



Review Paper

Functionalized and Electrospun Polymeric Materials as High-Performance Membranes for Direct Methanol Fuel Cell: A Review

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Article info

Received 2016-12-02
 Revised 2017-01-23
 Accepted 2017-03-11
 Available online 2017-03-11

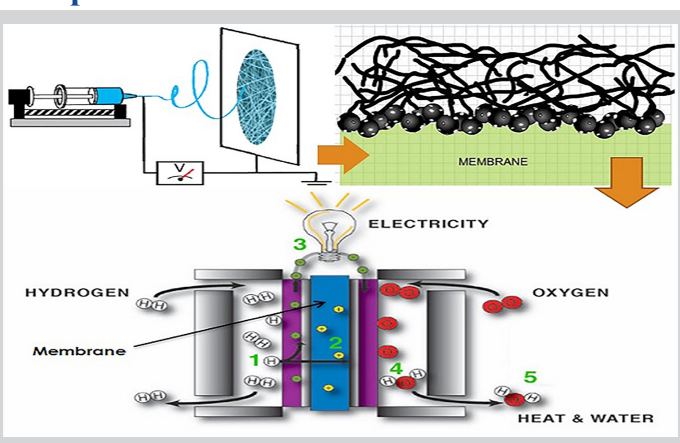
Keywords

Proton exchange membrane
 DMFC membrane
 Electrospinning

Highlights

- The function of a direct methanol fuel cell is highlighted.
- Types of polymeric membrane used for DMFC are reviewed.
- Electrospinning of nanofiber and their role in DMFC are discussed.

Graphical abstract



Abstract

Proton exchange membranes (PEM) for a direct methanol fuel cell (DMFC) have main drawbacks which are methanol permeability, reduced proton conductivity and the cost of the membrane. This paper reviews different polymeric materials such as fluorinated, non-fluorinated, acid-base complex, and composite membranes for DMFC. Currently, non-fluorinated membranes gain a lot of attention due to their low cost. Many researchers have developed functionalization methods for non-fluorinated polymer electrolyte membranes for DMFC application to reduce the methanol crossover. Finally, this review presents the *Electrospinning* technique and its parameter for fabrication of PEM with functionalized polymeric materials by using electrospinning to solve the proton conductivity and methanol permeability problem. The last part of the paper describes the current studies and future direction of PEM for DMFC.

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1. Introduction

One of the biggest challenges and major focuses of human civilization to finding alternatives of energy to reduce the fossil fuel depletion and environmental pollution throughout the world. The fuel cell is an alternative to reduce the use of fuel with a high efficiency and low/zero emission, have been attracting more and more attention in the recent decade. A fuel cell is an electricity generator device in which chemical energy converted into electrical energy. Proton exchange membrane fuel cells (PEMFCs) generally refer to the use of hydrogen as a fuel and direct methanol fuel cells (DMFCs) mainly comprises methanol and ethanol fuels. For hydrogen gas fed fuel cells at their current technological stage, hydrogen production, transportation, and storage, are the major challenges in addition to cost, reliability and durability problem. DMFCs are considering a suitable technology for power generation. Indeed, the liquid nature of methanol and simple refueling make it a good candidate for portable generators. [1,2].

There is increasing interest in direct methanol fuel cells (DMFCs) because it is not stored any electricity directly produced it. That is why they have desirable advantages over regular batteries such as increased operating time, reduced weight, and ease of recharging. The wide application range of fuel cells could also provide an alternative for stationary and transportation applications. The proton exchange membrane (PEM) is the core component of PEMFCs. The important roles of the PEM include transporting proton and separating the reactant fuels [3].

In the 21st century, the rapid growth of nanoscience and nanotechnology contributed their development in various applications in the different area. The nanocomposite electrospun fiber has flourished rapidly in PEM membrane and the research and development of the nanocomposite electrospun fiber are starting to grow by using the electrospinning method. These polymers have inherent properties to be conveyed into nanofibers for suitable applications. The properties of the nano-sized membrane material in proton exchange membrane (PEM) which can be used for improving the functionality of the membrane and have a large surface to volume ratio due to a smaller diameter, and have an excellent pore interconnectivity between each other itself [4].

Currently, commercially available Nafion (DuPont) membranes due to their excellent chemical stability and high proton conductivity [5]. Polytetrafluoroethylene backbone of nafion is made with perfluorinated vinyl ethers pendant side chains terminated by a sulfonate ionic group. In hydrated Nafion, Separation occurs in nano form due to hydrophilic and hydrophobic nature of the membrane because of amphiphilic composition in other words water soluble group attached to a water insoluble hydrocarbon chain [6]. The hydrated membrane produced good proton conductivity but it does not operate at above 80 °C temperatures. The main drawback of Nafion membrane the methanol permeability reduced the proton conductivity and dehydration of the ionic domain. The disadvantage of methanol crossover and hydrated swollen of membrane do not fulfill the requirement of the fuel cell which can be used at a temperature above 100 °C.

