Prospects on utilization of biopolymer materials for ion exchange membranes in fuel cells

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ABSTRACT

Cellulose and its derivatives, and chitosan are biopolymers that are touted as promising green alternatives for fuel cell ion exchange membrane (IEM) components due to their ubiquitous nature leading to low costs, environmental compatibility, and flexibility for modification. This review analyzes the various ways bacterial cellulose, nanocrystalline cellulose, cellulose nanofibers, cellulose acetate, and chitosan have been utilized in IEM synthesis. Key points realized from the rigorous literature evaluation are: (1) cellulosic and chitosan-based components were effectively used as both substrate and reinforcement, providing enhanced mechanical properties and additional sites for ion transport functionalization, (2) membrane fabrication involving grafting and crosslinking exhibited better mechanical and chemical stability compared to doping and impregnating techniques, (3) clever use of structures such as interpenetrating and semi-interpenetrating networks, like nanofiber skeletons, provided significant reduction in membrane swelling which is important in biopolymer-containing membranes due to its inherent hydrophilicity, and (4) the use of cellulosic materials had consistently resulted to improved methanol barrier characteristics for direct methanol fuel cell applications. However, a large portion of biopolymer-based IEM literature predominantly focused on proton exchange membrane research, and it is recommended that more attention should be shifted towards exploring biopolymer-based anion exchange membranes taking into consideration effective strategies that address the balance between swelling and performance.

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Introduction

Research into reliable, renewable, and clean alternative energy solutions continue to thrive as the world pushes for the mitigation and elimination of pollution from energy generation, amidst depleting fossil fuel reserves and soaring energy demands (1). Thus, considerable efforts have been put into developing ion exchange membrane fuel cell (IEMFC) technology which utilize carbon-neutral fuel such as hydrogen gas and methanol to generate electricity. At the forefront of IEMFC is the proton exchange membrane fuel cell (PEMFC), with the proton exchange membrane (PEM) at its core. In a PEMFC, hydrogen is oxidized at the anode while oxygen is reduced at the cathode through
noble metal (e.g. platinum) catalyst layers. This redox reaction is balanced by the migration of $\mathbf{H}^+$, produced at the anode, through the PEM to the cathode, and the flow of electrons, also produced at the anode, through an external circuit (Figure 1(a)). Thus, the effectiveness of the PEM in ion transport is an important aspect of electricity generation in a PEMFC (2).

Nafion® produced by Du Pont, is currently the most successful commercial PEM and is widely seen as the benchmark among researchers (3–5). It is constituted of a hydrophobic fluorinated backbone which provides thermal, chemical, and mechanical stability, along with hydrophilic sulfonic acid groups able to attract positive ions (6–8). The pronounced hydrophobic and hydrophilic domains produce hydrophilic channels conducive to ion transport within the membrane and impart Nafion® with ionic conductivities greater than 100 mS cm$^{-1}$ (3, 9). However, Nafion®’s reliance on hydration for ionic conduction leading to limited operating temperatures coupled with high membrane fabrication costs have hindered its widespread adoption (10). Various studies have been conducted to improve Nafion® by mitigating its disadvantages through pretreatment, utilization of reinforcing agents, formation of nanocomposites, and blending with other polymers (11–13). Researchers have endeavored to study other combinations of hydrophobic backbones with hydrophilic proton-conducting moieties to varying degrees of success (3), and some have also attempted combining membranes with protic ionic liquids (PIL) in both fluid and polymeric forms improving thermal stabilities but at lacking performance (14). Some PEM have also been designed for lower methanol permeability in direct methanol fuel cell (DMFC) applications, a subset of PEMFC which utilize methanol as fuel, since the current Nafion® membranes are susceptible to methanol crossover which have led to fuel loss and reduced performance (15, 16).

Anion exchange membrane fuel cells (AEMFC) operate in a similar principle to PEMFC but produce $\mathbf{OH}^-$ at the cathode through oxygen gas reduction and transport these through the anion exchange membrane (AEM) towards the anode (Figure 1(b)). Apart from this, AEMFC have the distinct advantage of having a faster oxygen reduction reaction than PEMFC which brings lower activation losses in effect permitting the use of cheaper non-noble metal catalysts for both electrodes (17–19). The possibility of cheaper fabrication costs has spurred research into numerous chemistries of AEM, employing similar strategies to PEM synthesis such as through formation of hydrophilic–hydrophobic phase separation for improved ionic conductivity, crosslinking of ionic clusters, and development of interpenetrating functionalized polymer networks (20). With all these considerations, researchers struggle to create the ideal IEM exhibiting high ionic conductivity and low fuel permeability while maintaining high durability and stability, all at an economical production cost (2, 21, 22).

**Biopolymers as ion-exchange membrane component**

Figure 2 shows the continuous and rapid growth of research publications involving IEMFCs for the past 20 years, wherein the blue bar represents the total number of publications for each year while a subsequent filter search with keywords ‘cellulose’ or ‘chitosan’ or ‘biopolymer’ was performed to obtain the green bar representing the number of reports for biopolymer-based IEMs. It is very clear from the illustration that synthetic polymer-based IEMs are predominantly the focus of research and biopolymer-based IEMs are greatly outnumbered in terms of research output for the past 2 decades. It is therefore noteworthy of closer scrutiny the preponderance of literature on synthetic polymer-based IEM, investigate the frailties and challenges of the use of biopolymer-based materials as IEM precursor, and to revisit the potential of biopolymer-based IEM as lucrative economical alternative.

Biopolymers have garnered attention for consideration as components in IEM fabrication mainly for their natural abundance translating to lower material cost, and their environmental compatibility, which is of increasing importance in today’s society (1). Some notable biopolymers are cellulose and its derivatives which have a global annual production of one trillion tons with sources varying from plant biomass, agricultural waste, algae, cellulose-producing bacteria, and tunicates (24–26). Cellulose is seen as a good candidate for membranes due to its high mechanical strength, good water retention, low gas and methanol permeability, and good thermal stability (27, 28). It is formable into membranes and nanofibers, as well as modified through grafting or crosslinking via conventional wet-chemistry and irradiation techniques to impart desirable properties such as ion-conducting capability due to the three available hydroxyl groups in each of its anhydroglucose units (Figure 3(a)) (29). These hydroxyl groups however also heavily influence the physical properties of cellulose as their capacity to form hydrogen bonds improve crystalline packing, and higher portions of crystalline regions, as opposed to amorphous regions, lead to higher mechanical strength and stiffness (30). The hydroxyl groups may be substituted with acetyl groups to produce cellulose acetate, a common derivative of cellulose which can be referred to as a mono-, di-, or triacetate depending on the degree of
substitution of acetyl groups (31). The diacetate form of cellulose acetate (Figure 3(b)) is preferred due to its solubility to common organic solvents such as acetone which allow for the use of easier forming techniques (32).

Another attractive biopolymer is chitin which is commonly found in the exoskeletons of crustaceans and insects, as well as the cell walls of fungi (33). It is second only to cellulose in natural abundance and has an estimated annual production of $10^{12}$–$10^{14}$ tonnes (34, 35), with about $10^6$ tonnes in crustacean waste from the food industry (36). The structure of chitin differs with cellulose in that where cellulose has three hydroxyl groups per anhydroglucose unit, chitin has only two hydroxyl groups and an amine group covalently bonded to an acetyl group forming what is known as a N-acetyl D-glucosamine unit (Figure 4) (37, 38). Deacetylation of chitin by over 50% produces a bio-degradable derivative known as chitosan which is soluble in acidic aqueous solutions unlike its precursor (35, 39).

**Bacterial cellulose**

Bacterial cellulose (BC) is a highly crystalline extracellular matrix made by multiple types of bacteria including those from the genera *Gluconacetobacter* and *Komagataeibacter*, with high-yield species such as *Gluconacetobacter xylinus* (also known as *Acetobacter xylinum* and *Komagataeibacter xylinus*) exhibiting promising potential for use in industrial scale production (40–42). The nanofibrillar 3D structure is 100 times thinner than plant cellulose while having higher tensile strength, crystallinity index, and water holding capacity (43). It is also favored for its high purity, wherein lignin and hemicellulose typically found in plant cellulose are absent (44). The reactive hydroxyl groups present in the cellulose structure allow for chemical modifications such as attachment of functionalized groups which enable ionic conduction.

