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Polymer based Membrane Electrospun Fiber in Fuel Cell Application: A Short Review

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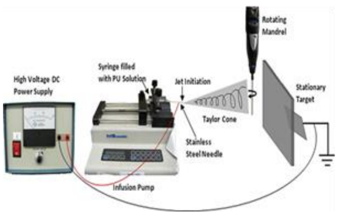
Graphical abstract



Abstract

Currently, the need of renewable energy becomes crucial due to the problem arising via fossil fuels usage which contributes to the environmental issues. Among the type of existing renewable energy, fuel cells is the most promising renewable energy sources since the energy can be directly converted from combustible of fuel. The proton exchange membrane (PEM) is the heart of the fuel cells system. The research and development on proton electrolyte membrane is keep burgeoned. Even though the studies of the electrolyte nanocomposite membrane for fuel cell application are quite various but only a few studies focused on the effect of electrospun nanocomposite membrane on the performance of proton electrolyte membrane. This review is focusing on the electrospinning process for the preparation of electrospun fiber membrane. This review is concentrates on polymer based membrane electrospun nanofiber and their influence on proton conductivity as well as on fuel crossover barrier properties. The proton conductivity and fuel crossover can be improved by fully exfoliated structure of nanocomposite electrolyte membrane via electropinning process and thus the membrane can be an alternative PEM for DMFC applications.

Keywords: Nanofiber; nanocomposite; electrospinning; fuel cell

1.0 INTRODUCTION

With the rapid growth of nanoscience and nanotechnology over the last 20 years and awareness of various applications contributed since 2000 [1], eventually give an insight the use of impregnation nanotechnology on proton electrolyte membrane (PEM). Targeted development of new one-dimensional (1D) nanostructures, such as continuous nanofibers (NFs), large aspect ratio nanowires (NWs) and nanorods (NRs), is attract much attention due to the reliance of their physical properties on directionality [2]. As essential one-dimensional nanomaterials, nanofibers have a very large specific surface area because of their small diameters, and have an outstanding pores interconnectivity between the fibers itself [3]. These specialties of the polymers themselves convey nanofibers with many desirable properties for sophisticated application.

Electrospinning seems to be an advanced and simple processing method of producing nanofiber. According to Liu *et al.* [4], the electrospinning process can be divided into several techniques such as vibration electrospinning, magneto-electrospinning, siro-electrospinning and bubble electrospinning. The first patent of electrospinning has been issued by Formhals in October 1934 [5]. The electrospinning process has proceeding become an interest topic within the past few years although the process has been known for almost 70 years [6].

However, the process of electrospinning has already burgeoned in 16th century ago when the very first electrostatic attraction of a liquid has been recorded by William Gilbert. In 1846, Christian Friedrich Schonbein had produced highly nitrate cellulose. Charles Vernon Boys described the process in paper on nanofiber manufacture in 1887. In 1900, John Francis Cooley filled the first electrospinning patent. John Zenely has published work on the behavior of fluid droplets at the end of the metal capillaries in 1914. His effort began the attempt to methametical model the behavior of fluid under electrostatic forces [7].

Most of the work issued by Formhals and Zenely are exclusively applied to the polymer. Compared with the conventional method such as wet spinning, dry spinning and melt spinning, the electrospinning can produced a much larger specific surface area and smaller pore size with fiber diameter in the range of 10~1000 nm whereas those conventional method only can produce fibers with a diameter in range of 5~500 µm [6].

Electrospinning technique which include the polymer is involves the use of high voltage electrostatic field to charge surface of the polymer solution droplet and thus will induce the ejection of a liquid jet through spinneret. At this rate, the electrostatic force overcomes the surface tension of the droplet and the formation of the Taylor cone is obtained when the solution exiting the tip of spinneret and eventually leading to the charged jet [2, 8-10]. The formation of Taylor cone is proportional to the applied voltage, the voltage is kept increasing until the equilibrium condition is achieved between the surface tension and the electrostatic force (Figure 1). The electric field controlled the route of charge jet and the solidified spun fiber was collected on the rotating or stationary conductive collector [2, 8-9, 11-12]. Setup for electrospinning is depicted in Figure 2.

