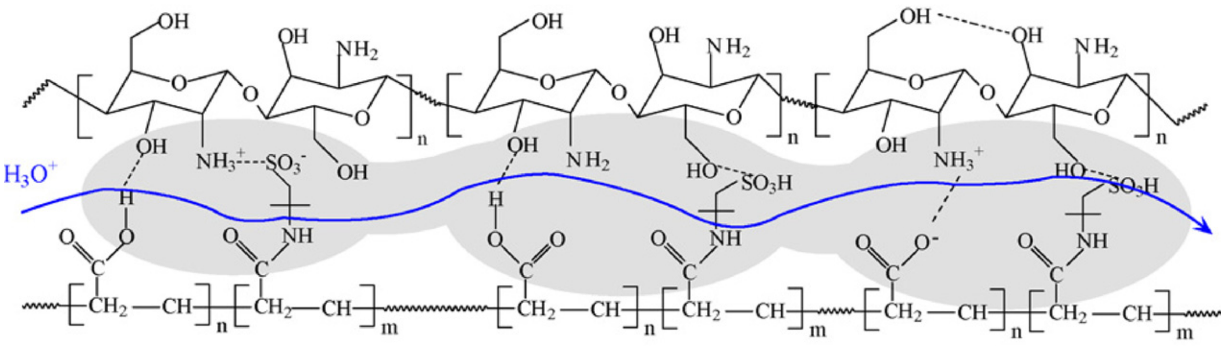
Anionic polyelectrolyte, acrylic acid-2-acrylamido-2-methylpropane sulfonic acid (P(AA-AMPS)) was also used to form polymer complex with CS. As shown in Fig. 11, P(AA-AMPS) has a high density of carboxyl and sulfonic groups, and serves as proton-conducting component. The complex membrane had a notable reduction in methanol permeability and an increase in proton conductivity as compared to pure CS membrane (Jiang, Zheng, Wu, Wang, & Wang, 2008). Vehicle mechanism and Grotthus or "jump" mechanism, as illustrated in Fig. 11, were reported to occur in the membrane and the latter seemed to be the predominant proton transfer mechanism. Oxidative durability was also improved by introducing the anionic P(AA-AMPS) into the cationic CS matrix.

A polymer complex of poly(4-styrenesulfonic acid-co-maleic acid) (PSSA-MA) and CS was prepared by cross-linking CS and PSSA-MA via both esterification reaction and ionic complex formation, as shown in Fig. 12. PSSA-MA contains both strong acid ($-SO_3$) and weak acid (−COOH), which can be used for ionic cross-linking and proton conduction (Seo, Koh, Roh, & Kim, 2009). Properties of blend membrane, such as mechanical property, and ionic conductivity, were found to be impacted by PSSA-MA content of the membrane.

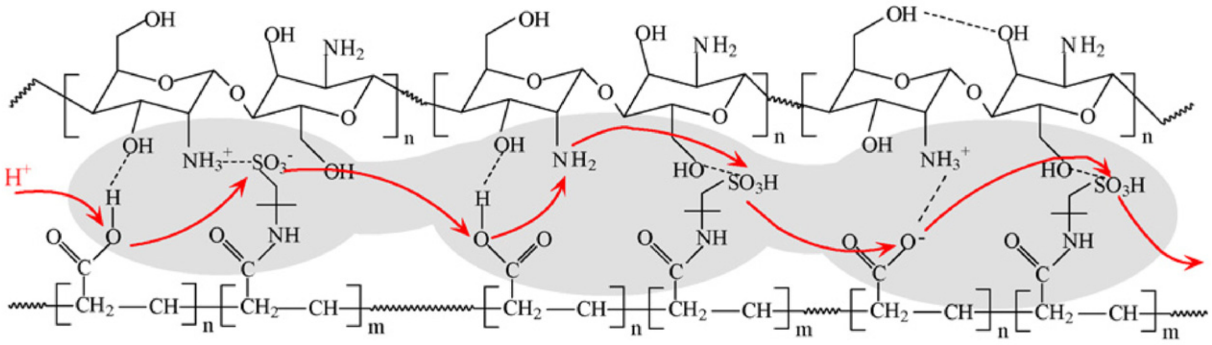
3.3. *Chitosan-based composite membrane*

3.3.1. *Chitosan/inorganic filler composite*

A composite membrane often has an inorganic moiety combined with a polymeric material. A review on organic–inorganic composite polymer electrolyte membranes for fuel cell applications can be found in Tripathi and Shahi (2011). The properties of the composite membranes made of interacting components not only depend on the nature of the polymeric and inorganic solid used but also on their amount, homogeneous dispersion, size and orientation of the solid particles dispersed in the polymeric matrix (Dupuis, 2011). Yuan et al. (2007) summarized two strategies for incorporating inorganic materials into a polymer matrix: (i) in situ formation of inorganic particles within polymer matrix through sol–gel reaction or crystallization. In some cases, the covalent bonds are formed between organic and inorganic components; (ii) physical mixing of organic solutions with inorganic fillers followed by



(a) vehicle mechanism



(b) Grotthus mechanism

▨ hydrophilic region ------- hydrogen or ionic bonding

Fig. 11. Tentative illustration of the proton transfer mechanism in CS/P(AA-AMPS) membranes: (a) vehicle mechanism and (b) Grotthus mechanism (Jiang, Zheng, Wu, Wang, et al., 2008).

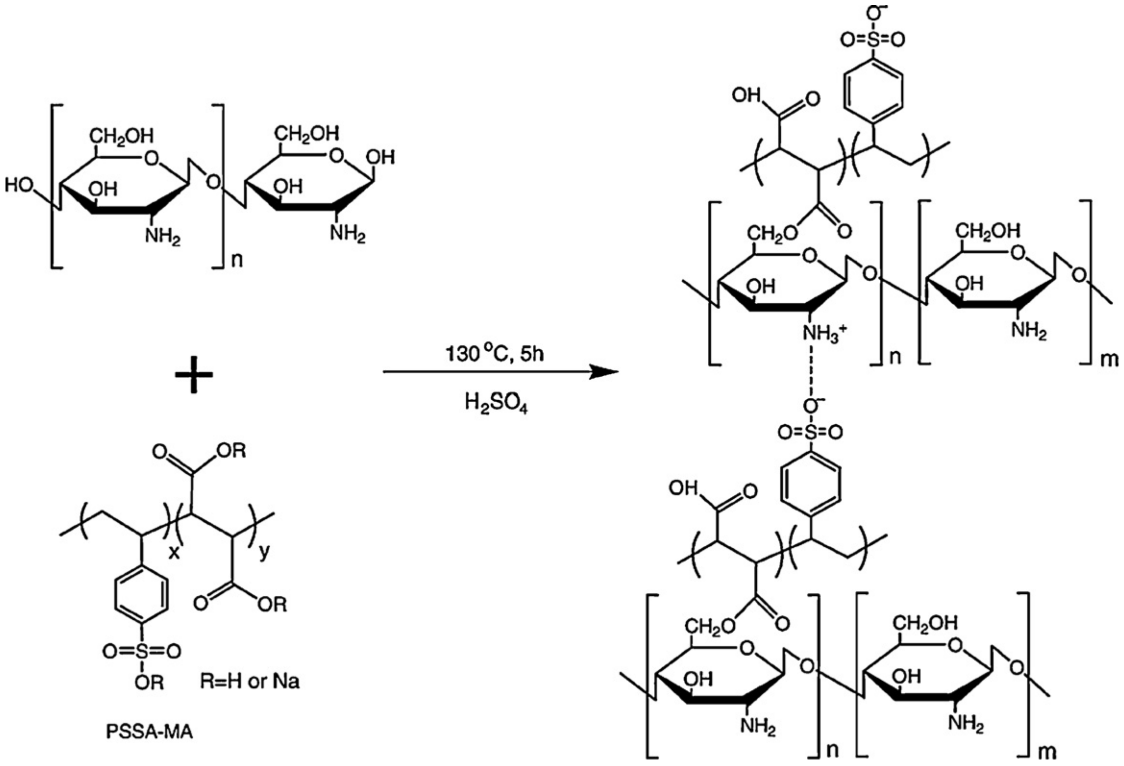


Fig. 12. Synthetic procedure for cross-linked membranes consisting of CS and PSSA-MA (Seo et al., 2009).

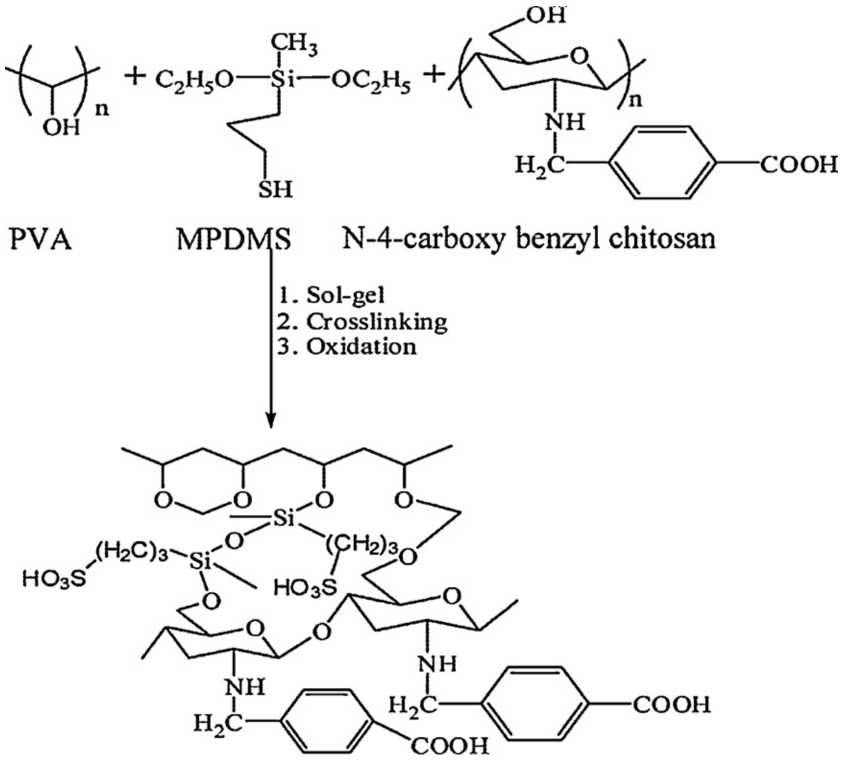


Fig. 13. Schematic reaction route for the preparation of sulfonated silica/N-p-carboxy benzyl CS/PVA hybrid membrane (Tripathi & Shahi, 2008).

simple casting. Organic and inorganic components usually interact through hydrogen bonding, van der Waals contacts, and/or electrostatic forces. The interfacial morphology of composite membranes has a significant impact on the overall membrane properties. Interfacial morphology is influenced by polymer chain flexibility and interfacial stress generated during membrane formation. There is a large choice of inorganic materials which serve to improve polymer membrane properties in various ways. The objectives for making chitosan–inorganic composite membranes reported in literature generally fall into the following categories: (1) balance hydrophilic-hydrophobic nature of chitosan; (2) reducing fuel crossover; (3) improving the mechanical and thermal strengths; (4) enhancing the proton conductivity by introducing solid inorganic proton conductors (Tripathi & Shahi, 2011).

