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Chemical Modifications of Chitosan Biopolymer as Poly Electrolyte Membranes for Full Cells: Article review

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Abstract: Fuel cells (FCs) have recently received much attention as alternative new and clean energy source. FCs are not only pollution-free, but they can also have more than two times the efficiency of traditional combustion technologies. Recently, tremendous efforts are being made to produce polymer electrolyte membrane (PEM) for fuel cells as replacement of Nafion due to its high cost, low ion conductivity at long operation times, poor mechanical strength, and decreased performance at high temperatures. An eco-friendly biopolymer chitosan (CS) has been devised as membrane in polymer electrolyte membrane fuel cells (PEMFCs). CS is amenable to chemical modification due to the presence of functional hydroxyl and amine groups in its backbone to convey distinct physiochemical and biochemical properties to the polymer without changing the basic structure. In the present article reviewing of different studies related to CS as biopolymer and outlines the chemical foundations of Cs and CS derivatives modification by sulfonation, phosphorylation and quaternization, to meet the requirements of a desired PEM for FCs. In additions, some recent preparation methods of PEM based on CS and CS derivatives are included.

Keywords: Fuel cell, membrane, chitosan, sulfonation, phosphorylation, quaternization.

1 Introduction

The vast increase in world population and urbanization over the last two decades has resulted in sever energy shortages. The European “World Energy Technology and Climate Policy Outlook” (WETO) predicts an average growth rate of 1.8% per annum in the period 2000-2030 for primary energy worldwide [1]. The increased demand is being met largely by reserves of fossil fuel that emit both greenhouse gases and other pollutants, e.g. carbon dioxide that leads to global warming. Beside, those reserves are diminishing and they will become increasingly expensive by 2030. CO_2 emissions from developing nations could account for more than half the world CO_2 emissions, thus countries should lead the development of new energy systems to offset this issue.

Fuel cells (FCs) have recently received much attention as alternative new and clean energy source. FCs are not only pollution-free, but they can also have more than two times the efficiency of traditional combustion technologies. A conventional combustion-based power plant typically generates electricity at efficiencies of 33-35%, while FCs systems can generate electricity at efficiencies up to 60%. FCs are compact design, environment friendly, produces no noxious emissions**,** operates quietly and have fuel flexibility**.** FCs can power almost any portable application that typically uses batteries, from hand-held devices to portable generators. In general, there are three main markets for fuel cell technology according to their applications: 1) stationary power either for primary or for backup power, or for combined heat and power (CHP), 2) transportation power (for cars, buses and other fuel cell passenger vehicles and 3) portable power which use fuel cells that are not permanently installed or fuel cells in a portable device. PEMFC in which the electrolyte is a polymer membrane, represent one of the important type of fuel cells. In general, PEMFC as shown in Fig. 1 are composed of electrodes i.e., anode (negative side) and cathode (positive side) with catalyst, electrolyte (solid or liquid), gas diffusion layers (GDL) that allows charges to move between the

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two sides of the fuel cell where the proton passes through the electrolyte, whereas the electrons create a current and interact with proton and oxygen to form water at the cathode, bipolar plates/interconnects and sometimes gaskets for sealing the stack and preventing leakage of gases. All of these components are arranged in a stack where the repeated stacks are linked in either series or parallel format to produce the appropriate voltage and current. The poly electrolyte membrane (PEM) separates both the fuel and the oxidant and preventing mixing and transporting protons from the anode to the cathode to complete redox reaction chemistry. The desired properties of PEMFC are good mechanical strength, good thermal stability, high stability in oxidative and reduction environment, good chemical and electrochemical stability, good processability for membrane electrode assembly (MEA), good barrier property for reactant species, low electro osmotic drag, zero electronic conductivity, high proton conductivity and long life above $100^{O}C$ temperature. Currently, Nafion (Dupont's prefluoro-sulfonated acids electrolyte membrane is the most widely-used as fuel cell membrane; however, it has some drawbacks such as a high price, low ion conductivity at long operation times, poor mechanical strength, and decreased performance at high temperatures [2-13].

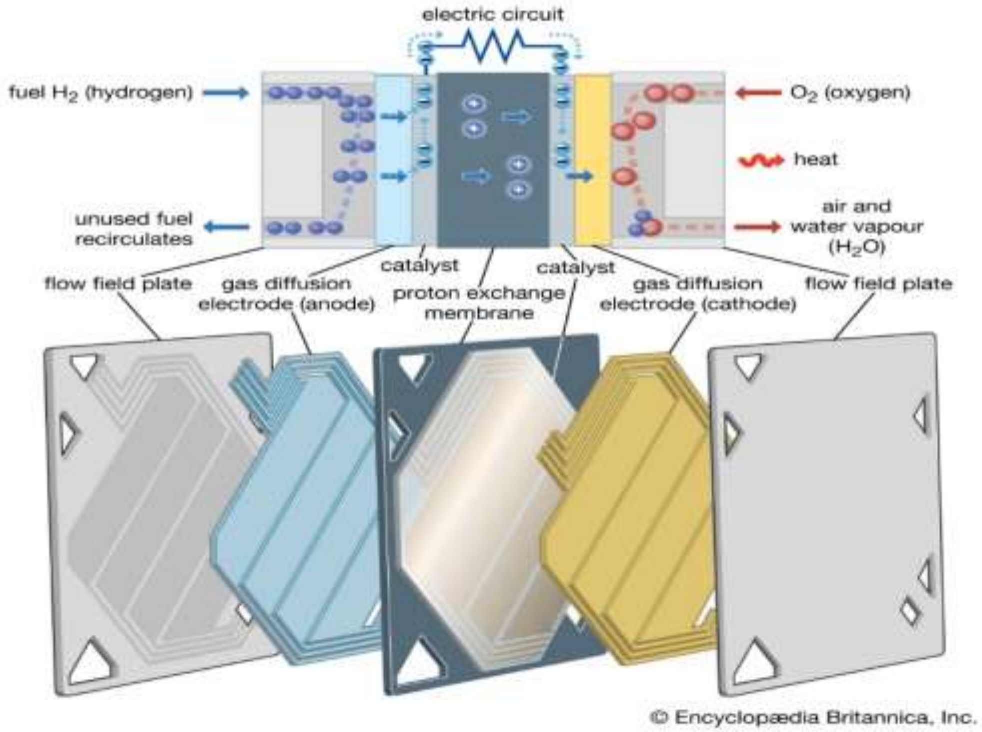

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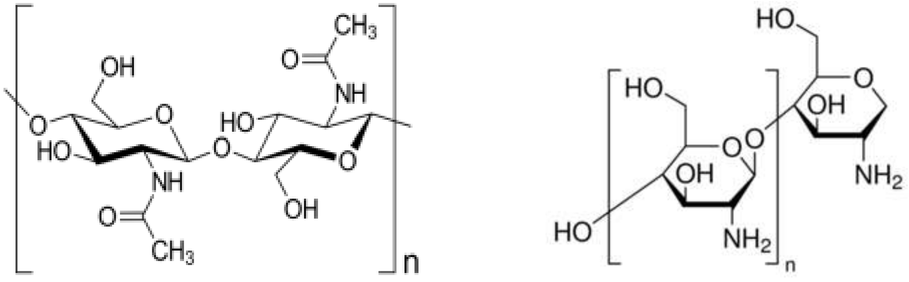
Fig. 1: Poly Electrolyte Fuel Cell.