One of the first attempts to utilize bacterial cellulose in ion exchange membranes for fuel cells was done by Choi et al. (45) for application in proton exchange membrane fuel cells (PEMFC). The membrane was prepared by synthesizing bacterial cellulose from *Acetobacter* sp strain JH232 and grafted with acrylic acid (AAc) through UV-irradiation. The scanning electron micrographs showed that the grafting with AAc filled the initially porous structure of BC (Figure 5(a)), thereby increasing the structural density with longer irradiation times (Figure 5(b)). The cross-linking between BC and AAc also increased the mechanical strength of the membrane, achieving up to 12 MPa tensile strength in wet conditions, which was comparable to the commercially available Tokuyama Neosepta CMX membranes which registered a tensile strength of 15 MPa under the same conditions. The study was also able to show that the imparted AAc caused the increase in ion exchange capacity (IEC) up to 3.1 mmol g$^{-1}$ due to its anionic head group.

Jiang et al. (46) took a different approach and soaked BC films, cultured from *Gluconacetobacter xylinus*, in phosphoric acid ($\text{H}_3\text{PO}_4$) and phytic acid (PA) to impart ion exchange properties resulting in $\text{H}_3\text{PO}_4$/BC and PA/BC proton exchange membranes. In this method however, the interaction of BC with the acid resulted in a plasticizing effect where the elastic modulus and yield strength both decreased generally with higher
concentrations of H$_3$PO$_4$ and PA. This was attributed to the hydrogen-bonding interactions between the acid and the crystalline regions of BC which led to a decrease in crystallinity and increase in amorphousness. Although there was a sharp decrease in modulus from ca. 1600 MPa for a pristine BC membrane down to the range of 120–180 MPa for the 7.2 M H$_3$PO$_4$/BC membrane and 280–360 MPa for 1.2 M PA/BC membrane, it was reported that commercial Nafion$^\circledR$ membranes exhibit an elastic modulus of around 185 MPa at similar measuring conditions indicating that the acid-doped BC membranes still possess viable mechanical properties for PEMFC applications. The PA/BC membranes reached a higher power density at ambient temperature than H$_3$PO$_4$/BC at 23.0 mW cm$^{-2}$ and 17.9 mW cm$^{-2}$, respectively, although the achieved power densities were still much lower than Nafion$^\circledR$ (i.e. in the order of 10$^2$ mW cm$^{-2}$). Jiang et al. (46) proposed possible routes for improvement such as using a crosslinking method to avoid leaching of the doping acid, and optimizing other aspects of the membrane electrode assembly (MEA) preparation.

Gadim et al. (47) harvested BC from *Gluconoacetobacter sacchari* bacterial strain and crosslinked with poly(4-styrene sulfonic acid) (PSSA), a polyelectrolyte ionic liquid with high proton-conductivity, using poly(ethylene glycol) diacrylate (PEGDA), in order to stabilize and prevent dissolution of PSSA in water. This resulted in a nanocomposite membrane where PSSA/PEGDA was entangled in the nano fibrillar matrix of BC through

![Figure 2](image2.png)  
*Figure 2. Number of research publications related to synthetic polymer-based IEM compared to biopolymer-based IEM from 2001 to 2020. (Source: Scopus website).*

![Figure 3](image3.png)  
*Figure 3. Chemical structures of (a) cellulose and (b) cellulose diacetate.*

![Figure 4](image4.png)  
*Figure 4. Chemical structure of chitin and its transformation to chitosan via deacetylation.*
crosslinks between the chains of the former. As expected, increasing the concentration of the crosslinker PEGDA increased the amount of PSSA crosslinked in BC, and the resulting PEMs exhibited IEC of up to 2 mmol g\(^{-1}\) at a combination of 80 wt% PSSA/PEGDA which translated to proton conductivities at 94°C of above 100 and 42 mS cm\(^{-1}\) at 98% and 60% relative humidity (RH), respectively. These conductivities were reportedly higher than those of Nafion® 117, with ionic conductivity typically at around 50 mS cm\(^{-1}\) at 95°C and 98% RH (48, 49). However, as similarly observed in the work of Jiang et al. (46), achieving ionic conductivities higher than Nafion® does not directly translate to power densities higher than that of commercial membrane. It is also notable that the membrane swelling did not exceed 25% at 94°C and 98% RH, even as the water uptake reached values of up to 185 wt%, which is a desirable property for membranes.

Gadim et al. (50) performed a subsequent study and focused on assessing the anisotropic effect of the preferential orientation of BC, as these are formed of nanofibrils, and the crosslinked PSAA on the protonic conductivity of the membranes. They found that the membranes exhibited over a half order of magnitude higher in-plane ionic conductivity rather than through-plane at 40% RH indicating a discontinuity in proton transport between PSSA and BC phases. At 98% RH however, the difference between in-plane and through-plane ionic conductivity reduced to 20%, showing the importance of keeping the membrane hydrated to establish hydrophilic domains across the BC/PSSA interface for improved proton transport. The study suggested that the observed anisotropy of proton conductivity is negligible in fuel cell operation since liquid water is generated when operating temperatures are less than 90°C, potentially keeping the membrane hydrated at 100% RH. The BC/PSSA membranes achieved through-plane ionic conductivity of up to 5.4 mS cm\(^{-1}\) at ambient temperature and 98% RH corresponding to a relatively high power density of 41 mW cm\(^{-2}\) under the same conditions, which is amongst the highest reported values for biopolymer electrolytes.

Rogalsky et al. (51) found a similar approach in PEM fabrication by devising their own polyelectrolyte ionic liquid, N-butylguanidinium tetrafluoroborate (BG-BF_4), and impregnating it into a BC matrix formed from Komagataeibacter intermedius IMBG291 strain (Figure 6(a)). BG-BF_4 on its own achieved a proton conductivity of 21–180 mS cm\(^{-1}\) from 25 to 180°C but its incorporation into the BC matrix at 80 wt% BG-BF_4 resulted in a drastic drop in ionic conductivity exhibiting values of 0.12–0.45 mS cm\(^{-1}\) from 25 to 180°C with an appreciable tensile strength of 35 MPa. Increasing the saturation of the ionic liquid to 95% increased the ionic conductivity from 1.6–52 mS cm\(^{-1}\) within the same temperature range but decreased the tensile strength to only 6 MPa. The researchers sought to further increase the ionic conductivity by polymerizing polyaniline (PANI), a proton conducting electrolyte, onto BC before impregnating with BG-BF_4.

As the BC/PANI system conducts protons through the Grothuss mechanism wherein the proton hops between negatively charged groups, the protons largely interact with the C=N quinone-imine nitrogens causing a synchronous elimination of H\(^{+}\) from the N-H groups, effectively moving the protons as seen in Figure 6(b). The resulting membranes exhibited a large increase of ionic conductivity in BC/PANI containing 80 wt% BG-BF_4 at 0.15–4 mS cm\(^{-1}\) with a decrease in tensile strength to 20 MPa. Similarly, a large increase in ionic conductivity was observed when the BG-BF_4 saturation was increased to 95%, achieving a maximum of 110 mS cm\(^{-1}\) at 180°C, but accompanied by a decrease in tensile strength to a worrying 4 MPa. The report noted that the further decrease in tensile strength was likely due to the lowering of intermolecular hydrogen bonds between PANI-coated cellulose nanofibrils. However,
the membranes still show promise since BC/PANI-BG-BF₄ (80%) \(^{(51)}\) has tensile strength, comparable to Nafton® in the same conditions, and possibly achieve similar power density to the BC/PSSA membranes of Gadim et al. \(^{(50)}\) due to similar ionic conductivity though at a much higher operating temperature of 180°C. The overall more stable and appreciable properties of BC/PSSA membranes over BC/PANI-BG-BF₄ may be due to the former utilizing a crosslinking method while the latter simply saturated the BC/PANI matrix in the polyelectrolyte.