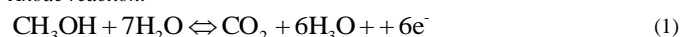
The engineering polymer such as Poly(ether-ether-ketone) (PEEK) has excellent chemical resistance and thermo-oxidative stability and low cost [7]. It was found that sulfonation of PEEK polymer used as a membrane which reduces methanol permeability and has adequate proton conductivity. The major advantage of SPEEK membrane is low cost. The conductivity and methanol permeability largely depends on sulfonation of PEEK and the degree of sulfonation [8]. It was reported that SPEEK membranes have a more life span than Nafion membrane which fulfills the fuel cell condition [9]. It is an alternative polymer which overcomes the methanol crossover drawback and reduces the loss of conductivity, hence researcher's developed desirable PEM by functionalization of polymeric materials. The aim of the paper to compare the properties of the membrane and development of the membrane by electrospinning.

2. Electrolyte membrane

In DMFC applications, an electrolyte membrane is called a "proton exchange membrane," which refers to the acid electrolyte. Direct Methanol Fuel Cell (DMFC) works created an electric potential by the reaction between methanol and oxygen specifically, it produces electricity through an electrochemical process without combustion and without the need for a reformed system for the fuel.

The electric potential is created using a polymeric membrane that is selective to certain chemical molecules, in this case, the membrane allows the passage of H⁺ ions (proton conductivity). On one side of the membrane, an aqueous solution of methanol (CH₃OH) is fed to the anode catalyst where the catalytic decomposition of methanol molecules, producing carbon dioxide (CO₂) and hydrogen (H₂) which is oxidized to H⁺ ions at the anode. The protons produced can migrate to the cathode of the cell through the membrane where the electrons (e⁻) produced to the anode, passing through an external circuit, reduce the oxygen (O₂) that is plugged in, allowing the formation of water (H₂O). The reactions occurring in the DMFC are as follows [10,11]:

Anode reaction:



Cathode reaction:



Overall reaction:



It is noted that the reaction occurs in the DMFC is the same as the combustion of methanol and is thus sometimes referred to as cold combustion. Actually, the cell is meant to control this reaction and use it to produce current directly. The standard cell voltage for a DMFC at 25 °C is 1.21 V. However, this potential is never obtained in reality. The open circuit potential is usually about 0.6 to 0.8V in the best case [10,11].

3. DMFC membranes

The types of polymer electrolyte membranes more representative for use in direct methanol fuel cells can be classified as [12]:

3.1. Perfluorinated membranes

They consist of chains of hydrophobic perfluorinated backbones and side chains, which are terminated in hydrophilic sulfonic acid groups thus leading to a complete phase segregation. Nafion is the most widely used commercial membrane and ionomer. Its chemical structure can be viewed in Figure 1.

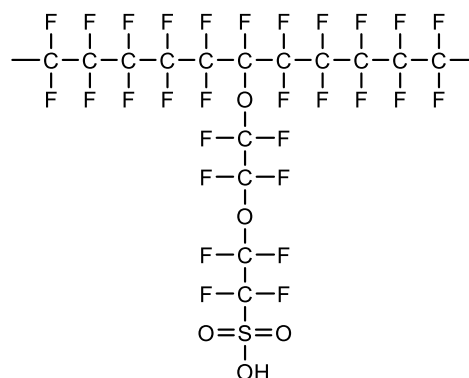


Fig. 1. Chemical structure of the perfluorosulfonic acid commercially known as Nafion [24].

This material has a very important role in the development of fuel cells. The strong bonds between the fluorine and the carbon make it durable to chemical attack and low polarizability. Another important property is the strongly hydrophobic and so it is used in fuel cell electrodes to drive the product water out of the electrode, and thus it prevents flooding. The perfluorinated polymer membrane is prepared by polymerization of monomers, which can be made either cationic or anionic by post treatment

[13]. These membranes have been developed by DuPont. The characteristic of the membrane is the fluorocarbon-based ion exchange membrane (Nafion) with good thermal and chemical stability. These are high equivalent weight perfluorinated membranes and have limited their use in fuel cells because they consume high power density [14]. Similar polymers are Flemion produced by Asahi Glass and Aciplex-S produced by Asahi Chemical. Among the three major types, the DuPont product is considered to be superior because of its high proton conductivity, good chemical stability, and mechanical strength [15].