Embedding nonporous or porous inorganic fillers with proper structure and pore size within the membrane play an important role in suppressing methanol crossover because they can interfere with polymer chain packing and create a more tortuous diffusion path. Hygroscopic oxides such as $(SiO_2)_n$, ZrO_2, TiO_2, and Al_2O_3 are used to increase water retention capacity of polymer composite at low relative humidity conditions, although they do not have significant intrinsic proton conductivity (Dupuis, 2011). A composite membrane of CS and oxide (MgO, CaO, SiO_2, or Al_2O_3) was found to possess conductivities between 10^{-3} and $10^{-2}\,\mathrm{S\,cm^{-1}}$ in wet state (Ramírez-Salgado, 2007). In many cases, proton conductivity decreases with an increase in filler content due to the relatively low proton conductivity of the fillers themselves and their considerable dilution effect on the proton exchange groups in the original polymer matrix. For instance, it was found that the proton conductivity decreased with the incorporation of silica particles (Wang, Zhang, Jiang, Yang, & Xiao, 2009). Thus, inorganic fillers are functionalized before embedding into CS membrane to reduce methanol permeability while simultaneously preserve or enhance proton conductivity. A series of surface functionalized silica submicrospheres with different functional groups (including sulfonic, carboxylic, and quaternary groups) were embedded into CS matrix. After modification of silica, proton conductivity increased, and sulfonated silica and carboxylated silica/CS demonstrated higher conductivity than pure CS membrane (Wang et al., 2009). A sulfonated silica/N-p-carboxy benzyl CS/PVA hybrid membrane was prepared using the sol–gel method and cross-linking with HCHO and H_2SO_4, followed by oxidation of the thiol group into the sulfonic acid group, as illustrated in Fig. 13 (Tripathi & Shahi, 2008). The hydrophobic aromatic ring introduced into CS is expected to alleviate the problem of excess swelling associated with CS membrane. Both —COOH on grafted CS and $—SO_3H$ on silica serve as proton conductor.

It was reported that the addition of titanate nanotubes improved methanol barrier property and also mechanical strength of CS membrane, and yet a decrease in proton conductivity with increased amount of titanate nanotubes was observed (Geng et al., 2010). The incorporation of phosphorylated titanate nanotubes not only improved methanol barrier property, but also increased proton conductivity by facilitating the proton transfer by constructing continuous conductive channels with the aid of P—OH groups and adsorbed water molecules (Wang, Zhao, et al., 2010). Organophosphorylated titania submicrospheres were synthesized by amino trimethylenephosphonic acid treatment of titania, and incorporated into CS membranes (Wu, Hou, Wang, Xiao, & Jiang, 2010). Ionic cross-linking occurred between $—NH_2$ groups on CS and $—PO_3H_2$ groups on organophosphorylated titania, which led to better compatibility between the inorganic fillers and the polymer matrix. Both increased ionic conductivity and reduced methanol permeability were achieved by this composite membrane as compared to pure CS membrane.

Another inorganic filler is zeolite which is aluminosilicates with a framework structure enclosing cavities that may be occupied by large ions or water molecules (Dupuis, 2011). Properties of CS/zeolite membrane are highly influenced by pore size and content of zeolite particles, and their hydrophilic/hydrophobic nature (Wang, Zheng, et al., 2008). For instance, appropriate addition of zeolite was found to enhance the mechanical strength, whereas excessive zeolite caused the reduction in mechanical strength of composite membranes due to the formation of too many interfacial voids at the interface of CS and zeolite (Wang, Zheng, et al., 2008). Incorporation of hydrophobic zeolites increased the diffusion resistance of methanol and consequently decreased the methanol permeability, whereas the opposite trend applied to hydrophilic zeolites (Wang, Jiang, Li, & Yang, 2010; Wang, Zheng, et al., 2008). Interfacial morphology of CS/zeolite membranes could be improved by homogenous incorporation of sorbitol as a plasticizer and appropriate control of membrane formation temperature (Yuan et al., 2007), and also by specific functionalization of zeolite particles (e.g. with silane coupling agent) (Wang, Jiang, et al., 2010; Wang, Yang, Zheng, Jiang, & Li, 2008; Wu et al., 2007), either of which contributed to a suppression of methanol crossover. Despite the advantage of some reported CS/zeolite membranes in methanol resistance, they had less proton conductivity as compared to pure CS membrane, possibly because incorporation of zeolite reduces the water uptake (Wang, Jiang, et al., 2010; Wang, Yang, et al., 2008; Wu et al., 2007). A way to improve ionic conductivity of CS/zeolite membrane is introducing $-SO_3H$ groups onto zeolite surface (Wang, Jiang, et al., 2010).

A great number of metal phosphates have been used as inorganic additives in polymeric composite membranes for fuel cells. Among them, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) has been demonstrated as a potential ion conductive material. Biomimetic mineralized hydroxyapatite particles were incorporated into CS matrices, and the CS/hydroxyapatite hybrid membranes exhibited enhanced ionic conductivity and reduced methanol permeability as compared to pure CS membrane (Zhao et al., 2011).

Solid superacids are used to improve properties of CS membrane, due to their hygroscopic and proton conductive properties as well as good mechanical properties. Commonly utilized solid superacids can be categorized into metal oxide supported sulfate ($M_xO_y–SO_4^{2-}$), heteropolyacid (HPA) and zeolite solid superacid. It was found that nanosized $TiO_2–SO_4^{2-}$ ($STiO_2$) enhanced mechanical strength and thermal stability of CS, since the presence of $STiO_2$ fillers inhibited mobility of CS chain. Meanwhile, the presence of $STiO_2$ particles within CS matrix induced a reduction of fractional free volume and a more tortuous diffusion pathway for methanol molecules, both of which reduced methanol permeability. However, the proton conductivity of the membrane decreased with the incorporation of $STiO_2$ particles possibly due to reduction in water uptake capacity (Wang, Zhang, Wu, Xiao, & Jiang, 2010).

HPAs, such as phosphotungstic acid ($H_3[P(W_3O_{10})_4]$), phosphomolybdic acid ($H_3[P(Mo_3O_{10})_4]$), and silicotungstic acid ($H_4[Si(W_3O_{10})_4]$), form insoluble complex with CS through strong electrostatic interaction. HPAs exhibit strong proton conductivity as high as 1.9×10^{-1} S cm^{-1} at 303 K (Nakamura & Ogino, 1982). It was found that CS/HPA membranes exhibited much larger break strength than CS membranes, but smaller elongation at break than CS membranes, attributed to the strong electrostatic interaction between HPAs and CS (Cui, Liu, Lu, & Xing, 2007; Cui, Xing, Liu, Liao, & Zhang, 2009). The ionic conductivity values of CS/HPAs were found to be higher than that of the CS membrane.

HPAs have the disadvantage of high solubility in aqueous media. Hence, HPAs are stabilized by ion-exchanging protons of HPAs with larger cations, such as cesium. Stabilized phosphotungstic acid was incorporated to a blend membrane of CS and hydroxyethyl cellulose which is a water-soluble non-ionic polymer and is blended with CS for the purpose of improving mechanical and hydrophilic properties of CS. As a result, hydrophilicity is further enhanced reducing the methanol sorption through mixed matrices. As illustrated in Fig. 14, the bigger molecular size and less polarity of the methanol molecule compared to water helps in restricting

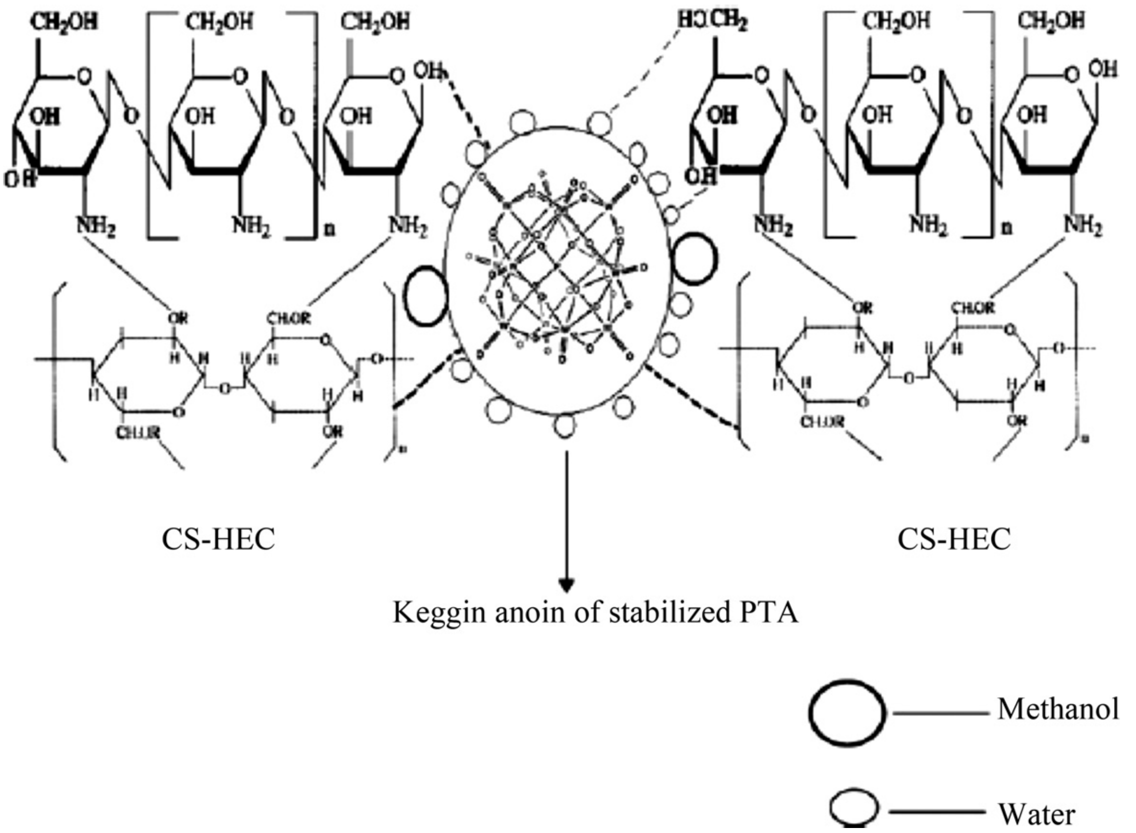


Fig. 14. Schematic representation of preferential water sorption from a methanol–water mixture in stabilized phosphotungstic acid (PTA)/CS/hydroxyethyl cellulose (HEC) membrane (Mohanapriya et al., 2009).