Vilela et al. \(^{(52)}\) sought to fabricate fully biopolymer-based PEM by using BC and fucoidan, an algae sulfated polysaccharide which exhibited proton transport capabilities. The two were crosslinked using tannic acid to stabilize the water-soluble fucoidan (Fuc). As the entire PEM was bio-based, thermal-oxidative analysis was performed and found that BC/Fuc was stable up to 180–200°C allowing comfortable operation in a PEMFC. Interestingly, membranes with higher fucoidan composition exhibited larger storage moduli (i.e. the amount of energy needed to induce elastic deformation), with BC/Fuc containing 75 wt% fucoidan registering up to 813 MPa at 180°C, which is 3 orders of magnitude higher than the storage modulus of Nafton® at the same temperature \(^{(53)}\). In contrast, BC/Fuc containing 50 wt% fucoidan had a storage modulus of 460 MPa at 180°C. Such observation may be attributed to the pore-filling effect of crosslinking fucoidan into the BC 3D network. A maximum ionic conductivity of 1.6 mS cm\(^{-1}\) was measured for BC/Fuc\(_{75}\) at 98% RH and 94°C, which is two orders of magnitude lower than Nafton® in the same operating conditions.

BC has also been used for application in other fuel cell types such as direct methanol fuel cells (DMFC). One of the first BC-based PEM for DMFCs was prepared by Lin et al. \(^{(54)}\) by UV-grafting BC with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). On its own, poly(AMPS) displayed a higher proton conductivity than Nafton® due to its sulfonic acid groups, but its highly hydrophilic nature required the introduction of a stable and strong copolymer such as BC. The resulting membranes showed an increasing trend in IEC with AMPS concentration, measuring 1.79 mmol g\(^{-1}\) at 20% AMPS. As expected, a positive trend in water uptake (WU) and proton conductivity followed as well, achieving maximal values of 264 wt% and 29 mS cm\(^{-1}\) respectively at 20% AMPS. The membranes were initially

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**Figure 6.** The (a) preparation of BC-PANI composite membrane and the (b) proton conduction mechanism in BC/PANI/BG-BF₄ composite membrane. Adapted from Rogalsky et al. \(^{(51)}\) with permission. Copyright 2018, Elsevier.
measured for their power density in PEMFC to promising results, with AMPS20-g-BC membranes achieving the highest values at 61−97 mW cm$^{-2}$ from 30 to 50°C. However, WU values exceeded 200 wt% with AMPS content greater than 15%, which could possibly translate to a loss of mechanical performance. Hence, the AMPS10-g-BC membrane was chosen for DMFC performance characterization instead. The methanol permeability of the membrane was one order of magnitude lower than Nafion®, at 5.64×10$^{-7}$ cm$^2$ s$^{-1}$ indicating a slightly lower susceptibility to fuel crossover and consequent loss of performance. However, when using a 2 M methanol solution in the DMFC, a power density of 16 mW cm$^{-2}$ was measured for the AMPS10-g-BC membrane, which was approximately 35% that of Nafion® under the same conditions. The power density decreased to 9 mW cm$^{-2}$ when a 10 M methanol solution was used, corresponding to 60% of Nafion®’s performance under the same conditions.

Nevertheless, the AMPS-g-BC membranes showed promise as methanol barriers and potential candidates as PEM in DMFC applications. BC-based membranes have also seen some development for AEMFC applications as seen in the study of Vilela et al. (53). The researchers took a similar approach to the study of Gadim et al. (47), wherein BC/PSSA nanocomposite membrane was produced, and synthesized a nanocomposite of BC and a poly(ionic liquid) namely poly(methacroylcholine chloride) (PMACC). The crosslinking of PMACC in-situ also resulted in physical entanglement within the BC matrix in place of chemical bonding while maintaining a macroscopically homogeneous membrane. It was demonstrated that crosslinking of PMACC in-situ decreased the functional polymer loss to negligible values of 1-2% from 20% loss seen in non-crosslinked samples. Due to the hygroscopic nature of PMACC, the water uptake values increased from 162 wt% in pure BC to 2057 wt% at 71 wt% PMACC and registered an IEC of 1.56 mmol g$^{-1}$. It is notable that such a high WU value had not been reported in AEMs until this study. Elastic modulus and tensile strength of the membranes were examined, though as dry membranes, and it was found that both properties decreased with increasing PMACC content in the nanocomposite membranes. The AEM with PMACC of 56 wt% showed the best combination of mechanical and electrochemical properties, with tensile strength and elastic modulus at 15.4 and 620 MPa respectively, andionic conductivity of 10 mS cm$^{-1}$ at 94°C under 98% RH.

In this section, we have discussed the applications of BC in different IEMFC and have found it to be successfully used as either the bulk or stabilizing matrix component of the IEM with modifications varying from grafting, to doping, and crosslinking, whether directly between polymeric chains or forming an interpenetrating network, to impart ionic transport capabilities. Doping and impregnation techniques provided the membranes with strong ionic conductivities, but at the cost of a large drop in mechanical performance which could lead to membrane failure over long operating periods. Furthermore, achievable power densities have not reached a level comparable to Nafion® even as some BC-IEM have attained ionic conductivities surpassing it. In-situ crosslinking with ionic liquids seems to have been more effective as mechanical properties such as elastic modulus are preserved to a greater extent resulting in strong membranes with appreciable performance as seen in the study of Gadim et al. (47).

The interpenetrating polymeric structure also exhibited an added benefit of suppressing membrane swelling to under 25% even as WU values approached 185 wt% in PSSA/BC membranes which would lend to the physical stability of the IEM under operation. BC has also proven itself to be a good methanol barrier, with a methanol permeability of up to one magnitude lower than Nafion® as seen in the study of Lin et al. (54).

**Micro/Nanocrystalline cellulose**

Cellulose, whether from plant or bacterial source, may be hydrolyzed with acid to dissolve amorphous regions and concentrate the crystalline components forming microcrystalline cellulose (MCC) which may be further refined into nanocrystalline cellulose (NCC) as seen in Figure 7. A rod-like form is typically achieved ranging from 50 to 200 nm in length (56). NCC may be incorporated into polymeric matrices to enhance mechanical properties such as tensile strength, bending strength, and stiffness with the prospect of chemical modifications (57).

In 2016, Ni et al. (58) aimed to synthesize a PEM based on fluorenyl-containing polyaryletherketone (FPAEK). They noted that although this polymer had a good balance of physical and chemical properties, its potential for high proton conductivity, provided by four sites for sulfonation in each fluorenyl group, was hindered by the accompanying excessive water uptake that could lead to the loss of mechanical strength and dimensional stability. To balance proton conductivity and mechanical properties, incorporation of nanomaterials was sought, and thus sulfonated FPAEK (SFPAEK) and sulfonated nanocrystalline cellulose (sNCC) were combined and solution casted to form a nanocomposite PEM. The study found that the tensile strength and elastic modulus of sNCC-reinforced SFPAEK in wet conditions increased...
by 10% and 14% from 25 and 519 MPa, respectively, when sNCC content was increased to 4 wt%. However, a decline in mechanical properties was observed at sNCC content higher than 4 wt% with corresponding decline in protonic conductivity. Water uptake and swelling increased with sNCC content due to the presence of sulfonates in both SFPAEK and sNCC. The report surmised that this was due to the possible agglomeration of the sNCC at higher concentrations, thus decreasing proton conduction due to the reduction of proton-conducting paths important in the Vehicle mechanism of conduction. The study aptly showed that the incorporation of functionalized sNCC up to 4 wt% definitively increased the performance of SFPAEK as proton-conducting membranes, with tensile strength and elastic modulus at 27.6 and 593.7 MPa respectively, and ionic conductivity of up to 234 mS cm\(^{-1}\) at 100°C.

Wei et al. (59) applied the same methodology to sulfonated poly(ether ether ketone ketone)s (SFPEEKKs) to obtain sulfonated sNCC-reinforced nanocomposite PEM. Similar to the results of Ni et al. (58), Wei et al. (59) found that increasing sNCC content up to 5 wt% showed an increase in tensile strength and modulus of elasticity of membranes in wet condition, followed by a decline in mechanical properties at higher concentrations. The effect of the degree of sulfonation of the SFPEEKK membranes were also considered, and it was found that higher sulfonation led to lower mechanical properties, most likely due to the increased water uptake. The research also noted that the reinforcing effect of sNCC up to 5 wt% may be attributed to the formation of hydrogen bonds between the hydroxyl groups in NCC and the sulfonic acid groups in SFPEEKK forming an interlock. The protonic conductivity again exhibited a positive trend peaking at 5 wt% sNCC. The observed decline in performance at higher sNCC loading was attributed to the agglomeration of sNCC that can block proton pathways for Vehicle mechanism conduction.