As most of the present-day polymers are synthetic materials, their biocompatibility and biodegradability are much more limited. For that recently researches are focused on natural polymers to overcome the draw backs of Nafion membranes. The advantanges of biopolymers to be used as PEMs are: 1) its low cost and eco-friendly; 2) the backbone of biopolymer has specific functional groups which allow modification to alter their properties. The present article are concerned with an overview of a CS as biopolymer, its structure and properties and its chemical modifications to be used to synthesis PEM for FCs [14].

2 Chitosan

The principal derivative of chitin is Chitosan (CS) which produced by alkaline deacetylation of chitin. CS is a copolymer of glucosamine and N-acetyl glucosamine. It also occurs naturally in some fungi. Commercial CS is derived from the shells of shrimp and other sea crustacean. Characteristics of CS is influenced by its molecular weight (from approximately 10,000-1 million Da) and degree of acetylation. CS is a natural organic product having both free hydroxyl groups and amino groups. The reactive position of amino group is at C2 position and the primary and the secondary hydroxyl groups are at C3 and C6 positions. These groups enable various chemical modification to tailor it for specific applications. CS is insoluble in water, and in most organic and alkali solvents. It is however soluble in dilute acids such as acetic, formic, and lactic acid. CS has high water attracting capacity. The basicity of CS is responsible for biocompatibility, hydrophilicity, non-toxicity and good membrane forming capability. Recently, research has been conducted in the application of CS and its derivatives to prepare of fuel cell membranes based on the site of the amino and hydroxyl group. It can function well as a PEM. The advantages of chitosan as a PEM refers to: 1) its environmental friendliness; 2) its low methanol permeability; 3) it has conductivity level of 3.87 x 10^{-7} S cm-1 and 4) presence of functional groups which can be chemically modified aiming specific properties 5) hydrophilicity which is a desirable property for use in high temperature and relatively low humidity [15-20]. The structures of both chitin and CS are presented in Fig. 2



Chitin

Chitosan ($C_{56}H_{103}N_9O_{39}$)

Fig.2: Structure of chitin and chitosan.

2.1 Chemical cross-linking of Chitosan

In polymer chemistry "cross-linking" usually refers to the use of cross-links to promote a change in the polymers' physical properties. The polymers can be either synthetic polymers or natural polymers such as CS. Special emphasis is placed on chemical cross linking reaction to improve mechanical and chemical stability of membrane. Structure and chemical interactions in covalently and ionically cross-linked CS are reviewed by Berger et al. [21] , they reported that 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: 1) CS cross-linked with itself, 2) 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 3) 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 are used to perform the covalent cross-linking on -NH_2 sites, forming stable bonds between amine groups of CS polymer and aldehyde groups. Besides dialdehydes, anchoring two epoxy groups, respectively, on two amino groups in different CS chains. Siti Wafiroh et al [22] found that chitosan has a poor thermal stability like other natural polymers which are not resistant at temperatures above 100°C. Thus, chitosan needs crosslinking like other inorganic materials as zeolite, bentonite and calcium oxide. This results in its mechanical properties improvement. Furthermore, the ion exchange capacity in absence of a crosslinker is 2.50 meq g-1, while that in presence of H_2SO_4 as a crosslinker increases to 5.66 meq g-1.

2.2 Chemical modification of Chitosan

Utilization of CS has been delayed, probably because of the difficulty to dissolve in general organic solvents. This is due to their rigid crystalline structure caused by the establishment of hydrogen bonding between their amino and hydroxyl groups within a chitosan monomer or monomers. To solve this problem, the structure of chitosan must be modified by hydroxy alkylation, carboxy alkylation, acylation, thiolation sulfation, quaternization, phosphorylation and graft copolymerization processes .

A highly reactive primary amino group of chitosan is convenient for chemical modification, having better solubility in organic solvents, makes it easier to compose with other polymer to get a homogenous blend. N-phthaloylation of chitosan with phthalic anhydride is an efficient way to improve its organic solubility.

Chemical modification of chitosan to generate new bifunctional materials is of primary interest because such procedure will not change the fundamental skeleton of chitosan, it will keep the original physicochemical and biochemical properties depending on the nature of the group introduced. Chemical modifications for chitosan are carried by sulfonation, phosphorylation and quaternization from the viewpoint of fuel cell applications to possibly generate ion exchange sites and improve ionic conductivity. Fig. 3 represents the general chemical modification reactions of chitosan to prepare membranes for FC as reported by Hans et al. [14].

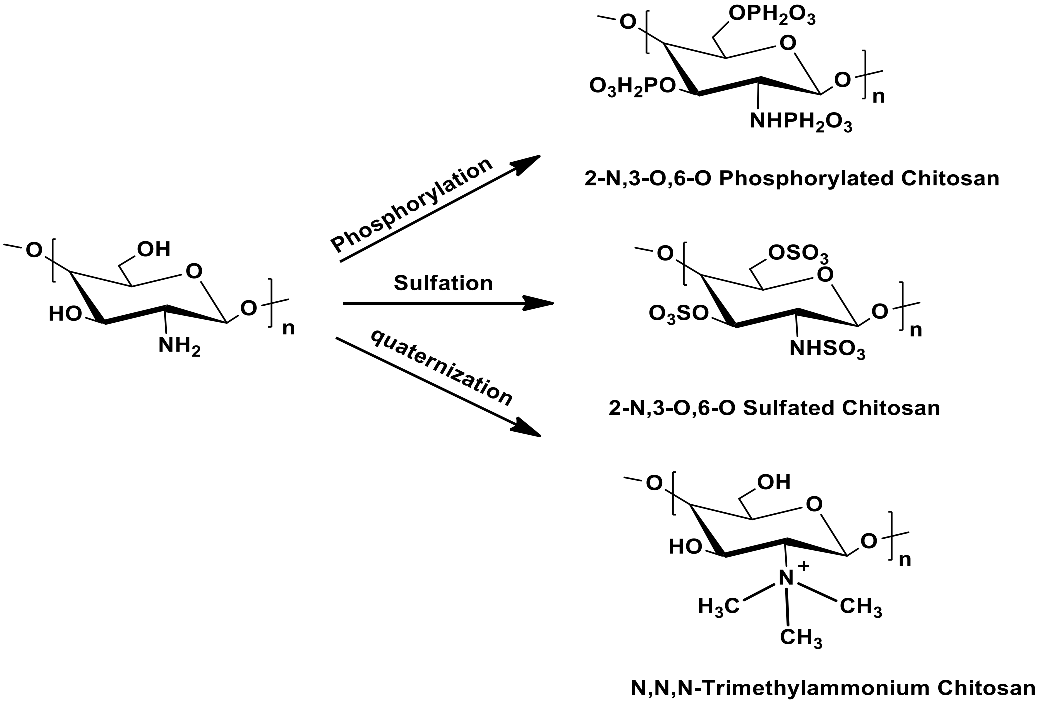


Fig.3: Chemical Modification to alter chitosan properties for membrane of FC.