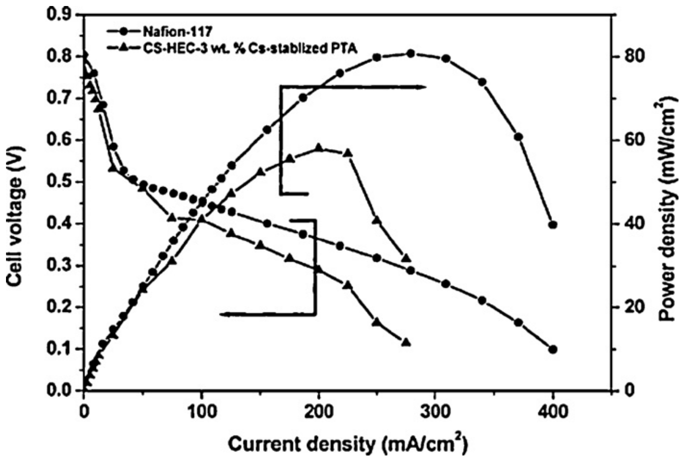


Fig. 15. Cell voltage and power density vs. current density at 343 K for Nafion 117 and stabilized phosphotungstic acid (PTA)/CS/hydroxyethyl cellulose (HEC) membrane (Mohanapriya et al., 2009).

methanol permeability through the mixed-matrix membrane. The incorporation of phosphotungstic acid was found to improve both mechanical properties and proton conductivity of CS/hydroxyethyl cellulose membrane, and yet the values were lower than Nafion 117 membrane (Mohanapriya et al., 2009). A DMFC with stabilized phosphotungstic acid/CS/hydroxyethyl cellulose membrane delivered peak power density of 58 mW cm^{-2} (as shown in Fig. 15), which was lower than with Nafion 117 due to lower proton conductivity for the former.

Stabilized silicotungstic acid was added to CS/PVA networks cross-linked with sulfosuccinic acid and glutaraldehyde. The addition of stabilized silicotungstic acid enhanced proton conductivity of CS/PVA membrane, and with optimized content of stabilized silicotungstic acid, the conductivity of blend membrane was higher than that of Nafion, as shown in Fig. 16(a). It was also shown that sulfosuccinic acid cross-linked membranes gave higher ionic conductivity than glutaraldehyde cross-linked membranes due to the extra proton-conducting paths provided by sulfosuccinic acid as shown in Fig. 16(b), and yet its methanol crossover flux was also higher. In addition to the benefit in proton conductivity, stabilized silicotungstic acid also serves to restrict methanol crossover. Tensile strength was found to increase while percentage elongation decrease in comparison to CS/PVA blends membranes due to membrane rigidity by addition of stabilized silicotungstic acid. CS/PVA/stabilized silicotungstic acid hybrid membranes crosslinked with sulfosuccinic acid and glutaraldehyde delivered peak power densities of 156 mW cm^{-2} and 88 mW cm^{-2}, respectively, in a DMFC at 70 °C, as illustrated in Fig. 17 (Meenakshi, Bhat, Sahu, Alwin, et al., 2012).

Organophosphorus acids (amino trimethylenephosphonic acid, ethylene diaminetetra(methylene phosphonic acid) and hexamethylenediamine tetra(methylene phosphonic acid)) were incorporated into CS/PVA blend (Jiang, Zheng, Wu, & Pan, 2008). Organophosphorus acid has, at the both ends of the alkyl chains, a couple of $-PO_3H_2$ groups which act as ionic cross-linking sites and also contribute to proton conduction. The addition of organophosphorus acids improved proton conductivity of PVA/CS blend membrane, and retained its methanol barrier property. The oxidation stability was also significantly improved by incorporation of organophosphorus acids. A certain amount of organophosphorus acid addition enhanced tensile strength, and yet reduced elongation.

CS was combined with plant hormones, either 1-naphthalene acetic acid (NAA), 4-chlorophenoxy acetic acid (CAA), or 3-indole acetic acid (IAA), to make proton conducting bio-composite membranes (Mohanapriya et al., 2011). These plant hormones belonging to the auxin group are involved in proton transport related process in biological system. It was found that the addition of plant hormones improved ionic conductivity and also tensile strength of CS membrane. As shown in Fig. 18, peak power densities of 11, 16, 18, 25 mW cm^{-2} were achieved by CS, CS/NAA, CS/CAA, and CS/IAA, respectively, in conformity with the proton conductivity values. However the values were much lower than that of Nafion 117 membrane.

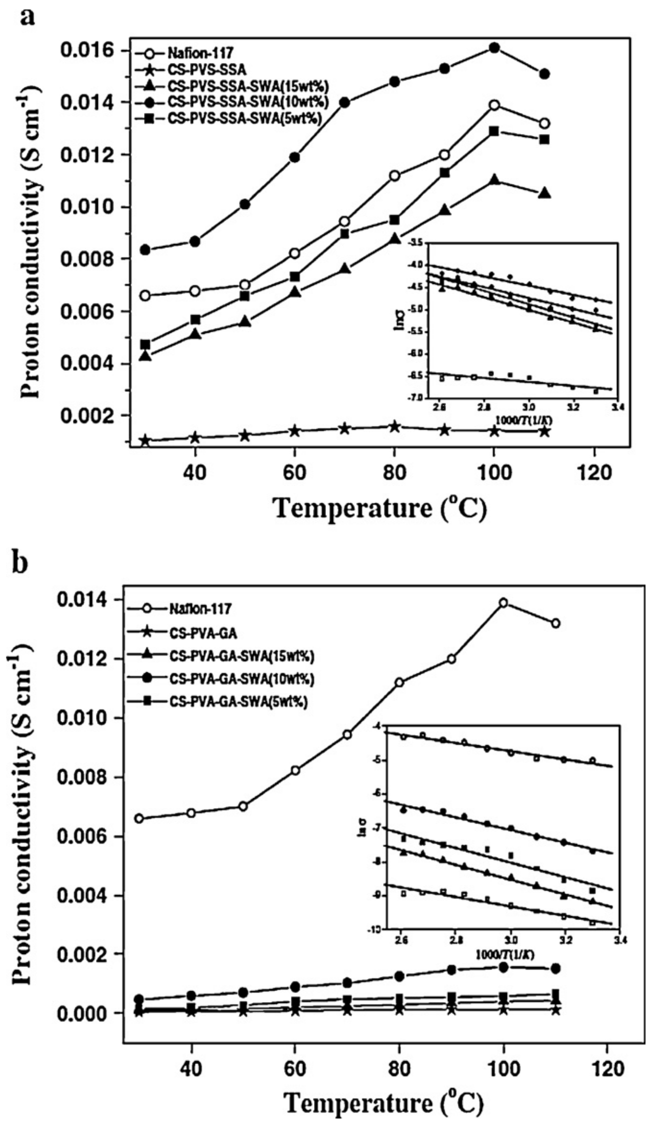


Fig. 16. Proton conductivity vs. temperature plot of (a) Nafion 117, sulfosuccinic acid (SSA) cross-linked CS/PVA, and CS/PVA/stabilized silicotungstic acid (SWA) membranes; (b) Nafion 117, glutaraldehyde (GA) cross-linked CS/PVA, and CS/PVA/stabilized silicotungstic acid (SWA) membranes (Meenakshi, Bhat, Sahu, Alwin, et al., 2012).

3.3.2. *Chitosan/polymer composite*

Inexpensive synthetic polymer, such as poly(aryl ether ketone), polysulfone, and polybenzimidazole are being investigated as alternative to Nafion, due to their desirable durability. These polymers can be converted to sulfonated polymer by sulfonation process, which improves their proton conductivity (Ahmad, Kamarudin, Hasran, & Daud, 2010). These synthetic membranes are used in combination with CS membrane to make polymer composite membranes with improved properties. A composite membrane of