3.2. Non-perfluorinated membranes

They are known as hydrocarbon membranes and nowadays are gaining a lot of interest as cheaper alternatives to Nafion. The advantages of hydrocarbon membranes are easily available, low cost and polar structure of the site allows the attachment of pendant groups in order to increase the water uptake [16]. These polymers are easily reused by a simple process. Non fluorinated membranes such as aromatic or aliphatic having a benzene ring structure in the bulk pendant groups from this membrane or in the polymer backbone of a membrane. In order to enhance stability at elevated temperatures, aromatic hydrocarbons can be (a) incorporated directly into the backbone of a hydrocarbon polymer or (b) polymers modified with bulky groups in the backbone to render them suitable for conduction of protons [17,18]. Their backbone is usually formed by phenyl units linked by functional groups such as a ketone, ether or sulfone. Sulfonation of the phenyl rings leads to the direct attachment of sulfonic acid groups for the proton conduction.

The aromatic rings are given the choice in the process of nucleophilic substitution and electrophilic. Polyaromatic membranes are high temperature rigid polymers with $T_g > 200$ °C owing to the presence of inflexible and bulky aromatic groups. Different types of non perfluorinated membrane among them ionomer membranes based on styrene [19], polyphenylene [20], Poly ether sulfones (PES) [21], poly (arylene ethers), sulfonated poly ether ether ketone [22]. The most considered materials are sulfonated poly ether ether ketone

(SPEEK) and sulfonated polysulfone [23]. Chemical structure of some non-fluorinated polymer in Figure 2.

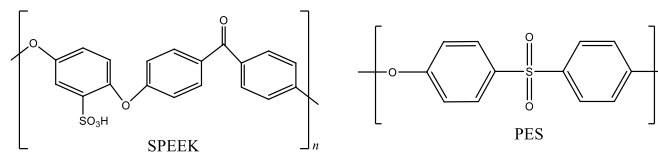


Fig. 2. Chemical structure of some non-fluorinated polymer [21,69].

A survey found that there are many choices non perfluorinated hydrocarbons. Table 1 shows a summary of previous studies on membrane synthesis for direct methanol fuel cells.

3.3. Composite membranes

They comprise a polymer matrix in which a solid filler is added. Inorganic oxide particles and zirconium phosphate are the most common fillers [31]. They can be modified with functional groups, e.g. sulfonic or phosphonic acids, attached on their surface [32]. Composite membranes containing micro to nanometer fillers including silica [33]; titanium oxide, zirconium phosphate [34]; molybdophosphoric acid, Aerosil (silicon dioxide powder) [35]; ORMOSILS (organically modified silicates), silane-based fillers [36]; hydroxyapatite, montmorillonite [37]; Laponite, zeolites [38]; and palladium [39] have been incorporated in a number of different polymer membranes including Nafion. High and low molecular weight composite like blends of poly (benzimidazoles) with phosphoric acid as a proton conducting component or phosphoric acid blended with other organopolymers [24,26,28,40]. The usual role of the fillers is enhancing the water retention capacity of membranes at lower relative humidities in fuel cells operating with hydrogen, while in DMFCs they contribute to decreasing methanol diffusion via the associated increase of tortuosity (see Figure 3) [41].

Table 1

Membrane synthesis and modification of polymers for direct methanol fuel cell.

Membrane Type	Modification information	Reference
Sulfonated polysulfone	Synthesized using sulfur trioxide-triethyl phosphate complex as the sulfonating agent. Good mechanical properties and relatively high IEC achieved.	[24]
Sulfonated polyethersulfone (SPES)	SPES was covalently crosslinked and synthesized using substituted diamine-sulfone to bring high proton conductivity and further mechanical strength for operations above 100 °C.	[24]
Poly (arylene)	Synthesis of sulfonated naphthalene type polyimide to achieve low methanol diffusion high proton conductivity and coefficients unlike PFSA.	[24]
Styrenic system of styrene divinyl benzene (SDVB)	Grafting SDVB to poly(fluoroethylene cohexafluoropropylene) (FEP), followed by sulfonation through attaining membranes very identical to PFSA.	[17]
Sulfonated polyetherether ketone (SPEEK) and sulfonated poly (4-phenoxy benzoyl-1,4-phenylene)	Sulfonating PPBP and PEEK using concentrated sulfuric acid. Thermal stability up to at least 200 °C was gained and a conductance of about 10–2 S/cm at 65 mol% Sulfonation in the case of SPPBP observed while SPEEK depicted conductance two orders of magnitude lower for the same mol% of sulfonation.	[24]
Sulfonated poly [bis (3-methyl phenoxy) Phoszene]	Sulfonating the base polymer with sulfur trioxide followed by yielding higher proton conductivity, crosslinking, lower water and methanol diffusion co-efficient besides excellent thermo and chemical mechanical stability when compared to Nafion®.	[25]
Sulfonated polyimide (PI)	Sulfonating PI using sulfur trioxide to achieve properties proportionate to Nafion 117.	[26]
Sulfonated polystyrene	Sulfonating polystyrene using acetyl sulfate as sulfonating agent. On increasing sulfonation, the ionic conductivity was equipotential to Nafion® (10-3 to 10-2 S/cm). Nevertheless, discontinuity in the properties at 15% sulfonation was noted.	[27]
Membrane Type	Modification information	Reference
Hydrogenated poly (butadiene-styrene) (HPBS)	Synthesized by heterogeneous sulfonation of poly (butadiene-styrene). On blending with polypropylene as an improvement in both the proton conductivity and thermal properties resulted.	[28]
Poly (aryloxyphosphazene) Polymers	Treatment of the aryloxyphosphazenes bearing bromo-phenoxy side groups with t-butylolithium followed by diphenylchlorophosphonate and conversion to phenyl phosphonic acid groups.	[29]
Sulfonated polyaryls	Polyetherketones were remodified by blending with polymers consisting of immobilized heterocycles for instance pyrazole, imidazole or benzimidazole as proton solvating species for resulting high proton conductivity. The water cross-over drastically reduced while keeping high proton conductivity.	[23]
Impregnating fleeces on polyte-trafluoro ethylene (PTFE) matrix	Impregnating polysulfone, microglass fiber and a composite matrix constituting of both the fleeces on a PTFE matrix. Unlike the two impregnated fleeces, the composite membranes did not exhibit a comparable or lower resistance than Nafion 117.	[30]
Sulfonimide compound	Crosslinking sulfonimide synthesized applying a macromolecular substitution method to result in phosphazene bearing pendant sulfonimide groups in achieving high proton conductivities.	[17]
Polystyrene graft polymer	Crosslinking styrene/acrylonitrile are obtained from N vinylpyrrolidone/2-acrylamide-2-methyl-1-propane sulfonic acid graft polymer using divinylbenzene to attain better stability in an oxidative environment.	[24]