There are two generally accepted mechanisms of proton transport inside the membrane: Grotthuss (60) and Vehicle mechanism (61). The Grotthuss mechanism describes the proton transport via hopping or jumping of proton (H\(^+\)) through the neighboring lone electron pair to that of another. This proton jump usually occurs in the regions where -OH ions are interacting with -SO\(_3\)H clusters by hydrogen bond (Figure 8). On the other hand, in the Vehicle mechanism, proton transfer proceeds via diffusion and movement of hydronium ion (H\(_3\)O\(^+\)) with water molecules through the hydrophilic channels in the structure of the composite membrane (Figure 8). Membranes with sulfonation degree of 2.34 and sNCC content of 5 wt% achieved better proton conductivities of 240 mS cm\(^{-1}\) at 80°C than the previously reported study by Ni et al. (58), though tensile strength...
and elastic modulus values were lower at 15 and 357 MPa, respectively.

A follow up study attempted to structure-optimize the previously reported SFPEEK/sNCC nanocomposite PEM (62). To do this, proper balancing of SFPEEK’s hydrophobic domains (which provide mechanical strength to the membrane and are represented by partially fluorinated segments) with its hydrophilic domains (which are essential to ion transport and represented by densely sulfophenylated fluorenyl segments) was considered. As hypothesized, membranes fabricated with 30% fluorenyl segments as repeating units had higher tensile strength and elastic modulus compared to membranes fabricated with 60%. The addition of sNCC still showed similar trends to the previous studies (58, 59) where the mechanical properties peaked at an sNCC content of 4% with SFPEEK-30/NCC-4 displaying the best mechanical properties at 43.2 MPa tensile stress and 961.7 MPa elastic modulus. Conversely, SFPEEK-60/ NCC-4 displayed the best electrochemical properties due to the higher number of hydrophilic segments and favorable reinforcement of sNCC achieving ionic conductivity of 245 mS cm$^{-1}$ at 90°C, with better tensile strength and elastic modulus than their previous study (59) at 25.5 and 578.2 MPa, respectively.

A subsequent investigation also explored the effect of crosslinking on SPAEK with carboxylic acid groups (SPAEEK-COOH-x) using sNCC as both performance-enhancing filler and crosslinking agent, where the hydroxyl groups of sNCC would react with carboxylic acid groups in SPAEEK-COOH-x to form crosslinks between chains (63). It was found that crosslinking increased tensile strength by up to 32.4% while maintaining similar ionic conductivity. The involvement of sNCC in crosslinking also shifted the peak of observed mechanical properties from around 4 or 5 wt% sNCC content to 8 wt%. The composition optimized membrane C/COOH-10/NCC-8 achieved a tensile strength of 32.3 MPa, elastic modulus of 892.1 MPa, and ionic conductivity of 192 mS cm$^{-1}$ at 90°C.

Zhao et al. (64) built upon the previous studies by investigating the effect of adding amine groups to sNCC (Am-sNCC) used as reinforcement and crosslinker in phenyl-containing SPEEK (Ph-SPEEEK) nanocomposite PEM. It was found that the addition of amine groups as proton-conducting groups increased the ionic conductivity observed in the membranes at higher temperatures by up to 40% at 100°C for Am3-sNCC-5 membranes compared to sNCC-5 membranes even though IECs were lower by 4% due to sulfonic groups providing more sites for proton exchange than the amino groups. This was attributed to the increased water uptake of Am-sNCC membranes providing better proton transport through Vehicle mechanism. Ion transport properties peaked at sNCC content of 5 wt% once again due to possible agglomeration at higher concentrations reducing the effectiveness of the Vehicle mechanism. Furthermore, membrane swelling was lower for Am-sNCC containing samples, though water uptake was higher due to the additional ionic interaction of the amino groups of the Am-sNCC and the sulfonic groups of the Ph-SPEEKK, which restricted the motion of the hydrated polymer matrix. The Am3-sNCC-5 membranes exhibited the best performance with ionic conductivity of 210 mS cm$^{-1}$ at 100°C and power density of 227 mW cm$^{-2}$ at 75°C under 100% RH, tensile strength of 42.3 MPa, and elastic modulus of 1177 MPa.

NCC has also been utilized as performance-enhancing filler in PEM for DMFC applications such as in the study of Hosseinpour et al. (65) wherein NCC was spray-coated between layers of Nafion® membranes to act as methanol barriers in a multilayer membrane setup. This application of NCC was found to reduce methanol flux density, pertaining to fuel crossover, by up to 11% compared to pristine Nafion® 115 and non-NCC treated membranes. Membrane ML-CNC-2 exhibited over 100% and 35% higher power densities than both its untreated counterpart and Nafion® 115, respectively, reaching up to 75.53 mW cm$^{-2}$ at 70 °C and 1M methanol. This was achieved despite the lower ionic conductivity of the NCC-treated membrane. The observed decrease in methanol crossover led to lower performance losses, demonstrating the potential for operations at either higher power densities or lower fuel volumes at similar power densities, the latter of which could reduce the size of the DMFC that is desirable for mobile or portable applications.

Another recent study conducted by Bagus Pambudi et al. (66) used regenerated microcrystalline cellulose (MCC) as the membrane matrix with proton conducting dopants imidazole or phosphotungstic acid (PTA) to form two distinct PEM for DMFC. XRD results showed that the regeneration of MCC reduced the crystallinity of the membrane from 80.6–66.5% and further reduction to 55.0% when doped with PTA or imidazole, respectively, suggesting a decrease in mechanical performance as was typical in other doped membranes discussed previously. The resulting membranes registered poor conductivities, with the imidazole-doped membrane reaching 0.214 mS cm$^{-1}$ and PTA doped membrane reaching 0.106 mS cm$^{-1}$ at ambient temperature. The methanol permeability was however lower by 60–70% compared to their Nafion® 117 reference at 3.54×10$^{-7}$ cm$^2$ s$^{-1}$ for the PTA doped membrane, which was attributed chiefly to the cellulose hydrogen bond network blocking methanol.
In 2011, Schmitt et al. \(^{67}\) used MCC to synthesize one of the first cellulose-based AEM. Due to the relatively fragile nature of available AEM at that time, the study aimed to make an AEM that utilized the high resistance of cellulose to mechanical strain and the strengthening effect of crosslinking techniques, while attaining significant anion transport through quaternary ammonium groups. Thus, in their study, MCC was dissolved and reacted with triethylamine and \(p\)-toluenesulfonyl chloride to get cellulose \(p\)-toluenesulfonate, which was then functionalized for anion exchange using diazabicyclo[2.2.2]octane (DABCO) and crosslinked using diiodobutane to obtain the AEM. Fabricated membranes had excessive water uptakes of over 200 wt% on average with ionic conductivity up to 5.4 mS cm\(^{-1}\).

The IEMs employing MCC as the bulk component showed poor performances in ion transport as cellulose inherently has low ionic conductivity, thus consequently rely on a selection of good functional groups to provide the needed ion exchange sites. Utilization of NCC, on the other hand, has generated IEM with excellent combinations of mechanical properties and ionic conductivity, with membranes such as Am3-sNCC-5 from Zhao et al. \(^{64}\) reaching power densities over 200 mW cm\(^{-2}\). However, such performance was largely dependent on the properties of the bulk matrix, with NCC acting as a performance-enhancing filler comprising only up to 8 wt% of the IEMs. Nevertheless, the strengthening effect of NCC and its capability to be functionalized to provide additional ion exchange sites were very favorable factors in crafting high performing IEM. Furthermore, both MCC matrix and dispersed NCC suppressed methanol crossover which ultimately improved membrane performance in DMFCs as seen in the study of Hosseinpour et al. \(^{65}\).

