

연료전지용 고분자 전해질 복합막의 최근 발전 동향

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(2018년 11월 1일 접수, 2018년 11월 14일 심사, 2018년 11월 20일 채택)

Recent Advances in Composite Polymer Electrolyte Membranes for Fuel Cell

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(Received November 1, 2018; Revised November 14, 2018; Accepted November 20, 2018)

Abstract

Composite polymer electrolyte membranes based on porous supports have been recognized as an alternative for fuel cell applications since it can provide both mechanical as well as electrochemical stabilities. This mini-review highlights recent advances in supported composite polymer electrolyte membranes using porous matrix and nanofibrous supports. In addition, a comprehensive table listing a wide range of anion and proton exchange pore filling membranes was provided at the end of the review.

Keywords: Composites, Electrospinning, Fuel cell, Polymer electrolyte membranes, Pore filling

1. Introduction

In the emergent advancement of polymer electrolyte membrane fuel cells (PEMFCs), the development of membrane electrode assemblies capable to operate at high temperatures and low relative humidity is essential. Those fuel cells do not require an external humidification system and hence expected to reduce the cost. Furthermore, higher operating temperature improves the fuel cell performance and overall efficiency of the system[1,2]. Current state of the art perfluorosulfonic acid ionomer based membranes (DuPont's Nafion) have limited their long-term application due to the high degree of dimensional change during the operation and reduction in conductivity due to dehydration at elevated temperatures and thus a drastic increase in IR overpotential[3]. Although various techniques have been developed in the last few decades, the durability and cost are still two major obstacles hindering its widespread application. Therefore, the research door is still open to design an innovative conductive and durable membrane for PEMFCs.

Development of organic-inorganic nanocomposites by incorporating nanofillers is a widely accepted facile approach to form continuous

proton conductive pathways and improve proton transportation through polymer electrolyte membrane (PEM). However, its tendency to form aggregate limits their ability to construct continuous conducting channels[4,5]. During the past five years, a number of publications relating to composite membranes have risen steeply. In recent times, the development of composite nanostructured systems comprising ion conductive polymer gel supported by a porous matrix or electrospun non-woven mats has emerged as a promising strategy to stabilize polymer electrolyte membranes and improve their properties for fuel cell application[6]. The main roles of the support in the composite polymer electrolyte are: (i) to reinforcing the membrane, which leads to better mechanical, dimensional and thermal stabilities and (ii) reduce the thickness of the membranes and improve ion conductivity. The purpose of this review is, to sum up the recent progress on PEMs based on pore filling and nanofibrous support composites.

2. Polymer Electrolyte Membranes

Polymer electrolyte membrane fuel cells using proton exchange membranes (PEMs) and alkaline anion exchange membranes (AEMs), due to their high energy conversion efficiency, environmental friendliness, and their flexibility for use in various kinds of electric vehicles as solid electrolytes are being considered as renewable and portable energy devices[7-9]. Perfluorosulfonic acid based membranes owing to their extraordinary chemical, electrochemical as well as mechanical stabilities with good proton conductivity have been widely employed in

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fuel cell systems. Unfortunately, the drawbacks such as high cost, high fuel permeability, and an adverse effect of dehydration which affects proton conductivity and hence performance drop at elevated temperature (above 80 °C) leads to considerable efforts to improve or finding an alternative membrane for fuel cell applications[10,11].

Hydrocarbon-based polymers such as poly(aryl ether ketone)s, polysulfones, polybenzimidazoles, poly(phenylene) and polyimides have been investigated as alternative electrolytes for fuel cells[12-16]. However, such hydrocarbon based proton exchange membranes have several drawbacks such as low electrochemical, mechanical and dimensional stability. In particular, the low thickness of the membranes prepared by casting process leads to poor mechanical strength properties. A variety of reinforced composite membranes has been developed by various researchers to solve these difficulties.

The concept of using a pore-filled membrane to control swelling and solvent permeation has been attracted much attention in the field of fuel cells to overcome the limitations of polymer blended membranes. The pore-filled membrane consists of two parts, namely a porous substrate to provide mechanical strength and a polymer electrolyte embedded in the pores of the substrate to allow proton conduction[17,18]. According to the synthesis strategies and structures, polymer electrolyte membranes are divided into two different categories in this review, including pore filling and nanofibrous composite membranes based on perfluorinated sulfonic acid and non-fluorinated hydrocarbon polymers.

2.1. Pore filling membranes

Recently, reinforced composite membranes consisting of mechanically stable porous substrates and proton conductive electrolytes have drawn considerable interest owing to their advantages in membrane thickness, mechanical strength, and dimensional stability than conventional reinforced composite membranes. Generally, the incorporation of ionically inert porous substrates causes unwanted loss of proton conductivity. Therefore, the composite membranes based on porous support filled with ion-conducting polymer appeared to be a promising approach to develop novel polymer electrolyte membranes[19].