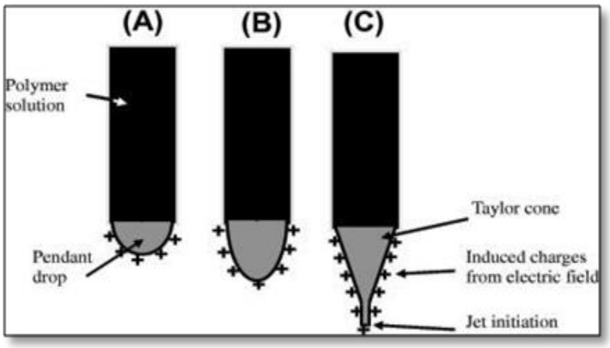


Figure 1 Formation of Taylor cone. Voltage is increased until the equilibrium between surface tension and electrostatic force is achieved as Figure 1(c) [13]

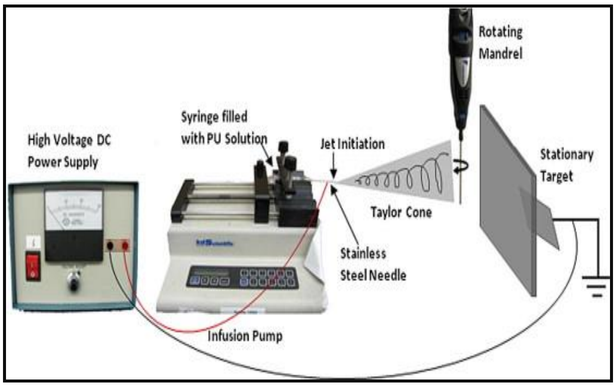


Figure 2 Electrospinning setup [14]

Other than electrospinning process, drawing, template synthesis, phase separation and self-assembly are the others method in developing nanofibers [15]. However, due to the versatility possessed by electrospinning process, thus makes it more favorable to be used in developing highly porous, patterned, nanofibrous polymeric materials of nanofibers [16].

■2.0 POLYMER BASED MEMBRANE NANOFIBER VIA ELECTROSPINNING

As stated above, the work issued by Formhals and Zenely are exclusively applied to the polymer and this becomes the first step towards the increasing in the development of electrospun nanofibers from various type of polymer. Nanofibers have been produced from hundreds various type of polymers [8] and only a few focusing on the effect of polymer based membrane electrospun fibers in fuel cell application. The following are a few polymer based membrane that have been mainly used recently for making nanofibers.

Nafion has been commercially used as polymer electrolyte membrane and it's shown a high performance in proton conductivity [17] which important for fuel cell. A new direction for Nafion has been persuaded in development of Nafion nanofibers by Dong *et al*. [18]. 0.1% of high molecular weight carrier polymer, poly (ethylene oxide) PEO (M_w = 8000 kg/mol) was used in their study. They successfully obtained higher purity of Nafion nanofiber with higher order of proton conductivity of magnitude as compared to the bulk Nafion film. The reduction in fiber diameter was found to improve the proton conductivity of the fuel cell.

The ionic morphology of polymer based membrane is also an important characteristic for proton conductivity enhancement. The orientation of ionic domains along the fiber axis direction is achieved due to the application of shear force during electrospinning process. The aligned ionic structures has resulting in a higher conductivity and this orientation can be extended if the used of shear forces increase in parallel with decreasing the fiber diameter [19].

Tamura and Kawakami [20] synthesized the membrane electrolyte comprised of sulfonated polyimide nanofibers and sulfonated polyimide for proton exchange membrane fuel cell. They found that the polyimides within nanofiber were significantly oriented when electrospun. This membrane showed an improvement in stability with increasing amount of aligned nanofiber and the gas crossover permeability decreased as compared to the membrane without nanofibers due to the aggregated structure within the nanofibers. Furthermore, the proton conductivity of the membrane in parallel direction showed a higher value as compared to the membrane in perpendicular direction and the sulfonated polyimide membrane without nanofibers that was prepared via solvent –casting method.