**Cellulose nanofibers**

Cellulose nanofibers (CNF) are commonly produced through mechanical treatment of plant biomass which are first treated with sodium hydroxide and sodium hypochlorite to separate from hemicellulose and lignin. Top-down methods (Figure 9(a)) such as high pressure homogenization, microfluidization, refining, and grinding introduce shear stress which defibrillate the remaining cellulose microfibrils resulting in nanofibers with diameters ranging from 10 to 200 nm and lengths in the microns \(^{68}\). CNF may also be produced in a bottom-up method (Figure 9(b)) through the hydrolysis of electrospun cellulose acetate which have the added advantage of producing longer fibers compared to the previously mentioned methods \(^{69}\). CNF retains the favorable mechanical properties of cellulose along with the chemical modifiability granted by its hydroxyl groups while forming a networked structure that may act as a matrix for support in composite systems. In the literature surveyed, CNF was commonly found to be applied in PEM for DMFC applications.

A study by Xu et al. \(^{70}\) reported embedding CNF into a sulfonated poly(ether sulfone) (SPES) matrix to improve water retention due to its hydrophilic nature and to impart additional proton-conducting channels through the reaction of the cellulose hydroxyl groups with the SPES sulfonic acid groups thereby increasing performance as a PEM. The ionic conductivity indeed increased with increasing CNF content, with the SPES/Cell-5 with 5 wt% CNF achieving a similar ionic conductivity with the Nafion® 117 test membranes of 130 mS cm\(^{-1}\) at 80°C under 100% RH. The water uptake and membrane swelling also exhibited a similar trend due to the hydrophilicity of CNF, with maximal values of ca. 40 wt% and 17%, respectively, for the SPES/Cell-5 membranes. The tensile strength also increased with increasing CNF content owing to the nanofiber skeleton imparted on the membrane, capping at 40 MPa for the dry SPES/Cell-5 membranes. Furthermore, methanol permeability decreased as CNF content increased gaining a reduction of up to 21% when comparing membranes with 5 wt% CNF content to pristine samples and recording a value of 4.45×10\(^{-7}\) cm\(^2\) s\(^{-1}\) at room temperature. These results showed that with comparable ionic conductivity and almost a third of the methanol permeability of Nafion® 117 (12.8×10\(^{-7}\) cm\(^2\) s\(^{-1}\) at 30°C \(^{71}\)), the SPES/Cell-5 membranes are good candidates for PEM in DMFC applications.

Zhao et al. \(^{72}\) improved on the study of Xu et al. \(^{70}\) by immobilizing proton-conducting fluorenylmethoxycarbonyl (Fmoc) group amino acid (FAA) clusters onto CNF before embedding these into sulfonated polysulfone (SPSF) to further increase proton conductivity. Similar to the previous study \(^{70}\), positive trends in water uptake and swelling were observed with respect to increasing cellulose- amino acid (cell-AA) concentration, with manageable values not exceeding 60 wt% and 30%, respectively. The addition of cell-AA also decreased methanol permeability compared to pristine samples due to the hindrance of the curved CNF skeleton on the movement of methanol molecules, as well as the hydroxyl group in cellulose and amino group in the FAA forming hydrogen bonds with the sulfonic acid group in SPSF which narrowed the methanol transmission channels. The cell-AA membranes achieved higher ion conductivity than pristine membranes due to the long-range proton-conducting pathways formed by the CNF structure and the ability of the FAA clusters to facilitate proton transport through the Grotthuss
mechanism using the sulfonic acid and amino group acid–base pair. In particular, the membrane with serine clusters (cell-Ser) exhibited the highest ionic conductivity of 213 mS cm$^{-1}$ at 80°C under 100% RH which was over 100% more than pristine SPSF membranes, and 60% more than Nafion® 117 under the same conditions. The ionic conductivity further increased to 264 mS cm$^{-1}$ when cell-Ser content was increased to 20 wt %. The water uptake also increased to ca. 67 wt%, but swelling decreased to ca. 15% due to the restricting effect of the CNF skeleton. The methanol permeability decreased to 6.8×10$^{-7}$ cm$^2$ s$^{-1}$, showing that the SPSF-Ser membranes had double the ionic conductivity while maintaining similar methanol permeabilities as compared to the previous study of Xu et al. (70). It is also reported that the cell-Ser membrane obtained a maximum power density of 87.22 mW cm$^{-2}$ at 60°C under 100% RH in a DMFC (2M methanol), proving excellent performance.

Wang et al. (73) took a similar approach with that of Zhao et al. (72) by embedding modified CNF onto SPSF. Cellulose was blended with UiO-66-NH$_2$, a zirconium metal organic framework (MOF) with 1,4-benzene-dicarboxylate (BDC) as linker (74), and electrospun to form nanofibers. The amino group in the MOF acted in a similar manner to the amino acid clusters previously discussed (72) that increased the proton conductivity and water uptake of the membranes, while the nanofiber skeleton reduced membrane swelling. The ionic conductivity of the MOF-containing membranes was reportedly higher than a recast Nafion® test membrane, with the Cell–UiO-66-NH$_2$-5/SPSF membrane corresponding to 5 wt% UiO-66-NH$_2$, exhibited the highest ionic conductivity of 196 mS cm$^{-1}$ at 80°C under 100% RH. The incorporation of the MOF was also shown to decrease methanol permeability by up to 46% when comparing Cell–UiO-66-NH$_2$-5/SPSF (5.5 × 10$^{-7}$ cm$^2$ s$^{-1}$) to unmodified SPSF samples. The Cell–UiO-66-NH$_2$-5/SPSF membranes also displayed double the power density of the pristine sample when tested in a DMFC (2M methanol) at 60°C under 100% RH, peaking at 78 mW cm$^{-2}$ which was about 10% lower than cell-Ser membranes.

CNF thus proves to be highly effective in increasing mechanical properties such as tensile strength while simultaneously improving the ionic conductivity of the membrane through functionalization, even exceeding 200 mS cm$^{-1}$ in the SPSF-Ser membranes synthesized by Zhao et al. (72). This form of cellulose also exhibits the desired effect of restricting membrane swelling previously seen in the BC-IEM crafted by Gadim et al. (47, 50), featuring an interpenetrating polymer network, due to the 3D nanofiber structure restricting the movement of the membrane matrix. The studies surveyed also once again prove that cellulose acts as an excellent barrier to methanol fuel.

**Cellulose acetate**

Cellulose acetate (CA) is a derivative of cellulose wherein the three hydroxyl groups in each anhydroglucose unit can be replaced by acetyl groups (Figure 3(b)). The degree of substitution (DS) dictates whether the CA is classified as a monoacetate (DS < 2.2), diacetate (DS =
2.2-2.7), or triacetate (DS = 2.7-3.0) (31). Replacing hydroxyls with acetyl disrupts the crystallinity of cellulose and enables solubility in common organic solvents. Cellulose diacetate, for example, is soluble in acetone, while cellulose is not, which allows for reshaping through spinning and other forming processes (32). One of the most common ways to prepare CA is by reacting cellulose with acetic anhydride in an anhydrous acetic acid solution with sulfuric acid as a catalyst. The reaction is performed in excess to produce cellulose triacetate which is then hydrolyzed to partially remove acetyl groups and achieve the desired degree of substitution. Notably, the hydrophilicity of the cellulose structure decreases as more hydroxyls are substituted with acetyl groups (75).

Ramly and Ali (76) crosslinked CA with sulfonated poly(ether ether ketone) (SPEEK) to diminish the high membrane swelling common with SPEEK membranes with high degrees of sulfonation. To perform crosslinking, UV-irradiation was used on varying concentrations of SPEEK and CA in solution which reportedly avoided the consumption of sulfonic acid groups in the crosslink process, avoiding unwarranted reduction in proton-conducting groups. The water uptake was shown to increase with CA content due to the numerous hydroxyl groups that form hydrogen bonds with water. However, only a minimal increase in water uptake is observed when the CA composition was increased to 0.4% before increasing rapidly up to around 2.3 times that of the pristine SPEEK membrane (ca. 15 wt% water uptake) at a composition of 99% SPEEK and 1% CA. The proton conductivity varied with the membrane composition, increasing until the 0.4% CA composition loading and decreased thereafter. The drop-off in ionic conductivity was attributed to a possible interaction between the acetyl and sulfonic acid groups thereby reducing the sulfonic acid groups available for proton conduction, and also the rigidity of the crosslinked structure hindering proton mobility and reducing space for retaining water around the sulfonic acid groups. SPEEK (99.6%)-CA(0.4%) membranes achieved conductivity of up to 155.6 mS cm$^{-1}$ at 50°C. It is however notable that the ionic conductivities of all membranes were not measured at higher temperatures due to excessive swelling.