2.2.1 Chemical modification of CS by sulfonation

Sulfonation is the process of directly attaching the sulfonic acid group, –SO_3H, to carbon in an organic compound**.** The final product of the sulfonation process is called the sulfonate. Biocompatibility of CS is increased upon sulfonation. There are different techniques to synthesize sulfated CS by using different combinations of sulfating agents. Harish P. et al. [20] reported that CS have both free hydroxyl groups and amino groups enable various chemical modification to tailor it as membrane for FCs by attaching the sulfonic acid group. 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 and adjusting reaction time, temperature, and reactant concentration, where the sulfonate groups can be attached to CS backbone. Tasi et al. [23]. reported that N-sulfonated CS with various sulfonation degrees can be prepared by using propane sultone. Chitosan powder is added to acetic acid with stirring followed by addition of 1,3 propane sultone. The sulfonated CS has a pendant alkyl sulfonic group attached to the side chain which can improve its hydrophilicity and water solubility. Preparation of N-sulfonated CS is presented in Fig 4.

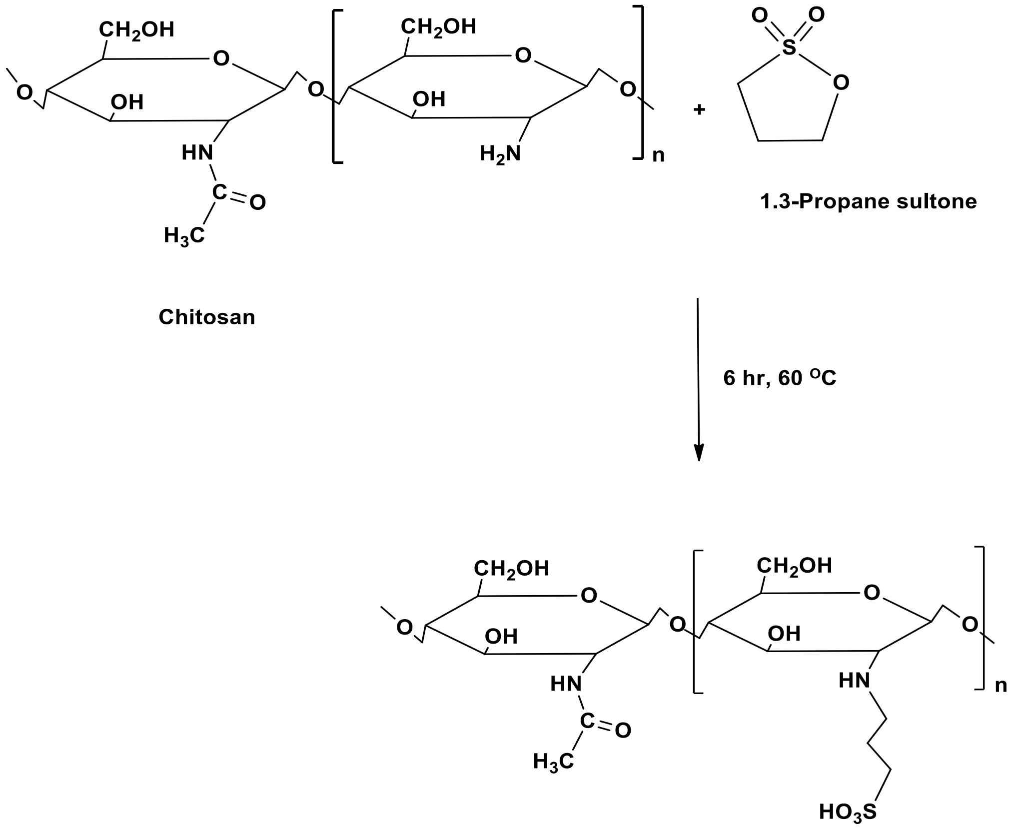


Fig. 4: Fig. 23 Schematic representation for preparation of N-sulfonated CS.

Preparing of O - sulfonated CS is described in a patent by Hayashi et al. [24]. Proper pretreatment conditions and solvent systems enable sulfonation to occur selectively on C3/C6-position (OH sites). SO_3 or chloro sulfonic acid with dimethylformamide complex can be used as sulfonating reagent as shown in Fig.5.

Fig.5: Synthesis of O-sulfonated CS.

Nagasawa et al [25] prepared sulfated chitosan by using sulfuric acid, tetrahydrofuran in presence of phosphorous pentoxide at −20°C (Fig.6). The average molecular weight and yield of the chitosan showed the extent of degradation of the polysaccharide structure by concentrated sulfuric acid

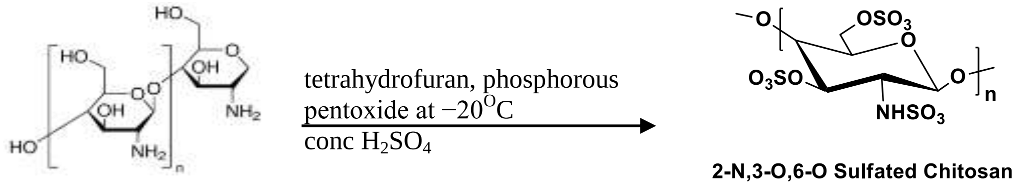


Fig.6: Preparation of 2-N,3-O,6-O Sulfated Chitosan.

Nudga et al. [26] prepared sulfo ethyl chitosan carrying sulfonic acid groups by using 2-chloro ethane sulfonic acid sodium salt in alkaline media. The sulfo ethyl chitosan was obtained with a degree of substitution of 0.11–0.35 and the sulfur content was found to be 1.39–5.32%. Substitution was involved both the O-6 and N-2 positions (Fig.7).

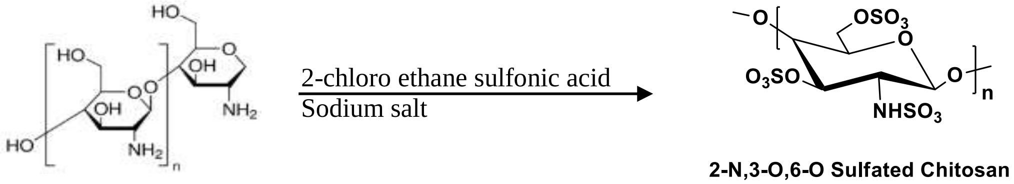


Fig.7: Preparation of 2-N,3-O,6-O Sulfated Chitosan sulfo ethyl chitosan.

Muzzarelli et al. [27]. Investigated the sulfonic acid function when introduced into chitosan by reacting with 5-formyl-2-furansulfonic acid, sodium salt, under the mild conditions of the Schiff reaction to avoid polymer degradation and O-substitution. Hydrogenation yielded N-sulfofurfuryl chitosan sodium salt as presented in Fig 8.