Perfluorosulfonic acid (PFSA) polymers with high ion exchange capacity (IEC) can impart high proton conductivity to the PEM at high temperatures and low relative humidity. Oshiba et al. proposed a pore-filling membrane, composed of a low equivalent weight (EW) perfluorosulfonic acid (PFSA) polymer and a mechanically strong thin (6 µm) ultra-high molecular weight polyethylene porous substrate. The high density structure of sulfonic acid groups inside the pores induced rapid proton conductivity and low hydrogen cross-over via packed acid mechanism. The prepared membrane electrode assembly (MEA) also exhibited higher fuel cell performance than that with Nafion 211 at high temperature and low RH. Low IR loss has been reported due to the effective transport of water from the cathode to anode and hence suppressing dehydration of the membranes at its lower thickness[2].

Over the years, a number of strategies have been adopted to mitigate the drawbacks associated with prototypical perfluorosulfonic acid membranes. Most of the alternative membranes are ranked below perfluorosulfonated (Nafion) membranes over an entire set of important

properties. Sulfonated hydrocarbon-based membranes developed still suffer from insufficient durability, which is largely determined by the rate of chemical degradation by hydroxyl and hydroperoxyl radicals formed during fuel cell operation and excessive swelling or shrinking in response to the change in relative humidity[20].

Poly(tetrafluoroethylene) (PTFE), polyimide, polypropylene, polyacrylonitrile, and polycarbonate are widely using as pore filling substrates. However, the membranes prepared using these substrates showed much lower conductivity than the pore-filled membranes because of the non-conductive nature of these substrates. In order to develop a dimensionally stable pore-filling membrane system with increased proton conductivity, porous substrates consisting of cross-linked benzoxazine-benzimidazole copolymers are developed for practical application of reinforced pore-filling membranes in polymer electrolyte membrane fuel cells operating at a temperature above 100 °C and a relative humidity of < 50%[21]. The porous proton conductive substrates were prepared by reacting PBI with sulfonated benzoxazine, using dibutyl phthalate (DBP) as a porogen followed by subsequent stepwise heating to 220 °C and extraction of DBP from the P(pS-co-BI) films. The resulting porous substrates exhibited mechanically robust cross-linked structures, tunable hydrophilicity, and proton conductivity. The pore-filling membrane prepared by impregnating the porous substrate with sulfonated poly(arylene ether sulfone) having the degree of sulfonation of 70 mol% displayed much improved dimensional stability and mechanical strength.

Even through alcohols are considered to be high energy density fuels, the main challenge that currently limits the performance of direct alcohol fuel cells (DAFCs) is the high permeability of alcohols through electrolyte membranes. Composite membranes consisted of a microporous polytetrafluoroethylene (PTFE) substrate filled with silane crosslinked sulfonated poly(styrene-ethylene/butylene-styrene) (sSEBS) developed exhibited long-term performance in direct alcohol fuel cells (DAFCs) and direct formic acid fuel cells (DFAFCs). The methanol permeability of the PTFE/sSEBS composite membrane was 30% lower than the Nafion 117 membrane. The selectivity of the PTFE/sSEBS membrane was $0.66 \times 10^4 \text{ cm}^3 \text{ Ss}$ at 60 °C which is higher than Nafion 117 and pristine sSEBS[22].

Highly sulfonated polymer membranes with higher ion exchange capacity exhibit severely lower dimensional and mechanical stability due to its excessive water uptake. In order to overcome issues associated with excessive swelling as well as degradation of polymer chains, cross-linked and pore-filled membranes have been actively investigated. PVDF membranes filled with cross-linked sulfonated polystyrene (CSPS) were directly prepared by Kang et al. using an organic-soluble sulfonate monomer without any highly acidic sulfonation step[12]. In their work, sodium 4-vinylbenzene sulfonate was treated with tetrabutylammonium hydroxide to synthesize organic-soluble tetrabutylammonium 4-vinylbenzene sulfonate (TVS). PVDF membranes were filled with TVS, N,N'-methylenebisacrylamide (cross-linking agent), and 2,2'-azobisisobutyronitrile (AIBN, initiator) in dimethyl sulfoxide (DMSO), followed by radical polymerization and subsequent washing with dilute hydrochloric acid solution to replace the tetrabutyl-