The researchers improved on the previous study by using methyl cellulose (MC), which contains methyl groups instead of acetyl groups, in place of CA and removing the suspected inhibiting interaction between acetyl groups and sulfonic acid groups (77). Benzoin ethyl ether (BEE) was also utilized as a crosslinker to promote C–C crosslinks between SPEEK and MC, suppressing the potential loss of conductivity due to the consumption of sulfonic acid groups in crosslinking. Increasing MC composition in the membrane indeed improved proton conductivity, with a maximum of 4.78 mS cm$^{-1}$. The vast difference in ionic conductivities compared to their previous work may be attributed to the proton-conducting properties of acetyl groups in CA, which are not found in MC.

On the other hand, Mohy Eldin et al. (78) utilized CA as the bulk membrane and modified it with phosphoric acid groups to produce a PEM for DMFC applications as shown in Figure 10(a). This was achieved by activating CA using epichlorohydrin (ECH) and subsequently mixing with varying orthophosphoric acid (OPA) concentrations. It was shown that increasing concentration of OPA increased the IEC of the membranes, up to 2 mmol g$^{-1}$ at 2 M OPA, due to the formation of a high concentration gradient between the liquid OPA phase and the solid CA phase which improved the interdiffusion and produced more ionizing sites. Phosphorization of the CA membrane with 0.5 M OPA almost doubled the water uptake to 18.7 wt% while halving methanol uptake to 4% compared to the pristine CA membrane. Membrane swelling was kept low with a maximum of 15.5% for both water and methanol. Methanol permeability was also reported at 2.4×10$^{-15}$ cm$^2$ s$^{-1}$ for the 0.5 M OPA-modified CA membrane which is several orders of magnitude lower than Nafton® 117.

Mohy Eldin et al. (79) also investigated the effect of using sulfonic acid groups in place of phosphoric acid groups on CA. ECH was again used to activate the CA before it was soaked in sodium sulfite (Na$_2$SO$_3$) to impart sulfonic acid groups (Figure 10(b)). The IEC of the sulfonated CA (SCA) membranes also increased with increasing Na$_2$SO$_3$ concentration up to 1.0 mmol g$^{-1}$ at 5% Na$_2$SO$_3$, which is about half of the IEC achieved with the phosphorylated CA (PCA). Unlike the PCA membranes however, both water uptake and methanol permeability decreased at higher concentrations of Na$_2$SO$_3$ which the study attributed to the low conversion of epoxy groups into sulfonic acid groups under the membrane surface creating a hydrophobic zone. This also explained the lower observed IEC compared to PCA. Minimal swelling of up to 3.45% in both water and methanol was observed due to the low uptake values of less than 10 wt% for both liquids, while methanol permeability was as low as 1.73×10$^{-17}$ cm$^2$ s$^{-1}$.

In a subsequent investigation, Mohy Eldin et al. (80) also used the same methodology in their previous studies to produce aminated CA (AMCA) using ethylenediamine (EDA). The AMCA achieved IEC of up to 5.32 mmol g$^{-1}$ (1 M EDA) which indicated a much better conversion of epoxy groups into amino groups, possibly due
to better diffusion of EDA into the membrane. Water and methanol uptake increased with increasing EDA concentration, with values of up to ca. 32 and 27 wt% respectively, which were higher than PCA (78) and SCA (79) membranes as reflected by the increased IEC. Membrane swelling was still manageable at up to 13.07% and 18.41% in water and methanol (at 1M EDA), respectively. The methanol permeability was still very low at $4.54 \times 10^{-17}$ cm$^2$ s$^{-1}$, proving that the CA-based membranes are effective methanol barriers.

Samaniego et al. (81) on the other hand, prepared CA-based membranes for AEMFC applications via a different approach. The CA was gamma-irradiated to graft vinylbenzyl chloride (VBC), providing functionalization sites for the subsequent quaternization with trimethylamine (TMA) as shown in Figure 11. The irradiation technique was preferred due to the relatively faster and simpler modification process compared to conventional grafting methods (82, 83). The combination of VBC and TMA was shown to impart better ionic conductivity and thermal stability compared to other amine and sulfide-based functional groups according to previous studies (84–86). The study showed that higher degrees of grafting (DOG) were achieved at higher radiation doses due to the increased amount of activation sites created by the higher amount of available energy. This reflected onto higher recorded IEC, wherein membranes irradiated at a 40 kGy dose attained IEC values of up to 2.15 mmol g$^{-1}$. It is also notable that the variation of initial membrane thickness had diminishing effects on measured DOG and IEC as radiation dose was increased, with similar measurements across different membrane thicknesses being apparent at higher doses.

The maximum dose used was 40 kGy as intrinsic properties of CA have been reported to deteriorate when exposed to over 50 kGy gamma radiation (87). The IEC of the membranes approached a constant value at 40 kGy dose, thus thinner membranes were preferred as these translate to lower ionic resistance. Hydrophysical data also indicated that thinner membranes were preferable as water uptake values vary from 176 to 424 wt% while swelling varied from 41.4–63.3% with lower range values found in thinner membranes across same doses. The ionic conductivities of the CA-AEMs were investigated, and a maximum of 163 mS cm$^{-1}$ was measured for B40 (40 kGy dose, 2.15 mmol g$^{-1}$ IEC), at 40°C and 100% RH. The B25 membrane (25 kGy dose, 1.41 mmol g$^{-1}$ IEC) achieved a stable performance of 92.5 mS cm$^{-1}$ at 70°C (100% RH) comparable to literature values for the commercial Tokuyama A201 AEM (88). The CA-AEM fabricated in this study are thus good candidates for AEM applications, though water uptake and swelling issues must be further balanced with desirable IEC.

Reports on the actual fuel cell performance of IEM based on CA were lacking and although the synthesized membranes, particularly the PCA and AMCA PEMs of Mohy Eldin et al. (78, 80), exhibited promisingly high IEC with low water uptake and swelling, the ionic conductivity and desired power densities cannot be ascertained. On the other hand, the studies mentioned that employed CA as a membrane precursor further stress the importance of balancing mechanical performance with ionic properties as excessive water uptake and swelling lead to limitations in operating temperatures of otherwise excellent IEM candidates. Meanwhile, measured values for methanol permeability indicate

Figure 10. Preparation of (a) phosphorylated CA (78) and (b) sulfonated CA (79) membranes. Adapted from Mohy Eldin et al. (78, 79) licensed under CC BY 4.0.
that CA acts as a superior methanol barrier compared to cellulose.

**Chitosan**

Due to the brittle nature of chitosan (Figure 4), it is commonly modified through blending with other polymers, doping with inorganic fillers, and forming organic–inorganic hybrids. Smitha et al. have produced a PEM by blending chitosan (CS) and poly(vinyl pyrrolidone) (PVP) in a 4:1 ratio for DMFC applications. While both components are hydrophilic, membrane swelling was controlled through crosslinking using glutaraldehyde (GA) and sulfuric acid which promoted a semi-interpenetrating structure. This structure reportedly limits the expansion of the ionic channels within the membrane thus limiting methanol crossover as well, with about a 20% reduction in methanol permeability ($7.3 \times 10^{-8}$ cm$^2$ s$^{-1}$) compared to non-crosslinked CS/PVP membrane and about a third that of the methanol permeability of Nafion® 117. The ionic conductivity of the crosslinked CS/PVP membrane was 24 mS cm$^{-1}$ at

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**Figure 11.** Mechanism of CA-based AEM preparation via gamma irradiation and subsequent functionalization. Reprinted from Samaniego et al. (81) with permission. Copyright 2020, Wiley.
room temperature which was only around 28% that of Naion® 117 in the same conditions. However, this is not necessarily reflective of the membrane’s performance in a DMFC compared to Naion® 117 as the lower methanol permeability of the crosslinked CS/PVP would lead to lower fuel crossover, thus better exhibiting its potential performance.