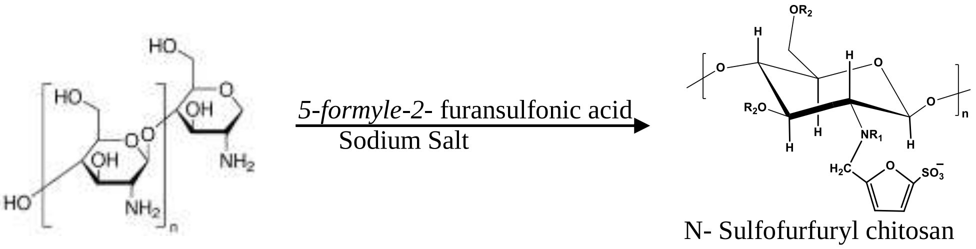


Fig.8: Preparation of N- Sulfofurfuryl chitosan.

Meyer et.al. [28] and Gilbert et al. [29] reported that the common difficulty of the sulfonation of polysaccharides is that their action is performed in a heterogeneous medium, because most of the poly saccharides are insoluble or only slightly soluble in the organic solvents which used as reaction medium in the conventional sulfation procedure. Consequently, it can be assumed that the constitution of the product is heterogeneous. Pseudo-homogeneous method of sulfated chitosan was prepared by Gamzazade [30] using 2% chitosan solution, anhydrous mixture of DMF-dichloro acetic acid with chloro sulfonic acid at room temperature for 1h as shown in Fig.9, followed by the formation of gel, then the gel was diluted with water, neutralized by NaOH and precipitated with methanol.

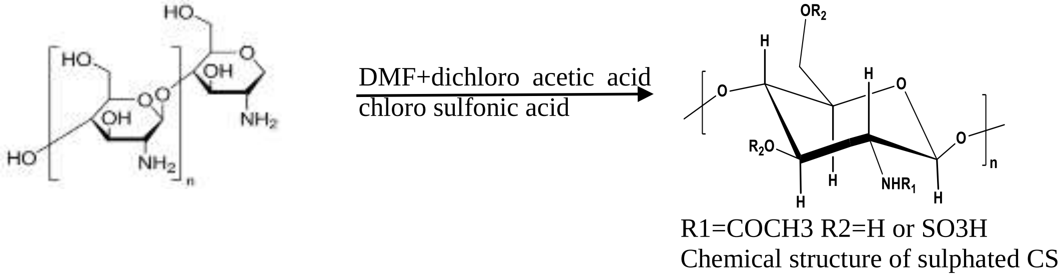


Fig.9: Preparation of sulfated chitosan.

Sulfated chitosan was also synthesized by Park et al. [31] by treating chitosan with sodium carbonate anhydrous and tri methyl amine sulfur trioxide (Me3N–SO3) as presented in Fig.10. The sulfated chitosan were obtained with 90% yields as a white, fluffy, water soluble material and degree of substitution was 0.76.

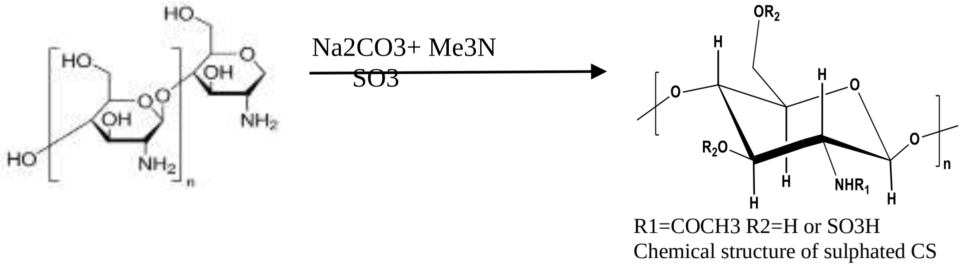
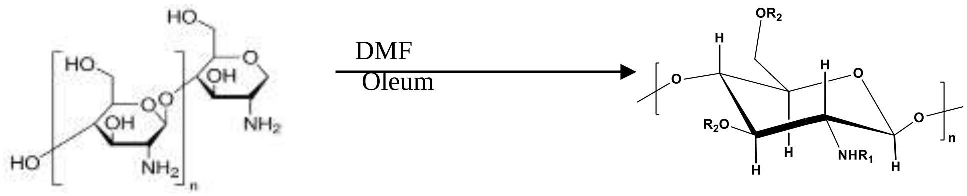


Fig.10: Preparation of sulfated chitosan.

Fig.11: represents the sulfated chitosan as prepared by Vikhoreva et al. [32] where chitosan was reacted with oleum and DMF. The degree of substitution was 1.10–1.63.

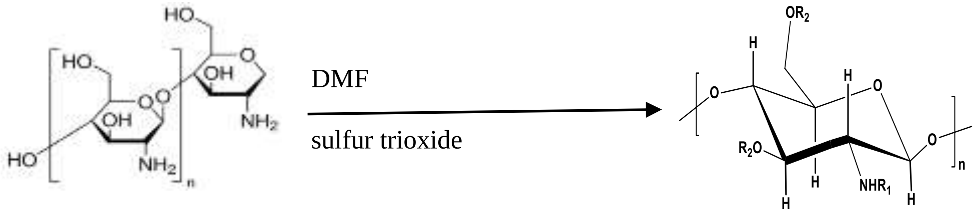


R1=COCH3 R2=H or SO3H

Fig.11: Preparation of sulfated chitosan.

Hirano et al. [33] prepared N,O-Sulfated chitosan by using chitosan, N,N-dimethyl formamide (DMF) and sulfur trioxide as presented in Fig.12.

5.



R1=COCH3 R2=H or SO3H
N,O-Sulfated chitosan

Fig.12: Preparation of N,O-Sulfated chitosan.

In addition CS derivatives were used as stating materials for preparation of different sulfonated compounds by many authors. Hirano et al. [34] synthesized O-Sulfated N-acetyl chitosan by reacting N-acetylated chitosan, DMF with sulfur trioxide. Also they prepared sulfated O-CM-chitosan by using O-CM-chitosan, DMF and sulfur trioxide. All the products were isolated in sodium or sodium acid salts to get high yield. Similarly. Hagiware et al. [35] prepared sulfated O-CM-chitosan by using O-CM-chitosan and prepared O-sulfated N-hexanoyl by treating N-hexanoyl chitosan, DMF with sulfur trioxide. In addition CS sulfate was prepared by Vongchan et al. [36] by treating 6-O-trityltchitosan, dichloroacetic acid with SO3-pyridine complex.. The crystallinity of chitosan was decreased after sulfonation. The sulfated-6-O carboxymethyl chitosan were prepared by Youn et al. [37] by using N-(2,3-dihydroxy) propyl chitosan derivative, DMF, sulfuric acid with dicyclohexyl carbodiimide. Sulfonation of B-chitosan increases the water solubility of the sulfated chitosan. N-Alkyl-O-sulfated chitosan derivatives were prepared by Zhang et al. [38] by treating N-octyl-chitosan with DMF and chloro sulfonic acid. The crystalline structure of modified chitosan was appeared as amorphous. These result suggested that the ability of forming hydrogen bond was decreased after chemical modification. The thermal stability of N-alkyl-O-sulfated chitosan was less than the original chitosan. Introduction of substituents into polysaccharide structures should disrupt the crystalline structure of chitosan, especially by the loss of hydrogen bonding. The reaction equations of CS derivatives as stating materials for synthesis of different sulfonated compounds are presented in Eq.1-5.