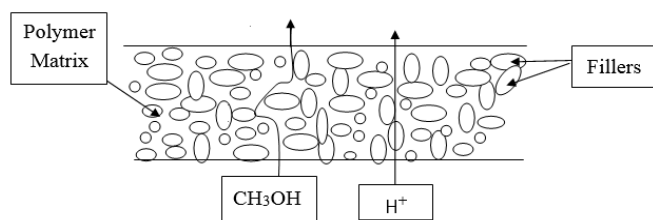


Fig. 3. Reduction of methanol permeability due to increased path tortuosity in composite membranes. Proton transport can be less affected if acid-functionalized fillers are added [41].

Three methods are reported for the preparation of organic-inorganic hybrid membranes [42]:

Physical blending: The filler in the form of inorganic (nano) particles is vigorously mixed with the polymer solution and afterward a membrane is cast from this slurry.

Sol-gel: A chemical precursor of the filler is dissolved in the polymer solution and then a membrane is cast. The precursor contained in the membrane is then hydrolyzed and condensates thus forming inorganic phases within the polymer matrix.

Infiltration: A membrane is cast from the polymer solution and a chemical precursor of the filler is dissolved within a suitable solvent. Following, the membrane is placed in the precursor solution and the membrane correspondingly swells. The swollen membrane incorporates the filler precursor compound by diffusion. Finally, the excess solvent is removed from the membrane and the remaining precursor molecules are reacted and transformed into inorganic species.

3.4. Acid-base complex membranes

An acid polymer, i.e., containing sulfonic acid groups, is blended with a basic polymer, i.e. incorporating amino groups, and thus, ionic crosslinking are created instead of covalent bonds. Polypyrrole and PBI are some examples of basic polymers. Acid–base complexes have been considered as a promising alternative for membranes that can be used at high temperature without suffering from dehydration effect and shows higher conductivity. Currently, the acid-base complex considered for high performance of fuel cell membranes, which involves the addition of an acid component into the alkaline polymer base to boost proton conductivity.

Nowadays, an acid-base complex polymer such as phosphoric acid-doped polybenzimidazole (PBI/H₃PO₄) membrane widely studied because it has shown a great deal for medium to high temperature, fuel cell under ambient pressure [43]. Researchers have characterized and studied about PBI doped with phosphoric acid and continuous doping level of phosphoric acid decided the mole percentage of acid per repeat unit of the polymer. It has been observed that the conductivity of PBI membrane was about 4.6×10^{-2} S/cm at a temperature of 165 °C and 450 % doping. It was shown that as the doping level increase around 1600% the conductivity could reach 0.13 S/cm. In the case of conductivity, doped PBI does not depend on the humidity in contrast to nafion. However, such acid-base complexes are sensitive to the doping level and temperature. According to that observation doped PBI/H₃PO₄ membrane sustain at temperature 190 °C and atmospheric pressure yielding a power density of 0.55 W/cm² and a current density of 1.2 A/cm² for the fuel cell [44]. Even so PBI acid-base membranes generally known for their exceptional properties for fuel cell application.