A semi-interpenetrating structure was also explored by Wang et al. (93) in their synthesis of AEM from quaternized chitosan (QCS) and polystyrene (PS). The quaternization of CS was performed using epoxypropyl trimethylammonium chloride (EPTMAC) and subsequent crosslinking with glutaraldehyde (GA) as shown in Figure 12. As PS is stronger and more rigid than QCS, an increase in percentage of PS in the membrane resulted in higher yield stress by up to 60% from pristine to 21% PS (17.5 MPa), but a drastic decrease in elongation at fracture by over 80% (8.1 MPa) at the same composition. Even so, membrane swelling was shown to decrease from 187 vol% in QCS to 46 vol% in semi-interpenetrating QCS/PS with 21% PS. As the anion transport groups are found in the QCS component, both IEC and ionic conductivity decrease with higher PS to QCS ratios. Among the tested QCS/PS membranes, Semi-IPN-8 which contained 8 wt% PS obtained the highest IEC and ionic conductivity of 1.19 mmol g⁻¹ and 52 mS cm⁻¹ (at 75°C), respectively.

Summary and perspective

Table 1 shows the summary of the hydrophysical and mechanical properties, as well as the electrochemical performance data of the membranes discussed in this paper. On the other hand, Table 2 lists the commercial membranes that serve as benchmark for performance comparison of the mentioned fabricated membranes. In this review of ion exchange membranes (IEM) using cellulose and cellulose derivatives, and chitosan, the following observations are noted:

1. Bacterial cellulose (BC), nanocrystalline cellulose (NCC), cellulose nanofibers (CNF), cellulose acetate may be functionalized to impart ionic exchange capacity and ultimately allow or improve ion transport.
2. BC, NCC, and CNF improve membrane mechanical properties when used as reinforcement.
3. Membranes with dominant cellulose content have stronger hydrophilic character.
4. Grafting and crosslinking techniques provide better mechanical and chemical stability over doping and impregnating methods.
5. Swelling of cellulose- and chitosan-based membranes may be structurally inhibited through crosslinking techniques forming interpenetrating and semi-interpenetrating networks.
6. Membrane swelling may also be diminished by inclusion of nanofiber skeletons.
7. Cellulose and CA-based membranes exhibit lower methanol permeabilities than pristine Naion® membranes.

The literature surveyed have demonstrated that cellulose can be successfully incorporated into IEMs whether as the bulk component, copolymer, or performance
| Biopolymer                  | Process and modifications                                      | Membrane type | Application | Hydrophysical properties | Mechanical properties | Electrochemical properties and performance | Membrane code and Reference |
|-----------------------------|----------------------------------------------------------------|---------------|-------------|--------------------------|-----------------------|-------------------------------------------|-----------------------------|
| Bacterial Cellulose         | UV-irradiated to graft with acrylic acid                      | PEM           | PEMFC       | $T_i = 12$               | $\sigma = 4$          | $E_{\text{in}}$ = 1.26                | AAC-modified BC (45)       |
|                            | UV-irradiated to graft with 2-acrylamido-2-methyl-1-          | PEM           | DMFC        | $W_U = 154$              | $P_d = 15–35$ (30–50°C) | $P_{WU} = 1.06$ – 1.16                | AMSPE10-g-BC (54)          |
|                            | propanesulfonic acid (AMPS)                                    |               |             | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.6$        | $\sigma = 3.4$                     |                             |
|                            | Sulfonated then solution casted with sulfonated fluorenyl-     | PEM           | PEMFC       | $W_U = 264$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     |                             |
|                            | containing polyaroyl ether ketones (SFPAEKKs)                 |               |             |                          |                       | $\sigma = 3.4$                     |                             |
|                            | Crosslinked in-situ with poly(aryl ether ketone)s (SFPEEKK)   | AEM           | AEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     | Membrane D (55)            |
|                            | Crosslinked in-situ with fucoidan                            | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     | BC/Fuc_75 (52)             |
| Nanocry stalline Cellulose  | Sulfonated then solution casted with sulfonated fluorenyl-     | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     | SFPAEKK/NCC-4 (58)         |
|                            | containing polyaroyl ether ketones (SFPAEKKs)                 |               |             |                          |                       | $\sigma = 3.4$                     |                             |
|                            | Sulfonated then solution casted with sulfonated polyaroyl     | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     |                             |
|                            | ether ketone(s) (SFPEEKKs) to form nanocomposite membrane     |               |             |                          |                       | $\sigma = 3.4$                     |                             |
|                            | Sulfonated then solution casted with sulfonated polyaroyl     | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     |                             |
|                            | ether ketone(s) (SFPEEKKs) to form nanocomposite membrane     |               |             |                          |                       | $\sigma = 3.4$                     |                             |
|                            | Sulfonated then solution casted with sulfonated poly(aryl     | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     |                             |
|                            | ether ketone(s) with carboxylic acid groups (SFPEEKK-COOH-x)  |               |             |                          |                       | $\sigma = 3.4$                     |                             |
|                            | to act as reinforcement and crosslinker in nanocomposite      |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | membrane                                                     |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | Sulfonated then solution casted with sulfonated poly(aryl     | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     |                             |
|                            | ether ketone(s) with carboxylic acid groups (SFPEEKK-COOH-x)  |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | to form nanocomposite membrane                                |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | Sulfonated then solution casted with sulfonated poly(aryl     | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     |                             |
|                            | ether ketone(s) with carboxylic acid groups (SFPEEKK-COOH-x)  |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | to form nanocomposite membrane                                |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | Sulfonated then solution casted with sulfonated poly(aryl     | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     |                             |
|                            | ether ketone(s) with carboxylic acid groups (SFPEEKK-COOH-x)  |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | to form nanocomposite membrane                                |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | Sulfonated then solution casted with sulfonated poly(aryl     | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     |                             |
|                            | ether ketone(s) with carboxylic acid groups (SFPEEKK-COOH-x)  |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | to form nanocomposite membrane                                |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | Sulfonated then solution casted with sulfonated poly(aryl     | PEM           | PEMFC       | $W_U = 154$              | $\mu_p = 5.64 \times 10^{-3}$ | $\sigma = 3.4$                     |                             |
|                            | ether ketone(s) with carboxylic acid groups (SFPEEKK-COOH-x)  |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |
|                            | to form nanocomposite membrane                                |               |             | $\sigma = 3.4$          |                       | $\sigma = 3.4$                     |                             |

(Continued)
Table 1. Continued.

| Biopolymer | Process and modifications | Membrane type | Application | Hydrophysical properties | Mechanical properties | Electrochemical properties and performance | Membrane code and Reference |
|------------|---------------------------|---------------|-------------|--------------------------|-----------------------|------------------------------------------|-----------------------------|
| Cellulose Acetate | Phosphorylated with orthophosphoric acid (OPA) | PEM | DMFC | \( WU = 18 \) (10–80°C), \( \mu_m = 1.02 \times 10^{-12} \) | \( \sigma = 1.41 \times 10^4 \) (44.56–92.5) (30–70°C, 100% RH) | \( \text{IEC} = 1.19 \) | B25 (81) |
| | | | | \( T_s = 45 °C \) | | | |
| | Sulfonated with sodium sulfite (SS) | PEM | DMFC | \( WU = 3.6 \) (20–80°C), \( \mu_m = 3.45 \times 10^{-17} \) | \( \sigma = 2.15 \times 10^4 \) (130–162.7) (30–40°C, 100% RH) | | B40 (81) |
| | | | | \( T_s = 72 °C \) | | | |
| | Aminated with ethylene diamine (EDA) | PEM | DMFC | \( WU = 33 \) (20–80°C), \( \mu_m = 1.33 \times 10^{-17} \) | \( \sigma = 24–110 \) (30–120°C, 100% RH) | | GS-CS/PVP (92) |
| | Grafted with vinylbenzyl chloride (VBC) and functionalized with trimethylamine (TMA) | PEM | AEMFC | \( WU = 176 \) (45.9) | \( \text{IEC} = 1.41 \) | | B25 (81) |
| | | | | \( WU = 422 \) (63.2) | | | |
| | Crosslinked to semi-interpenetrating polymer network with poly(vinyl pyrrolidone) (PVP) | PEM | DMFC | \( WU = 52.1 \) (20–80°C), \( \mu_m = 7.3 \times 10^{-8} \) | | \( \text{IEC} = 1.99 \times 10^4 \) (25°C, 100% RH, 0.1 M KOH) | Semi-IPN-8 (93) |
| | | | | \( T_s = 92 \) | | | |
| | Chitosan | PEM | AEMFC | \( WU = 254 \) (92) | \( \text{IEC} = 1.19 \times 10^4 \) | | Semi-IPN-21 (93) |
| | Quaternized and crosslinked to form semi-interpenetrating polymer network with poly(styrene) (PS) | | | | | | |
| | | | | \( \mu_m = 0.36 \times 10^{-9} \) | | | |