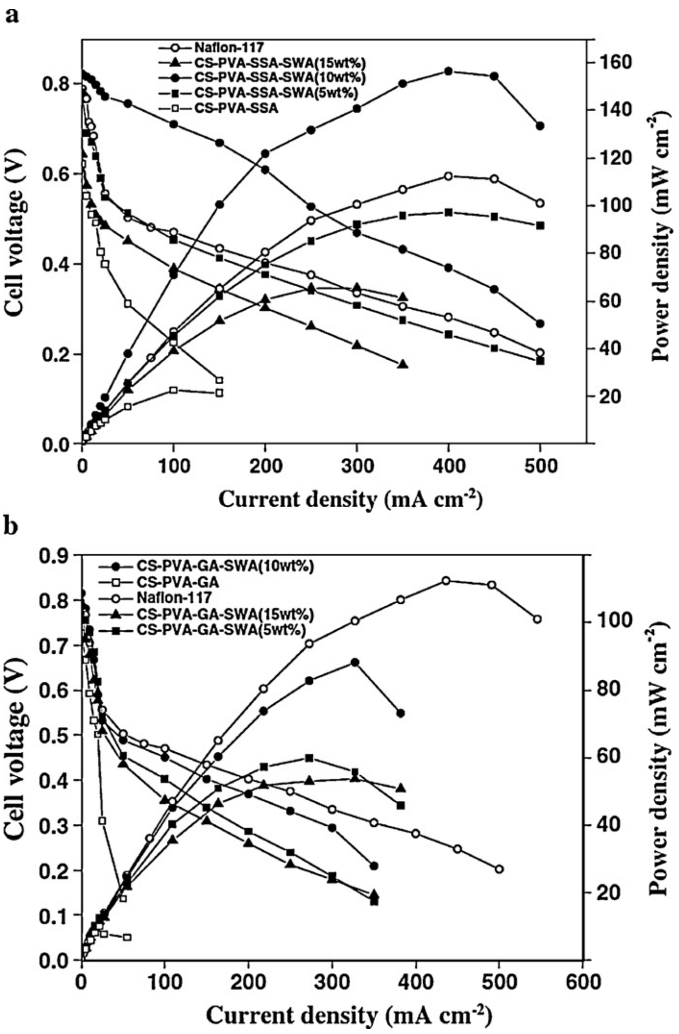


Fig. 17. Voltage and power density vs. current density plot for (a) Nafion 117, sulfosuccinic acid (SSA) cross-linked CS/PVA, and CS/PVA/stabilized silicotungstic acid (SWA) membranes; (b) Nafion 117, glutaraldehyde (GA) cross-linked CS/PVA, and CS/PVA/stabilized silicotungstic acid (SWA) membranes (Meenakshi, Bhat, Sahu, Alwin, et al., 2012).

CS/polysulfone (PSF) was prepared by casting CS layer on microporous sulfonated PSF substrate, followed by cross-linking CS with H_2SO_4 (see Fig. 19) (Smitha, Anjali Devi, & Sridhar, 2008). The interaction between PSF support and CS was enhanced through surface modification of PSF. Sulfonated PSF/CS composite demonstrated a higher ionic conductivity than CS membrane.

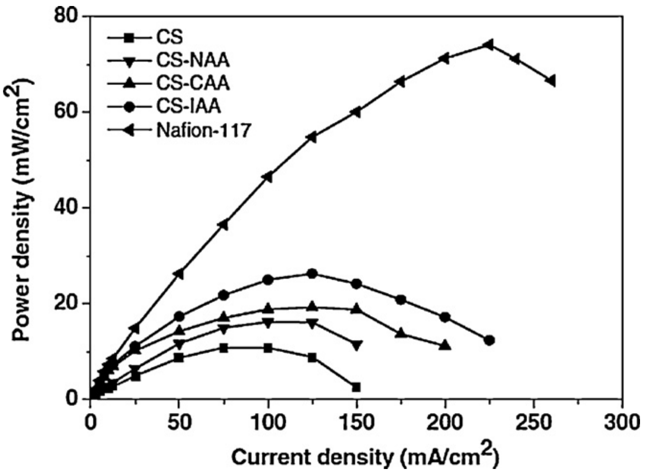


Fig. 18. Power density vs. current density curves for DMFCs operating with Nafion 117, CS, CS/IAA, CS/CAA and CS/NAA membranes at 70 °C (Mohanapriya et al., 2011).

CS was used to modify sulfonatedpoly(aryl ether ketone) (SPAEK) for reducing methanol crossover. SPAEK is a sulfonated aromatic polymer with a high sulfonation level to achieve sufficient proton conductivity. Large content of sulfonic acid groups leads to undesirable high swelling and excessive methanol crossover. A CS layer was coated on the surface of SPAEK membrane, followed by cross-linking CS with glutaraldehyde and sulfuric acid. The addition of CS layer was found to depress methanol crossover, and yet slightly decrease the proton conductivity of the original SPAEK membrane (Zhong, Cui, Fu, & Na, 2008).

A multilayer film was constructed onto the surface of SPAEK (bearing carboxylic groups) membrane by layer-by-layer self-assembly of polycationic CS and negatively charged phosphotungstic acid by sequential electrostatic adsorption, as illustrated in Fig. 20 (Zhao et al., 2009). The ionic conductivities of CS/phosphotungstic acid modified SPAEK membranes were superior to the pristine SPAEK membrane and comparable or even slightly higher than Nafion 117 membrane. Methanol resistance property was also greatly enhanced as compared to pristine SPAEK or Nafion membrane. Multilayer film of CS/phosphotungstic acid seemed to have positive effect on methanol resistance and yet negative effect on conductivity as compared to a bilayer film.

CS-based polymer and Nafion have been used in combination for the purpose of enhancing methanol resistance of Nafion and ionic conductivity of CS (Hasani-Sadrabadi, Dashtimoghadam, Majedi,

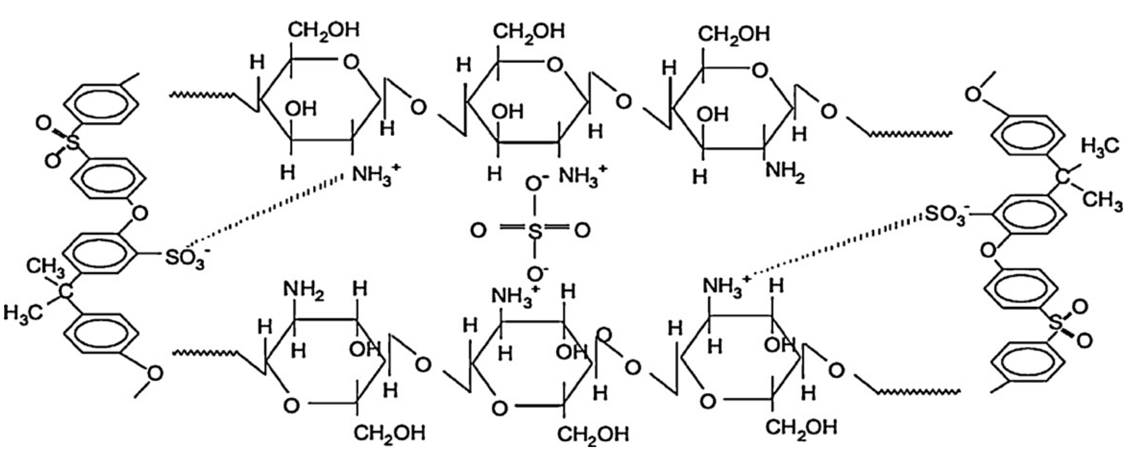


Fig. 19. Structure of CS and sulfonated PSF composite (Smitha et al., 2008).

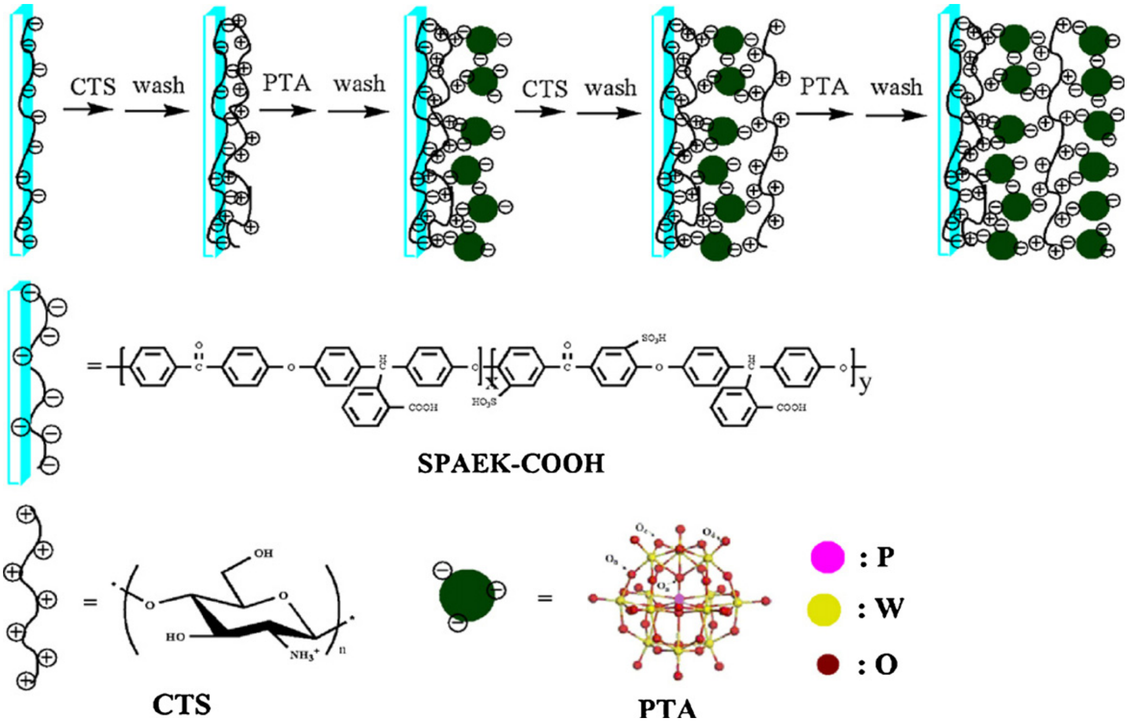


Fig. 20. Schematic representation of the fabrication of CS/phosphotungstic acid (PTA) multilayer films on SPAEK membrane (Zhao et al., 2009).

Emami, & Moaddel, 2011; Zhang, Cui, Liu, Xing, & Zhang, 2009). Two kinds of interaction could be expectable between CS and Nafion which are electrostatic interaction between ammonium ion of CS and sulfonic groups of Nafion, and hydrogen bonding between Nafion and hydroxyl groups of CS (Hasani-Sadrabadi, Dashtimoghadam, Majedi, & Kabiri, 2009). CS functionalized nanoclay montmorillonite was incorporated into Nafion and as a result a reduced methanol permeability was observed (Hasani-Sadrabadi et al., 2009, 2010). Cationic CS acted as an intercalating agent for functionalization of montmorillonite with negative surface. It was found that CS functionalized montmorillonite/Nafion had higher conductivity than unmodified montmorillonite/Nafion membrane. As shown in Fig. 21, CS functionalized montmorillonite/Nafion membrane obtained significantly improved power performance and efficiency as compared to Nafion 117 (Hasani-Sadrabadi et al., 2010).