SPEEK/PBI membranes were composed of sulfonated poly (ether ether ketone) SPEEK as the acidic compound and poly (benzimidazole) as the basic compounds were studied [45]. The membranes revealed good proton conductivities at ion-exchange capacities IEC of 1 meqg⁻¹, and they showed excellent thermal stabilities (decomposition temperatures. 270 °C). The experimental analysis proved that acid-base complex suitable for the direct methanol fuel cell.

It was also observed that blend membrane having acid-base interaction and covalent crosslinking more noticeable because significantly reduced water uptake and methanol permeability with only minimum loss of proton conductivity [46,47]. The researcher reported that the performance of DMFC at temperatures up to 130 °C suitable for a number of blend/crosslink membrane [48]. In a dry state, this membrane gives problem due to *Brittleness* of materials and to overcome the problem work in this area going on.

Many suitable polymer materials are used for providing to achieving desirable properties for proton exchange membrane. However, the favorable fabrication technique for membrane preparation still rarely studied. Hence, to increase the life of fuel cell it is important to be developed a new fabrication technique in order to fulfill the requirement of PEM fuel cell. Recently developed fabrication technique has been electrospinning. The fabrication technique is modifying the structure of the membrane by increasing the surface to volume ratio and give the interconnectivity to withstand the operating condition. All this property can be gained by electrospun nanofiber.

4. The principle electrospinning process

4.1. Background

Early studies on the interaction of electricity with liquids are dated in the late 16th century, in which William Gilbert noted that a spherical drop of water would change into a conical shape when an electrically charged piece of amber was placed on it [49].

Later, between the beginning and middle of the 20th century, some researchers set out to study this phenomenon experimentally and in 1934 Anton Formhals formalized a patent for producing polymer fibers by an electrostatic process [50].

However, those studies were not taken seriously by the British scientist Sir Geoffrey Taylor began to investigate the phenomena occurring when an electric field is applied to a liquid. Consequently, in 1969 he published that a drop of the polymer solution at the tip of a capillary subjected to an electric field adopts the form of a cone and that a filament emerges expelled from the vertex of such a cone, which is known as "Taylor cone" [51].

Thereafter, studies were mainly directed to investigate the morphology and characterization of nanofibers, and from the 1980s and particularly in recent times, many efforts have been focused on the optimization of the electrospinning process. This is due to the rise of nanotechnology and the promising applications of nanofibers in different areas such as filtration membranes, special fabrics, catalyst support, adsorbents, etc. [49].

4.2. Electrospinning process and set up

An electrospinning setup basically consists of a pump, a syringe pump in a lab scale, which transfers a polymer solution at a certain flow rate to a metallic capillary or needle (spinneret) connected to a high-voltage direct current power supply. When a high electric field is applied, the liquid solution becomes charged and the equilibrium of gravity, surface tension, and electrostatic forces lead to the formation of a Taylor cone (see Figure 3), and as a function of solution viscosity, drops or a continuous filament (jet) is formed. As the filament is extruded by the electrostatic repulsion (tangential component), it dries and stretches in flight. The nanofibers are finally deposited on a grounded collector which is often a metal plate or a rotating drum. The latter is preferred if aligned nanofibers are required [52].

Two innovative extensions of electrospinning are coaxial and melt electrospinning. In the coaxial electrospinning, two immiscible polymer solutions are injected one into the other at the tip of the spinneret. The outer fluid carries the inner solution to the Taylor cone and correspondingly core-shell nanofibers are obtained [52]. On the other hand, in the melt electrospinning, a melted polymer is electrospun thus eliminating the need for solvents [53]. However, due to the inherent high viscosity of polymer melts, the fiber diameters tend to be larger than those prepared by electrospinning of polymer solutions [54].

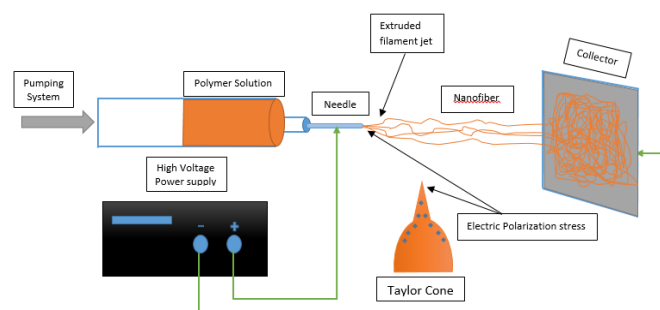


Fig. 4. Schematic representation of an electrospinning setup for the production of nanofibers from a polymer solution. The equilibrium of forces at the Taylor cone are also presented [4].