Legend: \( WU \), water uptake in wt%; \( MU \), moisture uptake in wt%; \( DS \), swelling in %; \( \mu_m \), methanol permeability in \( \text{cm}^2 \text{s}^{-1} \); \( T_s \), tensile strength in MPa; \( T_{fr} \), tensile strength in N; \( Y \), Young’s modulus in MPa; \( E \), storage modulus in MPa; \( \text{IEC} \), ion exchange capacity in mmol g\(^{-1}\); \( \sigma \), ionic conductivity in mS cm\(^{-1}\); \( P_{st} \), power density in mW cm\(^{-2}\). Note: The symbol ‘-’ indicates lack of information or absence of reported data.

enhancing reinforcement. A general trend is observed wherein mechanical properties such as tensile strength and stiffness improve when cellulose is integrated to ion-conductive components such as, through in-situ crosslinking with bacterial cellulose (BC), through dispersion of nanocrystalline cellulose (NCC), or by the bracing effect of a cellulose nanofiber (CNF) skeleton. Furthermore, the ion exchange capacity and corresponding electrochemical properties were shown to increase through functionalization of the cellulose.
components, though often at the expense of mechanical strength as the hydroxyl groups essential to crystalline packing of cellulose are reacted. As of writing, IEMs which utilized cellulose acetate (CA), with acetyl groups substituted into most hydroxyl groups, were not characterized for mechanical performance, but successful modifications for ion transport were conducted for both PEM and AEM.

Figure 13 shows the correlation between water uptake and cellulosic content of the discussed membranes and their corresponding description in Table 3. It is apparent that membranes which used cellulose as their bulk or backbone, particularly BC and CA, exhibited higher water uptakes which would also reflect through higher swelling. Cellulose has a hydrophilic character, and expectedly contributes to the high water uptake in these membranes. Similarly, chitosan-based membranes exhibited high water uptake with increased amount of chitosan component. However, it is also important to note that the water uptake of the membranes also highly depends on the other components present, especially those tethered functional groups responsible for ion transport. Nevertheless, increased water uptake and subsequent membrane swelling are issues that must be addressed with cellulose- and chitosan-dominant membranes in order to demonstrate its feasibility for service applications.

| Membrane designation | Membrane type | Application | Hydrophysical properties | Mechanical properties | Electrochemical properties | Reference |
|-----------------------|---------------|-------------|--------------------------|-----------------------|--------------------------|-----------|
| Naion* 115 PEM        | PEM/DMFC      | \(\mu_m = 1.33 \times 10^{-5}\) \(\mu_m = 9.45 \times 10^{-6}\) (70°C) \(\mu_m = 6.2 \times 10^{-6}\) (70°C) | \(\sigma = 39\) \(P_d = 45.7\) (2M methanol); ca. 15 (10M methanol) \(\sigma = 110\) (70°C) \(\sigma = 84\) (70°C, 1M methanol), ca. 80 (70°C, 2M methanol) \(P_d = 55\) (70°C, 1M methanol); ca. 40 (70°C, 2M methanol) | \(T_i = 9.47\) (50 mm min\(^{-1}\)) | \(WU = 30\) (30°C); 32 (60°C) \(DS = 9\) (30°C); ca. 27 (50°C) \(\mu_m = 8.4 \times 10^{-7}\) (60°C, 5M methanol); 1.99 \(\times 10^{-6}\) (80°C, 5M methanol) | (54) (94) |
| Naion* 117 PEM        | PEM/DMFC      | \(\mu_m = 1.28 \times 10^{-5}\) \(\mu_m = 8 \times 10^{-7}\) (30°C); \(\mu_m = 1.9 \times 10^{-7}\) (60°C) | \(\sigma = 13\) (30°C, 60% RH) \(IEC = 0.93\) \(\sigma = 15\) (30°C, 70% RH); 35 (60°C, 70% RH) \(P_d = 126.04\) (60°C, 2M methanol) | \(\sigma = 110\) (70°C) | \(WU = 30\) (30°C); 32 (60°C) \(DS = 9\) (30°C); ca. 27 (50°C) \(\mu_m = 8.4 \times 10^{-7}\) (60°C, 5M methanol); 1.99 \(\times 10^{-6}\) (80°C, 5M methanol) | (71) (95) |
| Tokuyama A201 AEM     | AEM           | –           | –                        | –                     | \(\sigma = 52.5\)–104 (25–80°C, 4M KOH, 2M ethanol) | (88) |
| Fumasep* FAA-3-50 AEM | AEM           | –           | \(T_i = 25\)–40          | \(IEC = 1.85\) \(\sigma = 40\) | \(IEC = 1.85\) \(\sigma = 40\) | (96) |

Legend: \(WU\), water uptake in wt%; \(DS\), swelling in %; \(\mu_m\), methanol permeability in \(\text{cm}^2\text{s}^{-1}\); \(T_i\), tensile strength in MPa; \(IEC\), ion exchange capacity in mmol g\(^{-1}\); \(\sigma\), ionic conductivity in mS cm\(^{-1}\); \(P_d\), power density in mW cm\(^{-2}\). Note: The symbol ‘-’ indicates lack of information or absence of reported data.

Figure 13. Comparison of water uptake (measured in ambient temperature or 20°C) and cellulosic content of membranes presented in this paper. Note: Squares denote membranes using BC, circles for NCC, triangles for cellulose nanofibers, and diamonds for CA. Cross marks denote CS and the corresponding wt% pertains to chitosan content instead of cellulose.
uptakes. This was exhibited in the BC and poly(4-styrene sulfonic acid) interpenetrating polymeric network by Gadim et al. (47, 50) and the CNF skeleton supported membrane by Xu et al. (70) and Zhao et al. (72) restricting membrane expansion. This was similarly observed in the Ph-SPEEEKK membrane reinforced and crosslinked by aminated and sulfonated NCC by Zhao et al. (64) where ionic interactions between amino groups in NCC and sulfonic groups in Ph-SPEEEKK inhibited the motion of the hydrated polymer matrix. This observation was not confined to cellulose-based membranes, as the chitosan (CS) and poly(vinyl pyrrolidone) (PVP) PEM of Smitha et al. (92) as well as the quaternized CS and polystyrene (PS) AEM of Wang et al. (93) forming semi-interpenetrating polymer networks demonstrated reduced swelling attributed to their structure. Cellulose and cellulose acetate were also consistently reported to act as better methanol barriers than Nafion® with methanol permeabilities lower by at least one to several orders of magnitude, making these good candidates for DMFC applications.

**Conclusion and future direction**

Research into biopolymer-based ion exchange membranes have grown over the past two decades, however they remain a small part of the overall focus despite the high potential in cost reduction and competitive performance with a greener approach. In this review, studies on various types of cellulose-containing membranes were considered and many positive prospects and strategies were found. Membranes with a good mix of mechanical and ion conducting properties were primarily observed in those utilizing biopolymer as an enhancement rather than as the bulk matrix, with multiple examples exhibiting comparable or better performance than commercial counterparts such as those with swelling-inhibiting structures (i.e. interpenetrating or semi-interpenetrating framework). Membranes with high cellulose content however, typically manifest heightened hydrophilic character, increasing water uptake and membrane swelling. The challenge therefore lies on the researchers to consider the application of cellulose and chitosan as the bulk component in IEM, while exploring effective modifications for ion transport functionalization and incorporating swelling-inhibiting macrostructures. Additionally, a large portion of existing literature investigates biopolymer utilization in PEM applications, and it is thus further suggested to explore its application in AEM fuel cells.

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