A triple-layer composite membrane comprising Nafion 105 membrane both sides coated with glutaraldehyde/sulfosuccinic acid cross-linked CS was prepared (Hasani-Sadrabadi, Dashtimoghadam, Mokarram, Majedi, & Jacob, 2012). Proton conductivity and methanol permeability measurements revealed a remarkably reduced methanol crossover and a higher conductivity for multi-layer membrane compared to Nafion 117. Moreover, DMFC tests revealed higher open circuit voltage, power density output, and overall fuel cell efficiency for the triple-layer membrane than Nafion 117, especially at concentrated methanol solutions, as illustrated in Fig. 22.

Layer-by-layer self-assembly was employed to prepare CS complex multilayer on Nafion membrane with superior methanol resistance property to Nafion (Lin, Zhao, Ma, Li, & Na, 2009; Zhang, Huang, & Shen, 2012). It was found that the proton conductivities of CS/silicotungstic acid complex layers on Nafion composite membranes decreased with increased number of CS/silicotungstic acid bilayers because the proton transfer in CS/silicotungstic acid complexes was less effective than that in pure Nafion (Zhang et al., 2012). A CS/SPAEK multilayer on Nafion composite membrane showed reduced water uptake, and methanol permeability while maintaining comparable proton conductivity to Nafion membrane (Lin et al., 2009).

4. Chitosan membrane for intermediate temperature polymer electrolyte fuel cell

Proton conductors with high proton conductivity under anhydrous and intermediate temperature (>100 °C) conditions have attracted much attention as electrolyte for a polymer electrolyte membrane fuel cell. The operation of the PEFC at higher temperatures improves the carbon monoxide tolerance of the platinum electrode and provides a higher energy efficiency. Due to its capacity of water retention, CS may serve as membrane material with reasonably good ionic conductivity at relative high temperature and low humidity conditions. Yamada and Honma (2004) prepared an anhydrous proton-conducting membrane using a composite of chitin phosphate and basic heterocycle imidazole. P—OH group of chitin phosphate is deprotonated on doping of imidazole and forms the P—O$^-$ group (see Fig. 23). This free proton strongly interacts with the nonprotonated imidazole —N= atom. A composite material of chitin phosphate and 200 wt.% imidazole showed a high proton conductivity of 7×10^{-3} S cm^{-1} at 150 °C under anhydrous conditions.

A CS/200 wt.% methanediphosphonic acid membrane was prepared and showed a proton conductivity of 5×10^{-3} S cm^{-1} at 150 °C under anhydrous conditions (Yamada & Honma, 2005). It was proposed that the phosphate group in the methanediphosphonic acid molecule forms the proton defect site (—P—O—) by the electrostatic interaction with the amino group in CS, and as a result, the neighboring proton in the methanediphosphonic acid molecule can transfer to the proton defect site without the assistance of diffusible vehicle molecules.

A microfluidic platform was developed for the synthesis of monodisperse (100 nm) CS based nanoparticles using anogelation with adenosine triphosphate (Majedi et al., 2012). As shown in Fig. 24(a), CS-adenosine triphosphate filled nanocomposites had higher conductivities in all ranges of temperature, which may be

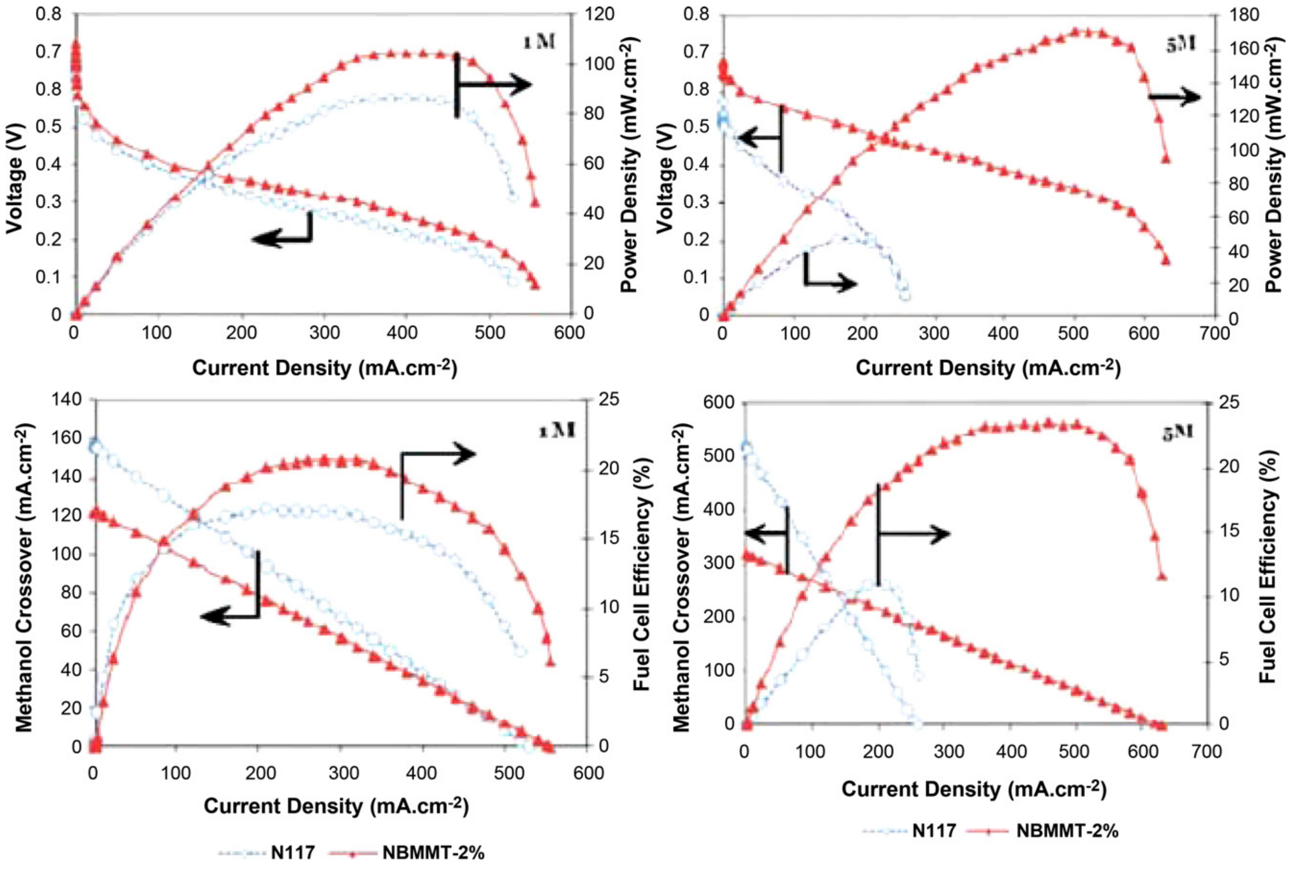


Fig. 21. Polarization curves of methanol–air single cells consisting of a NBMMT membrane and a Nafion 117, at (a) 1 M, and (b) 5 M methanol solution at 70 °C. Methanol crossover and fuel cell efficiency of corresponding fuel cells at (c) 1 M, and (d) 5 M methanol solution (Hasani-Sadrabadi et al., 2010). NBMMT stands for Nafion/CS functionalized montmorillonite (BMMT).

due to the creation of new proton transfer pathways. Moreover, the maximum power output of a PEM fuel cell based on the CS-adenosine triphosphate filled Nafion membrane was about three times higher than that for recast Nafion at the same thickness at 120 °C and 40% R.H. (see Fig. 24(b)).

5. Chitosan membrane for alkaline polymer electrolyte fuel cell

Wan et al. examined the ionic conductivity of different CS membranes, such as pure CS membranes with different degree of deacetylation and molecular weight (Wan, Creber, Peppley, & Tam Bui, 2003a), di-o-butyrylchitosan (Wan, Creber, Peppley, & Tam Bui, 2004), epichlorohydrin or glutaraldehyde cross-linked CS (Wan, Creber, Peppley, & Tam Bui, 2003b), and phosphorylated CS (Wan, Creber, Peppley, & Tam Bui, 2003c), and proposed that they can be possible candidate for use in alkaline fuel cells. When a CS membrane is swollen in water, its amino groups may be protonated and thus contribute to ionic conduction in the membrane. By using CS with high molecular weight and low degree of deacetylation, the ionic conductivity of membranes was enhanced (Wan et al., 2003a). In comparison with unmodified CS, CS with appropriate degree of cross-linking, di-o-butyryl CS, and phosphorylated CS, demonstrated increased ionic conductivity, as a result of increased hydrophilicity and decreased crystallinity (Wan et al., 2003b, 2003c, 2004).

An alkaline ion-solvated composite membrane was prepared by incorporating potassium hydroxide as ionic functionality and using CS as matrix. At room temperature, conductivity of this anion exchange membrane reached 10^{-2} S cm^{-1}. This CS-based alkaline composite membrane was tested in alkaline fuel cells, using hydrogen as a fuel, air as an oxidant, and achieved a current density of 35 mA cm^{-2} at 60 °C (Wan, Creber, Peppley, & Tam Bui, 2006; Wan, Creber, Peppley, Tam Bui, & Halliop, 2005).

An anion exchange polyelectrolyte is capable of transporting the hydroxyl anions and thus it needs cationic groups as anion exchange sites. Among various cationic groups, quaternary ammonium groups are more chemically and thermally stable than quaternary phosphonium and tertiary sulfonium groups (Couture, Alaaeddine, Boschet, & Ameduri, 2011). CS derivatives with quaternary ammonium group side chains could be fabricated into well-constructed anion conducting polymer electrolyte membranes (Xiong, Liu, Zhang, & Zhu, 2008). A CS-based anion exchange membrane was prepared by cross-linking quaternized CS derivatives (N-[(2-hydroxy-3-trimethylammonium)propyl] CS chloride) with glutaraldehyde. Cross-linked quaternized CS membrane was examined in alkaline fuel cells. A current density of 65 mA cm^{-2} was achieved at 50 °C (Wan, Peppley, Creber, Tam Bui, & Halliop, 2008). A high quaternization degree of CS results in increased ionic conductivity, and yet also high swelling which worsens membrane strength. It was found that glutaraldehyde was not effective enough for cross-linking quaternized CS with a high quaternization degree (>35%) because the resultant membrane showed poor mechanical properties. Thus, instead of glutaraldehyde, diethylene glycol diglycidyl ether, was introduced to prepare cross-linked quaternized CS (Fig. 25) (Wan, Peppley, Creber, & Tam Bui, 2010).