Pan *et al*. [21] in their studied has focused on developing a nanowire-based high performance in the application of the micro fuel cells. Nafion/poly (vinyl pyrrolidone) (PVP) nanowires (NPNWs) were synthesis by electrospinning. 1.27 g of Nafion (E.I.DuPont Company, equivalent weight (EW)=1100), 0.26 g of PVP (Sigma, MW~1300 000) and 2.1 mg tetramethylammonium chloride (Sigma) in 0.7 g ethanol were prepared as a precursor polymer solution for electrospinning. Plastic syringe with stainless-steel needle was used and 10 cm distance between the needle tip and the collector was applied. The voltage applied was at 16 kV. The used of PVP in this study was dedicated to the high molecular weight that possesses by PVP in order to successfuly electrospin Nafion without any contribution on proton conductivity.

Electrospun Nafion itself is hard to produce by its alone due to the properties which are not soluble in most common solvents which will eventually resulting in formation of micelles which contribute to the decreasing in chain entanglement [12]. Pan *et al*. [21] used the collector which composed of two conductive substrate (silicon) separated by a void gap.

They found that the transportation of protons to reach the cathode in NPNWs becomes more easily and consequently the proton conductivity of NPNWs was larger proportional to the decreasing in diameter due to the increase in the degree of the "texture" resulting from preferential orientation. They revealed that the proton conductivity can be enhanced by altering the diameter of the NPNWs to less than 2.3 µm. The others finding on electrospun fiber polymer based membrane for fuel cell application can be summarized in Table 2.1.

Table 2.1 Finding on electrospun fiber polymer based membrane for fuel cell application [2]

Based Polymer	Filler/Carrier Polymer	Proton Conductivity ($mScm^{-1}$)
Poly(vinyl alcohol)	Nafion®	22
Polyvinylidene fluoride	Nafion®	2
Sulfonated polyethersulfone	Nafion®	~85
Sulfonated random copolyimide	Sulfonated polyimide	Up to 370
Bromomethylated sulfonated polyphenylene oxide (BPPO)	Sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO)	30-80
3M perfluorosulfonc acid polymer	PEO	55
Nafion®	5wt% PVA or PEO	8.7-16
3M perfluorosulfonc acid polymer	PAA	498
Polymerised Ionic Liquid	poly(MEBIm-BF4) , PAA	7.1×10^{-4}
Sulfonated poly(ether ether ketone ketone)	None	37 (solvent DMF) 41 (solvent DMAc)
Sulfonated poly(arylene ether sulfone)	None sulfonated polyhedral oligomeric silsesquioxane (sPOSS)	86 94
Sulfonated copolyimide		~100
Polyvinylidene	Phosphotungstic acid (PWA, up to 12.8 wt%)	~0.4
Aquivion™	PEO (M_w $1x10^6$)	66
Sulfonated Zro_2	PVP, poly(2-acrylamido-2-methylpropanesulfonic acid) (pAMPS)	240

As we concerned, most of the previous studied focusing on polymer reinforce composite proton exchange membranes and the resulting membrane performance are dominant for proton conductivity rather than fuel barrier properties. A direct methanol fuel cell especially had shown a significant drawback on power density and efficiency if be compared to the polymer exchange membrane fuel cell which operate with hydrogen due to methanol crossover from anode to cathode [16, 22-23].

The latter approach (Table 2.2) which is on the preparing of new electrolyte composite membrane based on proton conducting materials that is currently being investigated for the past few years as a good proton conductivity as well as the methanol barrier properties. These new electrolyte composite membranes consist of dispersion fillers, such as silica, heteropolyacid, zirconium phosphate and etcetera within the polymer.