N-acetylated chitosan $\xrightarrow[\text{sulfur trioxide}]{\text{DMF}}$ O-Sulfated N-acetyl chitosan------------ (1)

O-CM-chitosan $\xrightarrow[\text{sulfur trioxide}]{\text{DMF}}$ sulfated O-CM-chitosan------------------ (2)

6-O-trityltchitosan $\xrightarrow{\text{dichloroacetic acid with..}}$ CS sulfate------------------------------(3)

N-(2,3-dihydroxy) propyl CS $\xrightarrow[\text{DMF Sulfuric acid}]{\text{dicyclorohexyl carbodiimide}}$ sulfated-6-O carboxymethyl CS- (4)

N-octyl-chitosan $\xrightarrow[\text{chloro sulfonic acid}]{\text{DMF}}$ sulfated-6-O carboxymethyl CS-----------(5)

2.*2.2Chemical modification of Chitosan by Phosphorylated*

Phosphorylated chitosan has attracted interests in recent years. The The literature has reported that the chemical modification of CS by phosphorylation is expected to improve its chelating properties and increase its biocompatibility. The phosphorylated of chitosan could be achieved through three reaction routes as reported by Kaipeng Wang et al. [39] in the presence of H_3PO_4/urea, $H_3PO_4/Et_3PO_4/P_2O_5$, P_2O_5/CH_3SO_3H and as shown in Figs. [13-15]. It was observed that in the reaction routes using H_3PO_4/urea in DMF as a reaction promoting agent and H_3PO_4/Et3 and PO4/P_2O_5, the amino groups were substituted instead of the hydroxyl groups. In the reaction route using P_2O_5/CH_3SO_3H, the amino groups were shielded by the ionic binding with CH_3SO_3H, and the C-6 hydroxyl groups were phosphorylated. Different structures of the phosphorylated chitosan were proposed based on the characterization results.

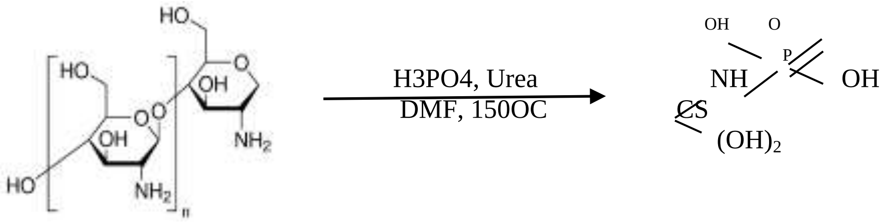


Fig.13: Phosphorylated by using H_3PO_4/urea.

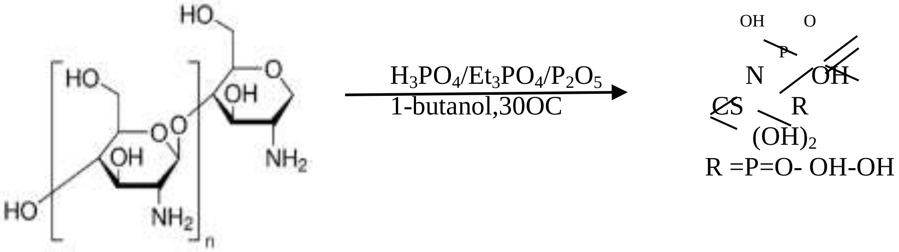


Fig.14: Phosphorylated of CS by using $H_3PO_4/Et_3PO_4/P_2O_5$.

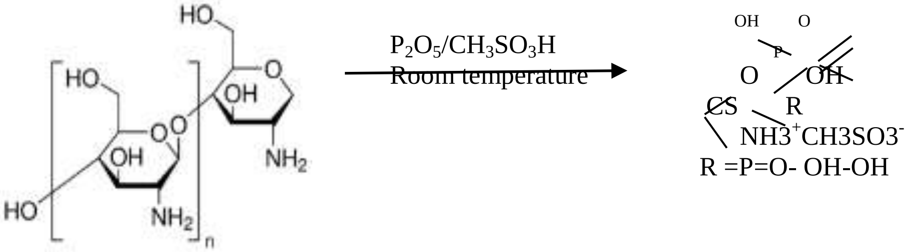
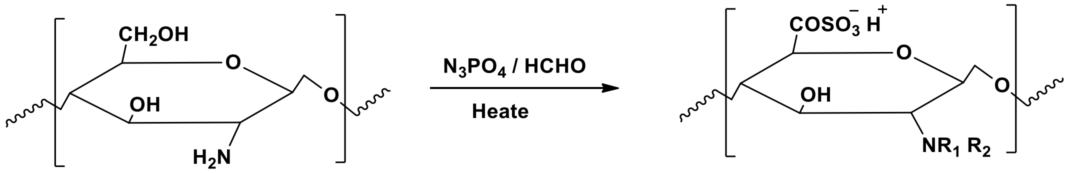


Fig.15: Phosphorylated by using P_2O_5/CH_3SO_3H.

Several methods have been developed to synthesize phosphorylated derivatives of chitosan (e.g., 2-N, 3-O, 6-O phosphorylated CS Fig.3). Yao et al. [40]. prepared CS phosphorylated CS by reaction of CS with phosphorous pentoxide in methane sulfonic acid. Ramos et al. [41] prepared an N-methylene phosphonic CS by using CS, phosphorous acid and formaldehyde as presented in Fig.16. An O-ethyl phosphonate CS was prepared by Palma et al. [42] by using KOH/methanol



R_1 = H, $R_2=CH_2PO(OH)_2$

R_1 = $R2=CH_2PO(OH)_2$

Fig.16: Synthesis of N-methylene phosphonic CS.

Waly et al. [43] reported that phosphorylated of CS can be prepared by using three mixtures: 1) mono and disodium phosphate mixture, 2) di ammonium phosphate / urea and 3) chloro methyl disodium phosphonate as shown in Figs 17-19.