Polystyrene (PS) was introduced to form an interpenetrating network with quaternized CS. Polystyrene is more hydrophobic than quaternized CS and has good mechanical strength. It was found that introduction of PS improved tensile strength, and yet

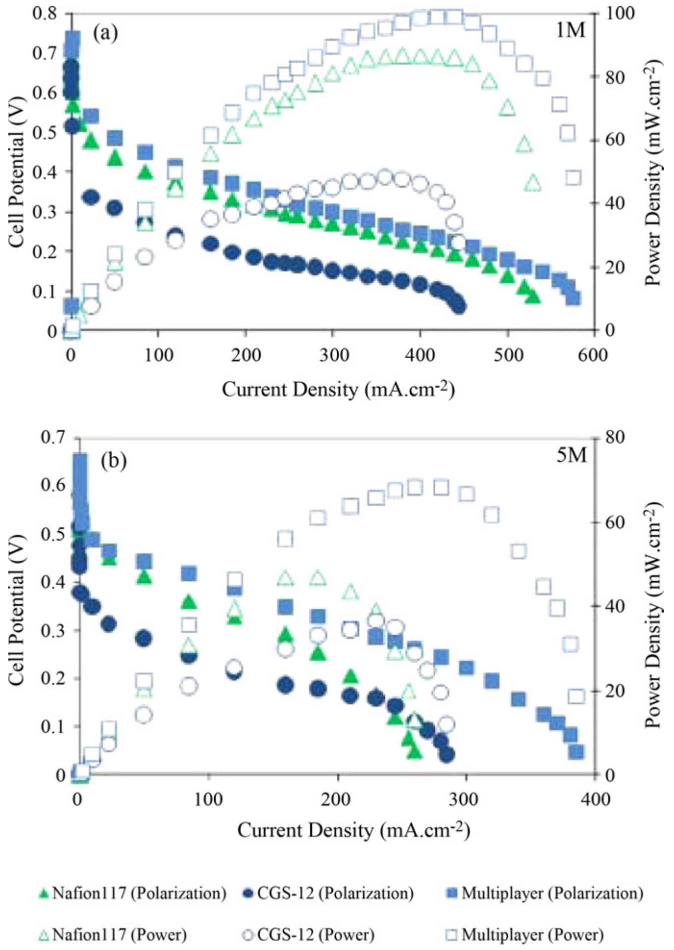


Fig. 22. Polarization curves of methanol–air single fuel cells consisted of a CGS-12, a CGS-12/Nafion 105 multilayer, and a Nafion 117 membrane, at 70 °C using (a) 1 M and (b) 5 M methanol solutions (Hasani-Sadrabadi et al., 2012). CGS-12 stands for 2 wt.% glutaraldehyde and 12 wt.% sulfosuccinic acid cross-linked CS.

reduced elongation. The addition of PS enabled the quaternary ammonia-based membranes to have a higher tolerance to bases. However, the membranes with a higher PS exhibited lower ionic conductivity because the PS is a nonionic conductor (Wang, He, & Che, 2011).

Recently, a CS hydrogel membrane was employed in a direct borohydride fuel cell (DBFC). The fuel for DBFCs is typically an aqueous solution of sodium borohydride in sodium hydroxide. During operation of a DBFC, Na^+ ions in case of a CEM, or OH^- ions in case of an AEM, are selectively transported across the CS membrane from anode to cathode chamber. As shown in Fig. 26, A DBFC using a CS membrane of similar thickness achieved a peak power density sig-

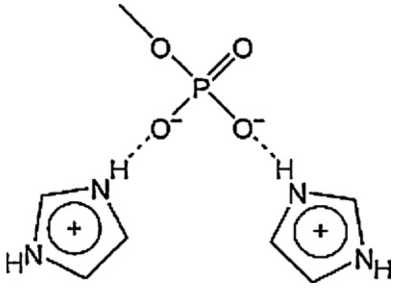


Fig. 23. Interaction between chitin phosphate and heterocycle imidazole (Yamada & Honma, 2004).

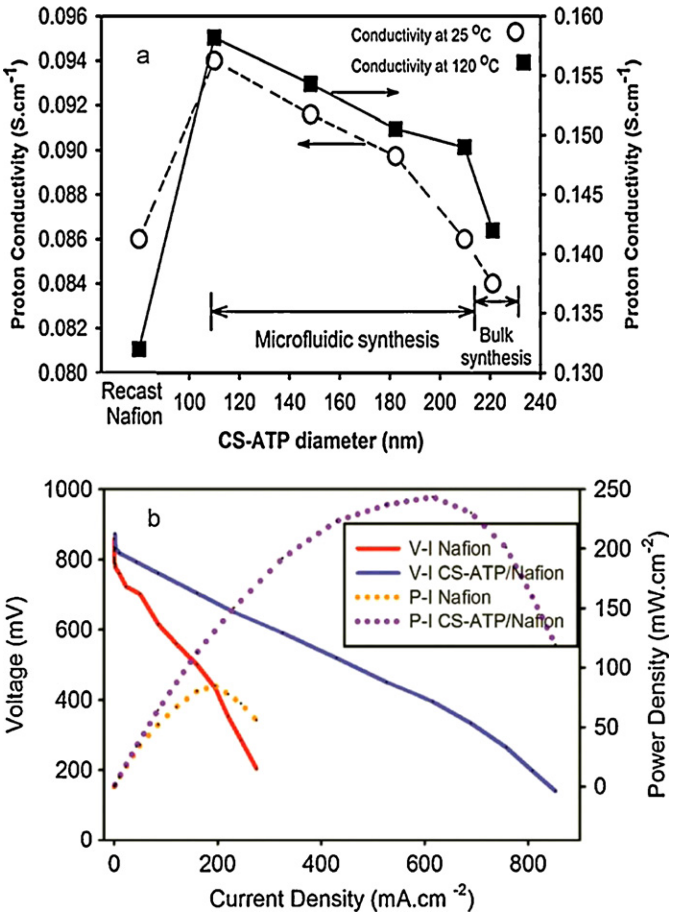


Fig. 24. (a) Size dependant proton conduction of the CS-adenosine triphosphate filled Nafion nanocomposite at 25 °C and 120 °C and (b) polarization curves of hydrogen–oxygen single cells consisting of a Nafion nanocomposite with 2 wt.% of CS-adenosine triphosphate as well as recast Nafion, at 40% R.H. and 120 °C (Majedi et al., 2012).

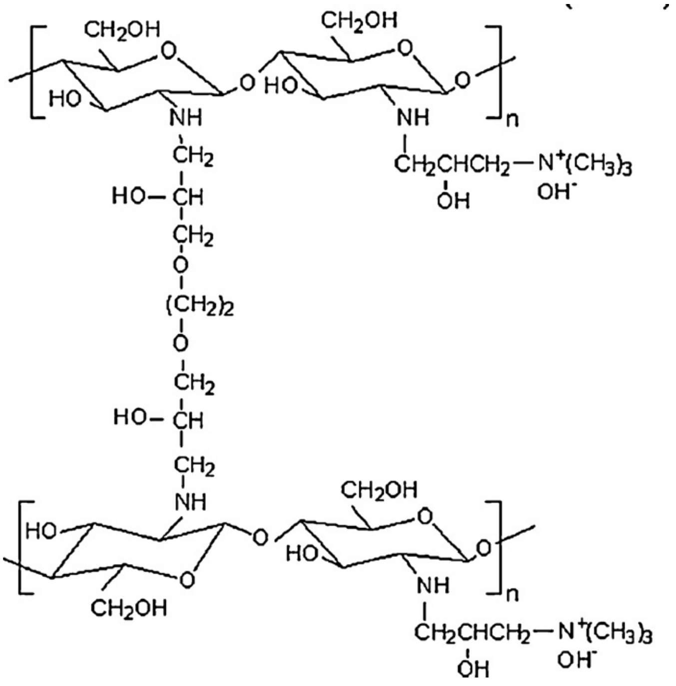


Fig. 25. The structure of diethylene glycol diglycidyl ether cross-linked N-[(2-hydroxy-3-trimethylammonium)propyl] CS (Wan et al., 2010).

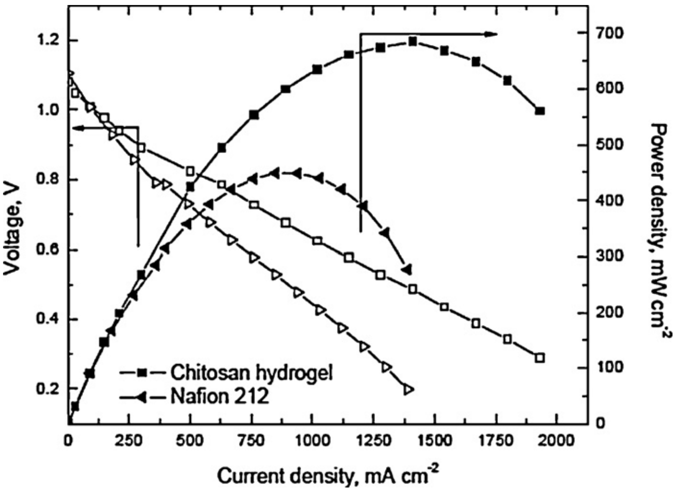


Fig. 26. Performance of a DBFC using CS hydrogel membrane, and Nafion membrane at 60 °C (Ma & Sahai, 2012).

nificantly higher than that obtained from a Nafion membrane (Ma & Sahai, 2012). Such improvement of CS-based DBFC over Nafion-based DBFC was due to the higher ionic conductivity of CS hydrogel membrane than Nafion membrane in alkaline medium, which was confirmed by electrochemical impedance spectroscopy study (Ma, Choudhury, Sahai, & Buchheit, 2011; Ma, Sahai, & Buchheit, 2012).