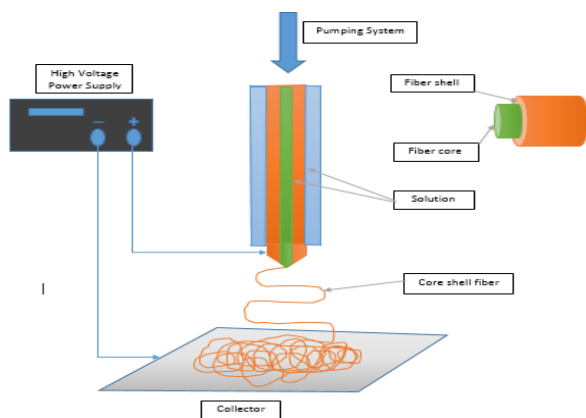


Fig. 5. Schematic representation of a coaxial electrospinning setup for the production of core shell nanofibers from a polymer solution [54].

4.3. Electrospinning parameters

The electrospinning process is a simple technique, but complex to optimize since it is influenced by many parameters which require a strict control. These parameters can be classified as a function of their nature [55].

Solution properties: The formation of nanofibers by electrospinning is dominated by the viscosity and surface tension of the polymer solution. Therefore, each polymer-solvent system to be electrospun needs finding the optimal conditions to succeed. For example, it is reported that smooth, but thicker nanofibers are formed with a polyethylene oxide (PEO) solution in water when the solvent changes to a water/ethanol mixture. This is interpreted as a consequence of a higher viscosity and lower surface tension of the solution with increasing ethanol concentration [56]. In general, nanofiber diameters and viscosity are directly associated [52]. Consequently, increasing polymer concentration, and thereby viscosity of the solution, causes enlargement of nanofiber diameters.

The morphology of the nanofibers, i.e. formation of smooth fibers or, on the contrary, beads or beaded fibers, is mainly driven by the surface tension, although the viscosity plays a role, too [56,57]. Decreasing the surface tension helps to eliminate the bead formation but promotes the formation of nanofibers with larger diameters. When water is used as a solvent, it is well known that surfactants must be added to the polymer solution for enabling electrospinning instead of electrospaying. In this case, the category of the surfactant (cationic, anionic, amphoteric or nonionic) also affects the aspect of the electrospun nanofibers [58].

Regarding the conductivity, it has been correlated that the net charge density carried by the moving filament is inversely proportional to the resistivity of the polymer solution [56], and therefore, directly proportional to the conductivity. Increasing the conductivity, and thus, the net charge density produces greater electrostatic repulsion forces which accelerate further the jet and in turn favors smaller diameters of nanofibers. Another advantage is that formation of beads diminishes with increasing net charge density [52,56].

Process variables: Generally speaking, increasing both the voltage applied between the needle and collector and the distance needle-collector contribute to decreasing the nanofiber diameters and bead formation. In the first case, this is attributed to the increment of net charge density with increasing voltage, and in the latter as a result of a greater extent of stretching associated with a larger distance of flight. On the other hand, the flow rate of the polymer solution must be conveniently fixed for achieving a stable Taylor cone at given conditions. However, as an empirical observation, relatively larger flow rates induce increased nanofiber diameters and even the formation of beads [52].

Environment effects: Relative humidity and surrounding temperature are the main factors which affect the production of the nanofiber. The relative humidity seems to shield the electric field between the needle and collector thus decreasing the effective electrostatic forces. Regarding the temperature, its effect is interpreted in terms of influencing the evaporation rate of the solvent. Pelipenko, Jan, et al have researched on the impact of relative humidity and temperature during electrospinning on morphology and mechanical properties. This study has shown that the diameter of electrospun nanofibers can be controlled by relative humidity during electrospinning. Lower relative humidity cause rapid solvent evaporation, resulting in the thicker nanofibers, whereas higher relative humidity causes slower solvent

evaporation, resulting in thinner nanofibers. The author concluded in electrospinning relative humidity can change the physical properties and expand its applicability [59].

4.4. Electrospun Polymer based nanofiber membranes

As mentioned above, the work done by Formhals is completely applied to the polymer and this becomes the great research area towards the increase the development of electrospun fiber from various types of polymer. Nanofiber has been produced from various different types of polymer [24]. The following are few electrospun polymer membrane nowadays that have been used for making nanofiber for fuel cell application.

Nafion showed excellent performances as proton exchange membrane, but it is still difficult to produce nanofiber by electrospinning because it is not soluble in most common solvents. This insolubility often results in the formation of micelles, which causes the decrease in chain entanglement and inability to the electrospun fiber without any addition of high molecular weight carrier [63].

An inorganic filler such as clay always used as reinforcement to reduce methanol permeability and increase proton conductivity mainly in direct methanol fuel cell Lee, Chanmin, et al in his study, had successfully electrospun SPEEK/SiO₂ composite. Nafion filled all the voids and interspace of fiber due to the highly porous structure of nanofiber. Good adhesion between the nanofiber surface and the Nafion matrix was also confirmed. In which he found that the presence of hygroscopic silica on the nanofibrous mat was advantageous in attracting more water than the cast films of Nafion and SPEEK. The Nafion- impregnated SiO₂/SPEEK composite nanofiber membrane performed better than the recast Nafion and SPEEK films, due to its better water retention and resistance to swelling, the proton conductivity of the nanofiber composite membrane [64].