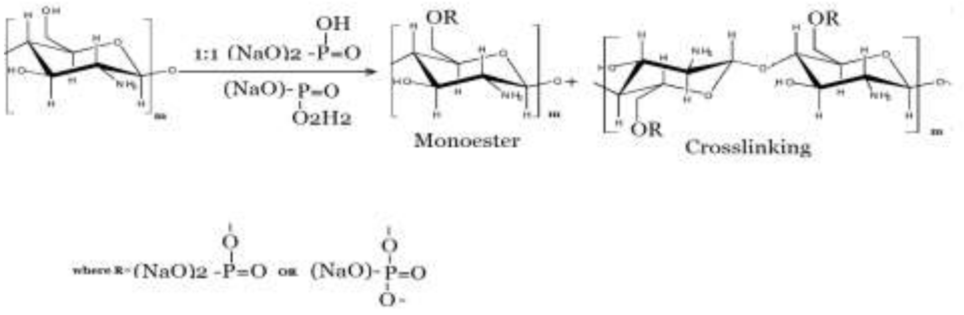


Fig. 17: phosphorylated of chitosan using mono and disodium phosphate mixture.

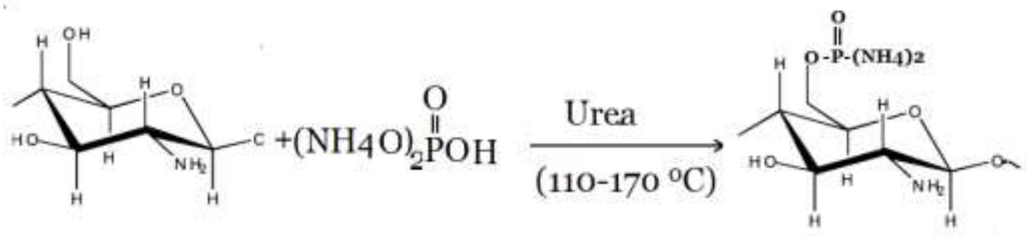


Fig.18: Phosphorylation of chitosan using mixture of di ammonium phosphate / urea.

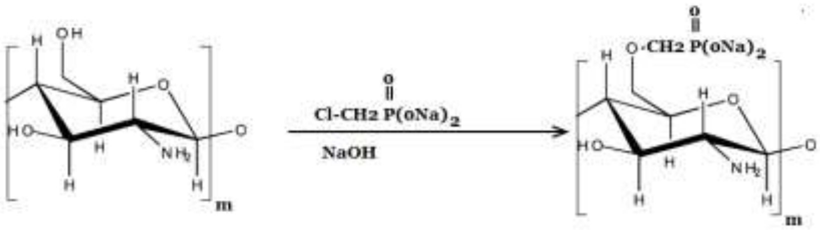


Fig.19: Phosphorylation of chitosan using chloro methyl disodium phosphonate.

2.2.3. Chemical modification of Chitosan by Quaternization

Chitosan is practically insoluble in aqueous solutions with a neutral or alkaline pH and becomes soluble only below pH 5.6. It is essential to derivatize chitosan in a way that substantially increases solubility. One efficient method is quaternization of chitosan or its derivatives, which converts the primary amino group into a quaternary ammonium ion and hence adds positive charges to the polymer [14,44,45]. Quaternization can be achieved either by reacting chitosan with alky halides such as iodomethane in one or two steps procedures, or dimethyl sulfate, or by reacting chitosan with compounds that contain the quaternary ammonium itself. Following are some of important published papers for preparation of chitosan quaternization:

Muzzarelli and Tanfani [46] were the first one to produce quaternized chitosan by reacting chitosan with formaldehyde followed by the reduction with sodium borohydride yielding N,N-dimethyl chitosan (DMC), which was then converted into N,N,N-trimethyl chitosan by the treatment with iodomethane in acetonitrile. Domard et al. [47] dissolved chitosan in N-methyl pyrrolidinone and reacted it with iodomethane in the presence of sodium hydroxide. The quaternization of chitosan produced was with efficiencies of about 60 to 65%. Substantial water solubility is obtained at degrees of quaternization of larger than 25%. Repeated reaction cycles proved increase of the degree of quaternization to more than 85%. Improving polymer stability, chemosensitivity, and water solubility were tester by combinations of the basic methods as reported by many authors [48-51].To avoid expensive alkyl halides for the synthesis of quaternized chitosans, which are, in addition, difficult to remove from the reaction product, de Britto et al. [52] used dimethyl sulfate as the methylation reagent. This method turned out to be more efficient than that based on iodomethane and resulted in a highly hydrophilic product with a degree of quaternization of about 52%. However, dimethyl sulfate is toxic, and the reaction is not selective for the preferred amino group [53]. O-Methylation was found to be favored over N-methylation with increasing temperatures, rapidly degrading chitosan. But the disadvantage of this method is that alkyl halides and dimethyl sulfate have toxic and carcinogenic properties. Therefore, in a recently published article, a novel strategy was presented to synthesize N,N,N- trimethyle chitosan TMCS in an ionic liquid using dimethyl carbonate as a methylation reagent [54]. Quaternization can also be achieved with reactants that carry a quaternary ammonium group themselves. For instance, when the primary amino group of chitosan is reacted with glycidyl trimethyl ammonium chloride [i.e., (2,3-epoxypropyl)trimethylammonium chloride], a quaternized, N-monoalkylated chitosan is obtained with an extended positively charged side chain at the amino group [55]. Quaternization can also be performed by the reaction of chitosan with 3-chloro -2-hydroxypropyltrimethyl ammonium chloride [56]. However, this method is less specific than O-alkylation , which occurs even at ambient temperatures. Very recently, Raik et al. [57] synthesized N-[4-(N,N,N-trimethylammonium)benzyl] chitosan chloride by the reaction of 4-formyl-N,N,N-trimethylanilinium iodide with the primary amino group of chitosan. The authors showed that the resulting polyplexes had a good solubility in water over a wide pH range, even at lower degrees of substitution. Alkylation of quaternized chitosan yields amphiphilic polymers due to the simultaneous presence of charged and hydrophobic side groups were investigated by many authors [58-64]. Trimethyl chitosan ammonium iodide was obtained by reaction of a low acetyl content chitosan with methyl iodide and sodium hydroxide under controlled conditions. The reaction was performed in several steps to obtain derivatives of chitosan at various degrees of quaternization with a limited value near 64% [65-66]. Glycidyl trimethyl ammonium chloride is also used as a quaternization agent because it has a quaternary ammonium group itself. A primary amino group at C2 position of CS reacts with glycidyl trimethyl ammonium chloride. The anion exchange conductor of quaternization CS is thus obtained by replacing hydroxide ions with chloride ions [67]. Following Figs. 20-22 are examples of quaternization of CS reactions.

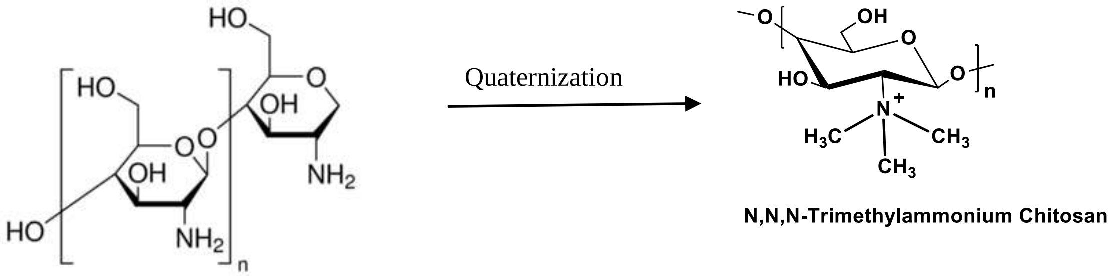


Fig.20: Quaternization of chitosan.