6. Chitosan for fuel cell electrode

An electrode in a polymer-electrolyte-based fuel cell usually consists of supported or unsupported catalyst with or without binder loaded on an electrode substrate or a gas diffusion layer. Polymeric materials are often employed as binder to bond catalyst particles and also provide ionic conduction. Glutaraldehyde cross-linked CS chemical hydrogel was employed as binding material for making electrodes in DBFCs. The CS binder exhibited better performance than a Nafion binder especially at elevated cell temperatures, ascribed to the hydrophilic nature and water retention characteristics of CS (Choudhury, Ma, Sahai, & Buchheit, 2011; Choudhury, Sahai, & Buchheit, 2011). In addition, the amount of CS binder required for making electrode is much less than that of Nafion binder.

Besides being an electrode binder, CS was used to improve properties of catalyst particles. Pt on carbon catalyst was entrapped in epichlorohydrin cross-linked CS (Phompan & Hansupala, 2011). It was indicated that CS chains existed in the primary pores of the carbon agglomerates, which extended three-phase-boundary and thus contributed to a decline in the activation overvoltage and improvement in cell performance of a H_2-PEM fuel cell.

There is an interest in using CS as catalyst support due to its high sorption capacities, stability of metal anions (such as Pt and Pd) on CS. A Pt or Pt alloy CS nanocomposite was prepared by chemical reduction of corresponding metal ions into zero valent nanoparticles in the presence of CS (Ekrami-Kakhki, Khorasani-Motlagh, & Noroozifar, 2011; Khorasani-Motlagh, Noroozifar, & Ekrami-Kakhki, 2011). It was found that the addition of CS into Pt catalysts improved the electrode performance for methanol electrooxidation, possibly due to the decrease in the poisoning effect and increased surface area.

Cogo et al. (2006) reported an approach of making CS and poly(vinyl sulfonic acid) (PVS) in layer-by-layer film adsorbed onto gold via ionic attraction. H_2PtCl_6 was deposited onto the layer-by-layer film, with CS/PVS layers serving as templates to yield metallic platinum. CS was chosen as a catalyst support due to its methanol resistance ability. PVS was used with CS for obtaining hydrophobic/hydrophilic separation. This Pt/CS/PVS film exhibited electrochemical stability, low permeability to methanol and conduction of proton, and thus may be used in membrane-electrode assembly of fuel cells.

Wang, Lu, Xiang, and Jiang (2011) reported a method to immobilize tungstophosphoric acid on Pt/C nanoparticles via the electrostatic interaction between negatively charged tungstophosphoric acid and positively charged CS which was attached to Pt/C nanoparticles (see Fig. 27). The CS/tungstophosphoric acid modified Pt/C catalyst demonstrated higher utilization efficiency as compared to pristine Pt/C catalyst. Electrochemical activity of CS/tungstophosphoric acid modified Pt/C catalyst for methanol oxidation and oxygen reduction reaction was reported to be significantly higher than that of unmodified Pt/C catalysts.

CS is a good dispersing agent for carbon nanotubes and thus is used in the preparation of carbon nanotube based catalyst or electrode of polymer electrolyte fuel cell (Nakagawa, Yasumura, Thongprachan, & Sano, 2011). Functionalization of carbon nanotube by CS introduces positively charged functional groups on the surface of carbon nanotube which serve as a medium to stabilize and anchor metal nanoparticles through electrostatic self-assembly, and also provides proton path for methanol electro-oxidation reactions, as illustrated in Fig. 28 (Wu et al., 2012). It is pointed out that the functionalization process is non-covalent and the structure of carbon nanotube should be rarely damaged, which

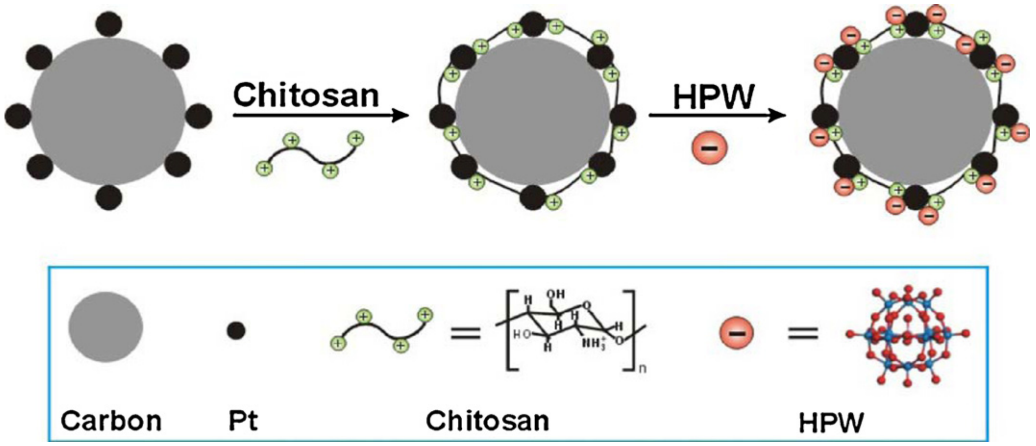


Fig. 27. Schematic diagram illustrating functionalization of Pt/C nanoparticles by CS, and self-assembly of tungstophosphoric acid (HPW) on CS-functionalized Pt/C nanoparticles (Wang, Lu, et al., 2011).

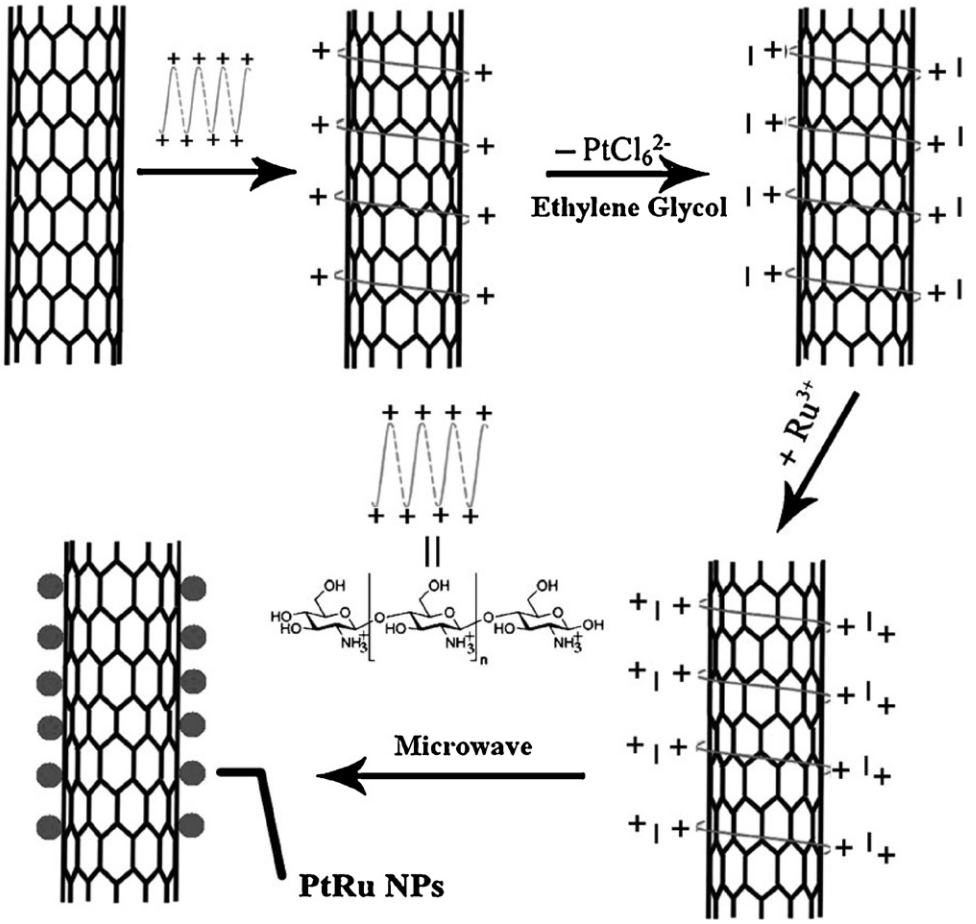


Fig. 28. Schematic diagram of preparation of PtRu/CS functionalized carbon nanotube (Wu et al., 2012).

is beneficial in preserving the good electronic conductivity and mechanical strength of the carbon nanotubes. Cyclic voltammetry studies indicated that CS functionalized carbon nanotube/PtRu had higher electrochemical surface area, electrocatalytic performance, and stability toward methanol oxidation compared to PtRu nanoparticles supported on the pristine carbon nanotubes (Cui, Li, & Jiang, 2011; Wu et al., 2012). Microchannelled 3D architectures composed of multiwall carbon nanotubes surface decorated with Pt nanoparticles and CS were prepared by ice segregation induced self-assembly process (Gutierrez et al., 2007). It was found that the CS functionalized carbon nanotube/PtRu provided good performance as anodes for DMFCs (e.g., current densities of up to 242 mA cm^{-2}).

Hollow CS nanospheres were used as both the template and the carbon precursor for hollow structure fabrication (Ding, Jin, Gu, & Xia, 2009). As illustrated in Fig. 29, the protonated amine groups in CS nanospheres provide sites for dispersing metallic precursors and subsequent nucleation centers for catalyst deposition in the pyrolysis process. Pyrolysis of the complex simultaneously results in the formation of metallic nanoparticles and the decomposition

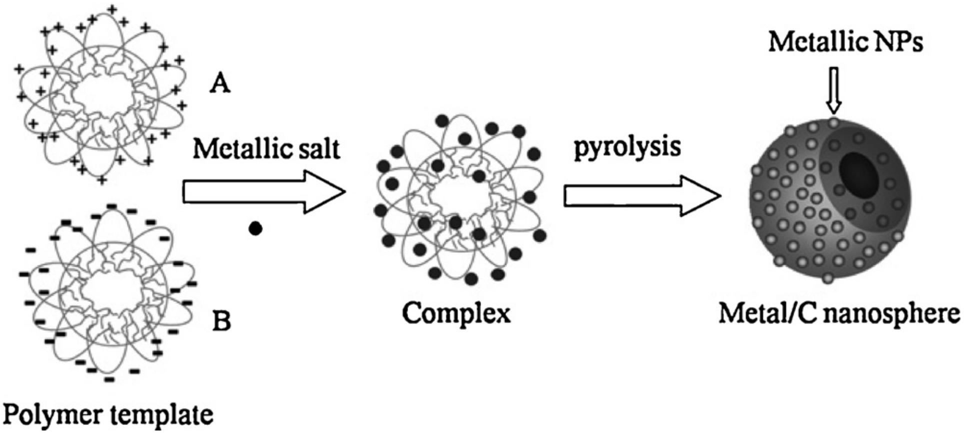


Fig. 29. Illustration of the synthesis process of hollow carbon nanosphere supported metal nanoparticles: hollow polymer templates with a positively (A, in case of CS) or negatively (B) charged surface (Ding et al., 2009).