Table 2.2 Finding on electrospun fiber polymer based membrane for fuel cell application [24]

Approach	Purpose
1. Modifying perfluorinated ionomer membrane/ prepare acid-base blends	Improve water retention properties at high temperature (>100 °C)
2. Modifying ionomer membrane	To improve conductivity
3. Preparing new electrolyte composite membrane based on proton conducting materials	To improve properties of polymer electrolyte membrane as desired properties of the two components which can combine in one composite

According to Kreuer [25], sulfonated polyetherketones (PEEKK and PEEK) were durable under the fuel cell operating conditions which over a several thousand hours. The hydrophilic property is needed since the presence of water molecules can facilitate the proton as well as increases the conductivity of the solid electrolytes which is crucial in fuel cell applications [26]. While clay minerals were used as a reinforcer in polymer membrane in order to improve the methanol crossover and water permeability for direct methanol fuel cell (DMFC) [27]. Lately, sulfonated poly (ether ether ketone) has been electrospun incorporated with SiO_2 as a supported proton exchange membranes for fuel cells application by Lee *et al.* [28]. In this study, they impregnated SiO_2/SPEEK nanofiber mat into Nafion solution in order to get a dense membrane for PEMFC applications. The Nafion impregnated SiO_2/SPEEK membrane show a comparative study with cast Nafion and SPEEK due to excellent proton conductivity.

Previous research conducted by Jaafar *et al*. [29] producing polymer-inorganic membrane consisted of SPEEK and Cloisite 15A® for DMFC application without the contribution of electrospinning process. The membrane was found able to reduce methanol crossover problem as compared to pristine SPEEK and Nafion 112 membranes. Bafna [30] had proved the advantages of clay composite over other nano-sized filler like nano-fibers. They found that the surface area to volume ratio (A/V) for nano-fibers is two times higher than clay layer and means that the nano-fiber would have higher surface area of the filler exposed to the polymer matrix and thus would have higher reinforcing ability compared to the clay layers.

However, when oriented strongly in a particular direction in the composite, the ability was served to the clay layers to reinforce the composite bi-ixially. In preventing the transport of gases or fluid through a particular composite direction, a large amount of filler surface area is required and for this highly oriented filler, the area would be significantly larger in clay composite. This gave a reason to Bafna in order to prepare a polyethylene-clay nanocomposite in their work. Depending on clay quantity and the dispersion state, clay can exhibit as a nucleating agent as well as an obstacle to the polymer mobility. But electrospinning process favors the elongation of the chains and the ordering of the polymer [31].

Smectites, which are a family of both montmorillonite (MMT) and hectorites are a valuable mineral class for industrial applications due to their high cation exchange capacities, high surface areas, high surface reactivity and high barrier properties compared to others natural clays [29]. Organoclays, Cloisite 15A® is the materials prepared from montmorillonite (MMT) and the cation di-tallow as mentioned. Tallow is the mixture of octadecyl (>60%), hexadecyl and tetradecyl. Cloisite is very crucial additive in polymer nanocomposite membrane since it was already being modified from MMT and the possibility in enhancing the compatibility with the organic polymers is expected to occur [32].

Thus, in order to produce an exfoliated polymer-clay nanocomposite membrane, the electrospinning process will be employed. SPEEK and Cloisite 15A® will be used as the base materials in dope solution. The Cloisite 15A is expected to exfoliate well within the polymer matrix via electrospinning process in order to hinder the polymer movement as well as barrier for the methanol crossover in regards with the crystalline structure of the clay [33].

■3.0 CONCLUSION AND OUTLOOK

The involvement of nanoclay within the polymer matrix is indeed give a bright sight in developing a sophisticated electrolyte membrane for fuel cell application in addition with a role played by electrospinning process which makes the membrane much better in reducing a methanol crossover especially for direct methanol fuel cell application. The choices of the nanoclay used within the polymer matrix also has been preliminary studied by other researchers but the challenges was there is only a few studied involved with electrospinning process in developing a nanocomposite electrolyte membrane. However, it can be expected that the research into developing a polymer based membrane electrospun fiber in fuel cell application will becomes more vigorously studied in future. In addition, we will fabricate the composite membrane consists of SPEEK/Cloisite15A nanocomposite fiber via electrospinning process for DMFC application.

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