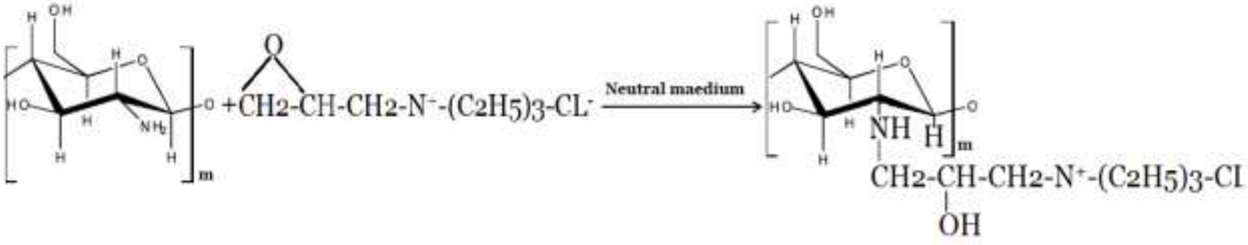


Fig.21: Cationization of chitosan using 2,3-Epoxy propyl triethyl ammonium chloride.

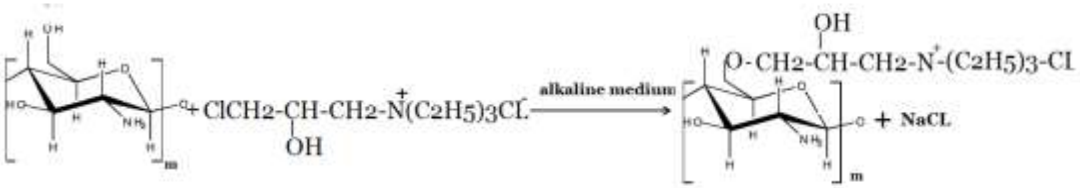


Fig. 22: Cationization of chitosan using 3-chloro propyl triethyl ammonium chloride.

3 Chitosan membrane preparations for FC

A composite material is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. The individual components remain separate and distinct within the finished structure, differentiating composites from mixtures and solid solutions. Hybrid materials are composites consisting of two constituents. If the two constituents are in nanometer or molecular level they are known as nano hybrid materials. Commonly one of these compounds is inorganic and the other one organic in nature. Thus, they differ from traditional composites where the constituents are at the macroscopic (micrometer to millimeter) level. Mixing at the microscopic scale leads to a more homogeneous material that either show characteristics in between the two original phases or even new properties. Following are some methods were attempted for preparations of hybrid and composite membranes to be used for FCs.

Chitosan-silica (CSSi) hybrid films have been fabricated by F. Al-Sagheer et al. [68] by sol-gel process using tetraethoxysilane (TEOS) Both organic and inorganic phases show increased interfacial interaction. The particles in the matrix were of homogeneous distribution with a particle size in the range of 2–7 nm. The thermal stability of the composites increases with the increase in silica concentration. 30 wt% silica was optimum. A gradual increase of 3.0 GPa in the modulus relative to the pure polymer is observed. The reaction is presented in Fig. 23.

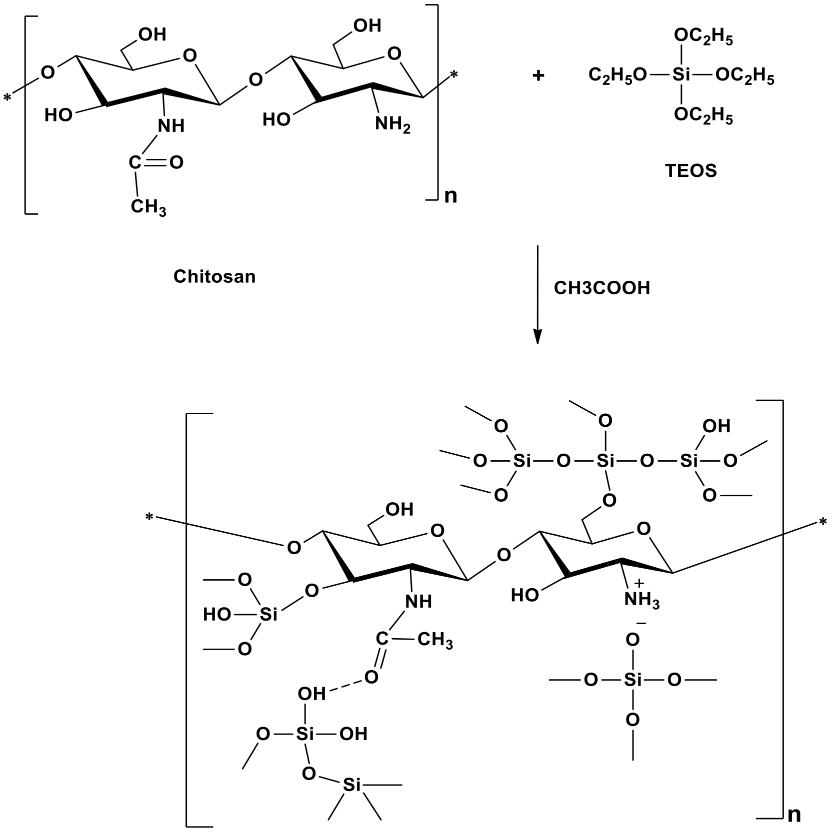


Fig. 23: Schematic representation for preparation of (CS-Si) hybrids.

Siti Wafiroh et al. [69] synthesized membrane for PEMFC by utilizing the natural polymer chitosan modified into hybrid zeolite. Zeolite was synthesized by hydrothermal methods. CS was dissolved in 1% acetic acid and mixed with different concentration of zeolite. A Hybrid zeolite A chitosan sulfonated membrane was formed by soaked the membranes for 2 hours in H2SO4 at room temperature. Then neutralized with washed using demineralize water, and then dried. Performance of hybrid zeolite A chitosan sulfonated membrane as proton exchange membrane was tested by proton conductivity test.

Nur Fatin et al. [70] reported that Proton exchange membranes (PEMs) based on chitosan (CS) and cellulose (CL) have been prepared using a solution-casting technique with sulfosuccinic acid (SSA) as an ionic cross linker and dimethyl sulfoxide (DMSO) to dissolve cellulose, and acetic acid was used to prepare CS solution. The proton conductivity of a cross-linked CS-CL membrane was on the order of 10-5 S cm-1, which is greater than the proton conductivity of a pure CS membrane.