Ju, Young-Wan and co-workers was investigating the electrochemical behavior electrospun polypyrrole/sulfonated-poly (styrene-ethylene-butylenes-styrenes) composite nanofiber and electrospun polypyrrole/poly (styrene-ethylene-butylenes-styrenes) by a casting method. By electrospinning, the fiber diameter 300 nm found and casting showed the granular microporous structure. The effect of electrospinning and 40% sulfonation results in higher electrochemical capacity due to the increase of doping level, high electrical conductivity, low interfacial resistance, and good electrospinning by more charge [65].

To increase the proton conductivity of the membrane sulfonated poly (aryl ether ketone) (SPAEK) have been extensively used due to their good mechanical and thermal stability after sulfonation and they show the very promising application of micro, nano, and ultrafine membrane mainly of the proton exchange fuel cell. Li and co-workers developed sulfonated poly ether ether ketone ketone (SPEEKK) nanofiber by electrospinning and increase proton conductivity up to 0.37 S/cm. The author investigated SPEEKK by solution casting and electrospinning he found that electrospun membrane shows much more clearly phase separation than the convenient SPEEKK membrane and proton conductivity of the membrane 37 times higher than that of the membrane prepared by solution casting. By electrospinning, the proton conductivity increases and show promising membrane for the proton exchange fuel cell application [66].

A good proton exchange membrane for fuel cell application should complete with intrinsic properties, especially on methanol crossover and proton conductivity properties. To obtain these properties, the electrospinning parameter such as voltage, distance, relative humidity, and the concentration of solution need to be controlled in order to produce excellent nanofibers for proton exchange membrane (see Table 2). Mostly, electrospinning parameters depend on types of polymer used. However, electrospun nanofiber shows mechanical strength problem due to its small diameter, which makes the electrospun nanofiber easily break [67]. Thus, a holdup or reinforce material is needed in order to keep higher the mechanical strength of the electrospun nanofibers and equivalently the durability of the electrospun nanofibers membrane to withstand elevated temperature and pressure. Table 3 lists some of the previous researches on electrospinning parameters, which were used in fabricating the electrospun nanofibers for fuel cell application.

Generally, proton conductivity and methanol permeability are mainly due to the formation of ionic alignment during electrospinning as well as it gives the tortuous path for methanol to enter into matrices. Furthermore, the present of filler within the polymer matrix will restrict the methanol crossover and improve the barrier properties of the membrane. As a conclusion, high surface area to volume ratio and small diameter of electrospun fiber with an excellent proton conductivity and higher resistance to methanol permeability can be obtained by applying different parameter of electrospinning equipment.

Table 2
Electrospinning parameters and their effects on fiber morphology and fiber diameter.

Parameter	Remarks	Reference
Applied voltage	Deposition pattern of fibers changes from random orientation into a straight arrangement. Fiber bead density increases with increasing instability due to the increase of the applied voltage. Increasing applied voltage, thinning the fiber, reducing the average diameter of the fiber, and causing multiple jets. Higher applied voltage broadens the distributions of the diameters of fiber.	[54,55]
Distance between tip and the collector	The jet diameter decreases with increasing distance. At a short distance, the fibers are not completely stabilized and eventually the cross-sections of spun fiber become flatter and some fibers stick together becoming bundle fiber. At long distance, the fibers exhibit a straight; cylindrical morphology indicates the fiber, mostly dried when reaching the collector.	[59]
Concentration	Below a critical concentration, the fiber jet will break down due to the generation of a mixture of fibers and droplets jet. Above the critical concentration, a stable jet is difficult to form. Bimodal distribution of fiber diameters is possible to form from higher concentration solutions. Decreasing the concentration will reduce the diameter of electrospun fiber; further decrease will form beaded fibers.	[59,60]
Viscosity	The too diluted solution is difficult to form a stable jet; the jet will break, whereas too viscous solution will make it difficult to form fiber due to the solution drying on the tip. Higher viscosity produces fiber without beads.	[54,61]
Surface tension of solution	Reduced surface tension will produce fibers without beads. Reduced surface tension will form a larger diameter of the fibers. (Depending on polymer and solvent.)	[54]
Net charge density	Adding NaCl or salts will increase the net charge density and reduce the diameter of the fiber.	[54,59]
Feeding rate	At higher feeding rate, this will exceed the delivery rate of a solution with applied voltage and eventually result in tiny drops of the jet on the collector. At low feeding rate, the solution is ejected faster and the shift of the mass balance will result in the sustained, but unstable jet which eventually forms a fiber with beads.	[62]
Molecular weight	Molecular weight affects the manipulated concentration in order to electrospin fine fibers. Low molecular weight can easily form nonuniform fibers with bead. High molecular weight will be able to produce uniform fibers without a bead.	[59]

Table 3
Summary of electrospinning parameters on electrospun nanofibers membrane in fuel cell application.