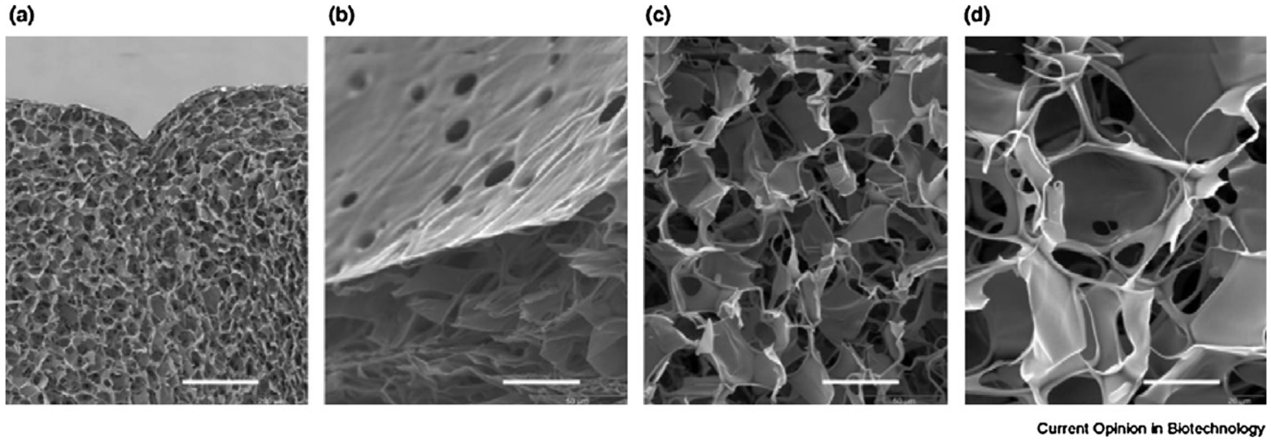


Fig. 30. Scanning electron micrographs of CS scaffolds. Scale bars: (a) 200 μm, (b) 50 μm, (c) 50 μm and (d) 20 μm (Minteer et al., 2007).

of hollow polymer nanospheres into hollow carbon nanospheres. Electrochemical results showed that the hollow carbon nanostructure supported PtRu catalyst had high electrochemical activity and stability toward the oxidation of methanol, outperforming the commercial PtRu/XC-72 catalyst.

7. Chitosan for biofuel cell

A biofuel cell is a type of fuel cell that employs biocatalysts. Microbial and enzymatic biofuel cells employ living cells and enzymes, respectively, as catalyst for fuel oxidation. Microbial biofuel cells have long lifetimes (up to five years) and are capable of completely oxidizing simple sugars to carbon dioxide. However, they deliver low power densities owing to slow transport across cellular membranes (Minteer, Liaw, & Cooney, 2007). By contrast, enzymatic biofuel cells typically possess orders of magnitude higher power densities, but can only partially oxidize the fuel and have limited lifetimes (typically 7–10 days) owing to the fragile nature of the enzyme (Minteer et al., 2007).

To develop a stable enzymatic biofuel cell, a matrix for enzyme immobilization is critical to retain the activity of enzyme in a long period (Deng, Shang, Wen, Zhai, & Dong, 2010). Carboxyl and amine side groups of CS can serve as protein-binding ligands for enzyme immobilization (Falk, Garramone, & Shivkumar, 2004; Liu, Wang, Zhao, Xu, & Dong, 2005; Wei, Cruz, & Gorski, 2002). Hydrophobically modified CS has been used for enzyme immobilization and stabilization at bioelectrodes in enzymatic biofuel cells (Lau, Martin, Minteer, & Cooney, 2010).

Three-dimensional electrodes possessing multidimensional and multidirectional pore structures are possible solution to improve performance of a biofuel cell. Porous CS scaffolds of defined pore structure were fabricated through a thermally induced phase separation (Ho et al., 2004). Fig. 30 shows scanning electron micrographs of CS scaffolds. Freezing temperature, freezing time, acetic acid concentration, and CS concentration were found to affect the final pore structure of CS scaffolds (Cooney et al., 2008). CS scaffold was used to fabricate enzymatic electrode that oxidizes glucose and produce electrical current more effectively than the same electrode made of a CS film (see Fig. 31) (Cooney et al., 2008). The large pore size of CS scaffold enables it to support bacterial colonization of internal pores without increasing flow resistance (Higgins, Foerster, et al., 2011).

The CS scaffolds can be made electronically conductive when doped with carbon nanotubes at relatively low weight percents (Liu et al., 2006). These CS/carbon nanotube scaffolds have demonstrated effectiveness in supporting either direct or mediator based electron transfer systems in biosensors (Li, Liu, Liu, Liu, & Yao, 2005; Tan, Li, Cai, Luo, & Zou, 2005; Zhang, Smith, & Gorski, 2004). It was reported that carbon nanotube/CS nanocomposite bioelectrode enhanced the electricity generation of a microbial fuel cell (Higgins, Lau, Atanassov, Minteer, & Cooney, 2011; Katuri et al., 2011; Liu et al., 2011).

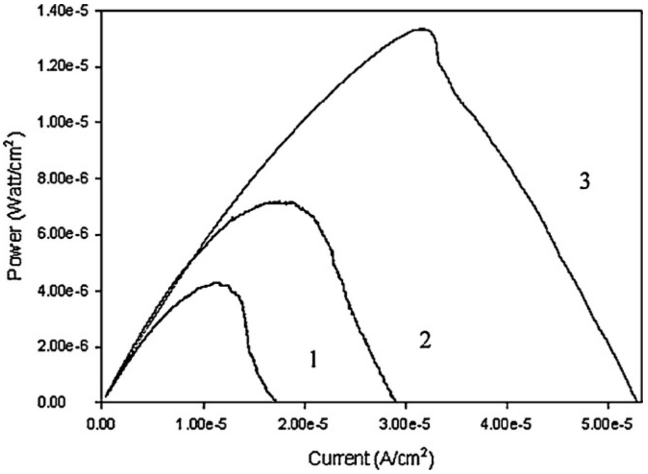


Fig. 31. Power vs. current curves for glucose biofuel cells employing CS anodes immobilized with NAD-dependent glucose dehydrogenase. Curve 1 corresponds to the "thin film" electrode. Curve 2 corresponds to the "scaffold" electrode that was dried at −20 °C and lyophilized. Curve 3 corresponds to pre-cooling the casting solution to 4 °C before casting on the electrode at −20 °C (Cooney et al., 2008).

Fe_2O_3 nanorod and CS were used to modify conventional carbon/graphite/indium tin oxide anode of a microbial fuel cell using layer-by-layer self-assembled technique. This modification strategy ensured a relatively high content of Fe_2O_3 nanorod within the polymer matrix. The microbial fuel cell with Fe_2O_3/CS modified anode produced a higher quantity of electricity output with 320% enhancement comparing with bare anode (Ji et al., 2011).

8. Summary and perspective

As a natural abundant biopolymer, chitosan is receiving great interest as materials for both membrane electrolyte and electrode in various fuel cells, such as polymer electrolyte-based fuel cell (including low to intermediate temperature polymer electrolyte fuel cells, direct methanol fuel cells, alkaline polymer electrolyte fuel cells), and biofuel cells. Considering that polymer membrane electrolyte is the most expensive component of a polymer electrolyte-based fuel cell, the use of low-cost chitosan-based membrane might bring down cost of a fuel cell.

Various CS-based membranes, both anionic and cationic, have been extensively examined for fuel cell applications. These CS-based membranes generally do not offer significant advantages over traditional Nafion membrane, as far as proton conductivity is concerned, and as a result the corresponding power density of related fuel cells is also lower than Nafion-based ones. Thus, the intrinsic ionic conductivity of CS-based membrane needs to be further improved for fuel cell applications. The mechanical strength and shelf life of CS also need further enhancement, which have not been given extensive attention. Efforts have been made to improve properties of CS membrane, including chemical modification, formation of CS blend and composite. These methods improve some properties of CS with or without sacrificing the others. Chemical modification, such as sulfonation, phosphorylation, and quaternization, is able to generate ion exchange sites on CS backbone, and may serve to improve ionic conductivity. However, these chemical modification increase solubility of CS in aqueous medium and thus may worsen its mechanical strength. Several CS hybrid membranes demonstrate ionic conductivity of the same order of magnitude of Nafion. Incorporating solid inorganic proton conductors is an effective way of improving proton conduction (e.g. a stabilized silicotungstic acid/CS/PVA membrane had higher conductivity than Nafion). Blending with tough polymers or incorporating reinforcing fillers is needed to improve mechanical and chemical stability of CS membrane. Functionalization of inorganic fillers serves to enhance properties such as ionic conductivity of CS-based composite membrane. Being a hydrophilic polymer, CS has potential use alone or combined with Nafion or other synthetic polymer, for intermediate temperature polymer electrolyte fuel cells.

Most if not all of CS-based membranes examined have much lower methanol permeability than Nafion due to hydrophilic nature of CS, and methanol permeability can be further reduced by using CS blend or composite, which makes CS meets at least one of the requirements for application in a DMFC. CS is used in combination with Nafion to enhance methanol resistance of Nafion and improve proton conductivity of CS.

CS-based anion exchange membrane has also been investigated. Interestingly, CS exhibits excellent power performance as membrane electrolyte and also electrode binder in a DBFC, which make it a promising material for use in a DBFC or other alkaline fuel cells.

Besides in polymer electrolyte membrane, chitosan was successfully used in electrode as binder and ionic conductor, and in catalyst preparation to improve catalyst properties. Recently, many efforts have been made in producing biofuel cell electrode with improved properties using chitosan. Chitosan proves to be effective in enzyme immobilization and in construction of three-dimensional electrode architecture for use in biofuel cells.

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