A. Muthumeenal et al. [71] modified CS by phthaloylation using an excess of phthalic anhydride at 130 ^{O}C and blended with the sulfonated polyethersulfone (SPES) to produce composite blend membranes. In particular the introduction of the phthaloyl group into the chitosan matrix increases its solubility in organic solvent, film formability, flexibility, low methanol permeability and with suitable ion conductivity. SPES and Nphthaloyl chitosan (NPHCs) blend membranes with various compositions were prepared and detailed investigation on water uptake, proton conductivity and methanol permeability has been conducted for its suitability in fuel cell environments as reported by

Ionically cross-linked polyelectrolyte complex (PEC) membranes of cationic chitosan (CS) and anionic poly(acrylic acid) (PAAc) were synthesized by B. Smitha et al. [72] which assessed for applicability in fuel cells. CS and PAAc were blended in different weight ratios and the resulting membranes were post treated to enable the formation of the polyelectrolyte complex. The ionic cross-linking occurring on blending the polyelectrolytes excludes the need of using other cross-linking agents. Methanol permeability and proton conductivity were estimated and compared with respective values for Nafion 117. PEC membranes exhibited high ion exchange capacity (IEC), high proton conductivity (0.038 S,cm-1), low methanol permeability, and adequate thermal and mechanical stability. Above all, the cost-effectiveness and simple fabrication technique involved in the synthesis of such PECs makes their applicability in DMFC quite attractive.

V.Vijayalekshmi et al. [73] prepared a series of novel ionic cross-linked chitosan (CS) based hybrid nanocomposites by using polyaniline/nano silica (PAni/SiO2) as inorganic filler and sulfuric acid as an ionic cross-linking agent. The CS/P Ani/SiO2 nanocomposites show enhanced mechanical properties and improved oxidative stabilities. These nanocomposites can be effectively used as environmental friendly proton exchange membranes. Fig. 24 represents the reaction formation of CS/P Ani/SiO2 nanocomposites.

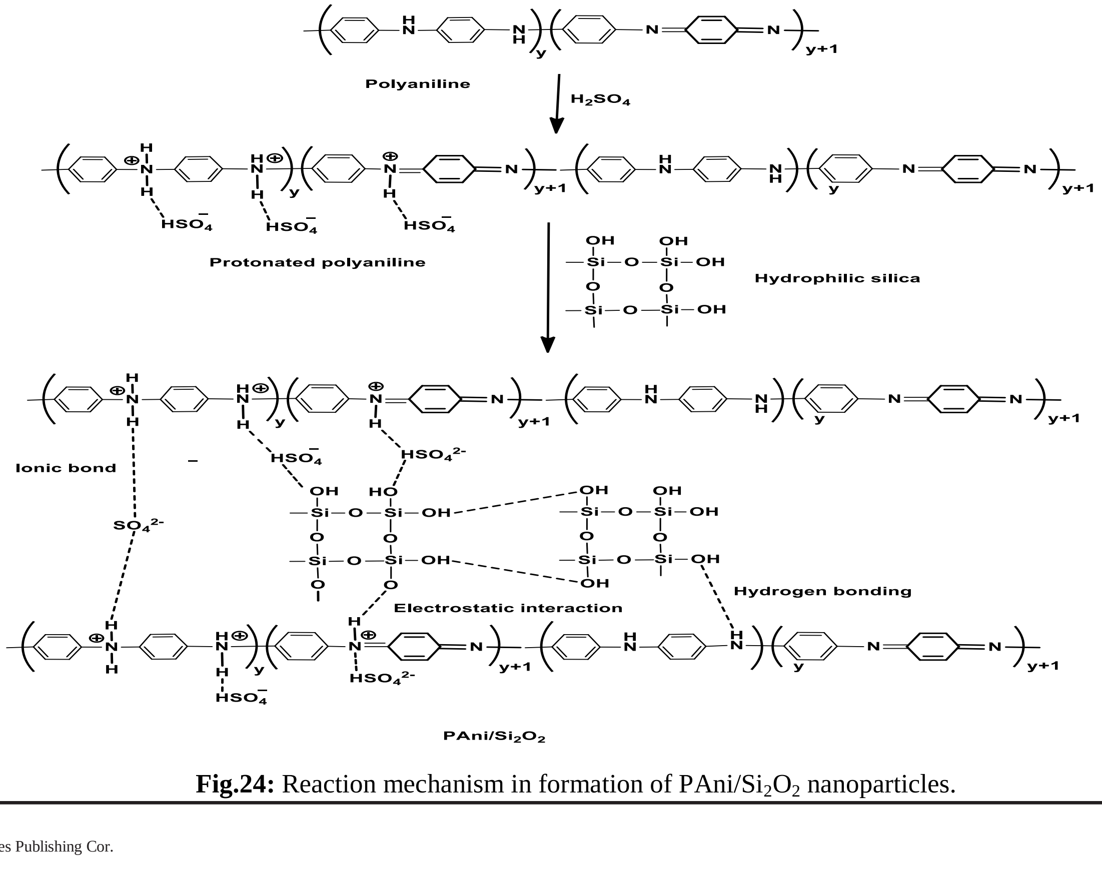


Fig.24: Reaction mechanism in formation of PAni/Si_2O_2 nanoparticles.

Siti Wafiro et al [22] prepared of a sulfonated chitosan-calcium oxide (CaO) composite membrane to be used as a fuel cell proton exchange membrane. Production of membranes was done by mixing dope of a chitosan solution with CaO powder of varying concentration (0 %, 10 %, 15 %, 20 %, 25 % and 30 %). The crosslinking process is carried out with the participation of glutaraldehyde, while the sulfonation proceeds in H_2SO_4. The optimum characteristics obtained in presence of 25 % CaO refer to ionic exchange capacity of 1.517 meq/g, swelling of 28.207 %, methanol permeability of 1.211 x 10-4 kg/m^2s, and proton conductivity of 6.415 x 10-5 S/cm.

Balappa et al [74] prepared functionalized graphite oxide and subjected it to sulfonation via a simple procedure in the presence of 1,4-butane sultone (BS) and sodium dodecyl benzene sulfonate (SDBS). The resulting sulfonated graphite oxides were incorporated into polystyrene sulfonicacid-co-maleic acid (PSSA-MA) crosslinked sodium alginate in different mass% to enhance the water uptake, mechanical stability and proton conductivity of the membranes. Among the developed proton exchange membranes (PEMs), membranes containing 16 mass% of graphite oxide sulfonated with BS and SDBS respectively exhibited the highest proton conductivity of 0.133 and 0.145 S/cm at 80^{O}C. The ion exchange capacity (IEC) of these membranes was found to be 1.40 and 1.52 meq/g, respectively. The performance of the membranes was evaluated using fuel cell workstation at 80^{O}C. The proton conductivity was found to be dependent on the concentration of the ionic cross linker. Eqs 6 and 7. represents the reactions steps.

4 Conclusion

In this article, reviewing of large studies for preparation of CS derivatives to meet the requirements of desired membrane for FCs are covered, where chemical modifications of CS were carried out by sulfonation, phosphorylation and quaternization. In addition some methods for synthesizing of CS membranes are included.

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