Polymer	Supporting material	Electrospinning parameter	Remark	References
Polyvinyl alcohol, PVA	Nafion	Distance from needle to collector: 20 cm Solution flow rate: 1.2 ml/h Voltage potential: 20 KV I.D. needle: 0.8mm Collector: copper collection roll	More straight and less tortuous effect on Nafion/PVA nanofiber which leads to increase in proton conductivity of the membrane and reduction in membrane crossover with a thickness of $\sim 50 \mu\text{m}$.	[68]
SiO ₂ /sulfonated Poly (ether ether ketone), SPEEK	Nafion	Distance from needle to collector: 10 cm Voltage potential: 15 KV I.D. needle: 0.15mm Humidity: below 15% RH	Thickness of SiO ₂ /SPEEK nanofiber membrane 45 μm incorporation with Nafion produces high proton conductivity compared to cast Nafion and SPEEK. The maximum power density of SiO ₂ /SPEEK incorporation with Nafion is 170mW/cm ³ double than cast Nafion.	[64]
Polyvinyl alcohol, PVA	Nafion	Distance from needle to collector: 25 cm Solution flow rate: 0.5ml/h Voltage potential: 16 KV	Succeeds in producing PVA nanofiber having diameter of 200–300 nm Contribution of Nafion as support the material has indeed increased the mechanical and thermal properties of the composite membrane with a thickness of composite membrane at 46–47 μm . PVA nanofibers have indeed increased the barrier properties on methanol crossover.	[4]
Sulfonated poly (ether sulfone) (SPES)	Nafion	Distance from needle to collector: 15 cm Voltage potential: 19 KV Collector: rotating cylindrical stainless steel	Proton conductivity of the bilayer SPES/Nafion barely changes compared to the Nafion 117/112 The methanol crossover is reduced due to the SPES nanofibers within Nafion matrices.	[40]

5. Current studies and future direction

As stated in above rapid growth in non-fluorinated polymeric based PEMs such as Sulfonated PEEK could prove that it has better potential and a viable strategy to overcome the high cost currently used Nafion membrane. However, at the high degree of sulfonation of parent SPEEK reduced its performance in DMFC due its high methanol crossover problem [69]. To overcome such drawback several modifications and functionalization have been investigated such as:

1. The conductive polymer such polypyrrole and polyaniline interaction will lead to the compatibility of the blending polymers. This will lead to the reduction of swelling, improvement of mechanical properties and a further decrease in the methanol crossover of membranes.
2. Mixing of acidic and basic molecules generally form a protonically conductive pathway. Blending with amine polymers will lead to the formation of proton transport channels from the protonated-amine groups to the sulfonated groups when the membranes are hydrated.
3. Adjusting SPEEK by blending technique: The most current compatible blends reported occur between SPEEK-polyether sulfone (PES), SPEEK-polyether imide (PEI) and SPEEK-polybenzimidazole (PBI)

Besides, Electrospinning has proven to successfully resolve the drawbacks of the PEM membrane by improving the morphological, structural of electrospun membranes, thus improving the performance of DMFC, as discussed in the prior topic. However, it is important to emphasize that the parameters involved in the electrospinning process need to be optimized in order to fully utilize the advantages of electrospinning thus providing a complete exfoliated structure, membrane even at the small amount of additive loading in which ultimately produced a high performance PEM with less cost.

6. Conclusions

The selection of functionalized polymeric membrane and electrospun polymer electrolyte membrane for a direct methanol fuel cell (DMFC) has gained a lot of attention from researchers due to its capability in sustaining proton conductivity and reduce methanol permeability. A significant amount of work has been done in preparing to functionalize sulfonated PEEK and electrospun sulfonated PEEK for fuel cell application, However, several existing challenges in electrospinning process still need to be overcome prior to formation of smooth electrospun fiber, such as solution parameters, controlled parameters, and ambient parameters and also few weaknesses need to be improved on morphology of functionalized polymeric membrane.

Abbreviations

PEMFCs	Proton exchange membrane fuel cells
DMFCs	Direct methanol fuel cells
PEM	Proton exchange membrane
PEEK	Poly ether ether ketone
SPEEK	Sulfonated poly ether ether ketone
PES	Poly ether sulfones
SPES	Sulfonated polyethersulfone
SDVB	styrene divinyl benzene
SPI	Sulfonated polyimide
HPBS	Hydrogenated poly (butadiene-styrene)
PTFE	Poly tetrafluoro ethylene
PBI	Polybenzimidazole
PEO	Polyethylene oxide
SPAEEK	Sulfonated poly (aryl ether ketone)
SPEEKK	Sulfonated poly ether ether ketone ketone
PEI	Polyether imide
IEC	Ion exchange capacity

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