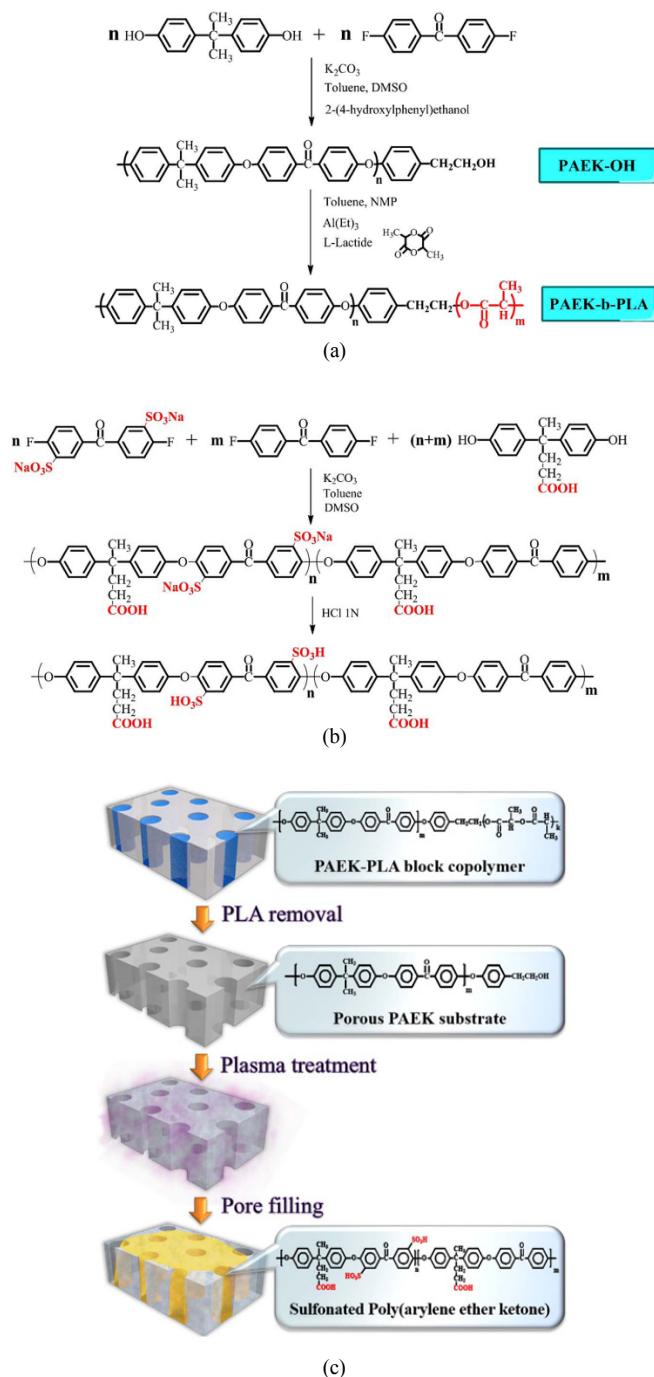


Figure 1. Synthetic schemes of (a) PAEK-OH and PAEK-b-PLA; (b) polymeric filler SPAEK (DS = 80%); and (c) preparation of pore filling composite membrane (Reproduced with permission from Elsevier).

lammonium ions with protons and to remove any unreacted cross-linking agent together with the monomer. The pore filling showed improvement in mechanical strength and conductivity greater than Nafion-212. However, those membranes are suitable only where high oxidation stability is not required. Poly(p-phenylene sulfonic acid-ran-2,5-benzophenone) (PPSP-BP) along with vinyl sulfonic acid (VSA) and triallyl isocyanurate (cross-linker) impregnated into poly-

ethylene microporous membrane followed by electron beam irradiation cross-linking produced membranes with high ion exchange capacity ($4.0\text{--}5.1\text{ meq g}^{-1}$) and stability in water. Moreover, the membranes showed low gas permeability and high dry-wet durability[23].

The pore-filled membranes composed of a similar structured porous substrate and polymeric filler using poly(arylene ether ketone) based material was proposed to enhance interfacial compatibility and hence diminish the leakage of polymeric filler. The porous poly(arylene ether ketone) (PAEK) membrane was chosen as a pore-filling substrate and sulfonated PAEK with 80% degree of sulfonation as polymer filler for proton conduction. Plasma treatment on porous surface were also given to improve adhesion between the hydrophobic porous substrate and hydrophilic polymer filler. Figure 1 illustrates the synthesis routes for the polymer filler, substrate and composite membrane. The pore-filled composite membranes exhibited thermal resistance up to $230\text{ }^{\circ}\text{C}$, as well as excellent dimensional stability from room temperature to $90\text{ }^{\circ}\text{C}$. However, the proton conductivity was still lower than Nafion-117, but the methanol permeability was much lower so that the selectivity was better than Nafion-117[24].

Kim et al. reported a series of pore filling membranes containing a porous cross-linked benzoxazine-benzimidazole copolymer P(pBUa-co-BI) substrates with sulfonated poly(arylene ether sulfone)s (SPAES)s having different degree of sulfonation for fuel cells operating at high-temperatures ($> 100\text{ }^{\circ}\text{C}$) and low humidity ($< 50\%\text{ RH}$) conditions, it shows much improved dimensional stability and mechanical properties than SPAES membranes. The ultra-thin pore filling membranes ($15\text{--}20\text{ }\mu\text{m}$) also exhibited high chemically bound water and hence displayed improved fuel cell performance at $120\text{ }^{\circ}\text{C}$ and $40\%\text{ RH}$ [25].

The use of ionic liquids as conductive fillers allows tuning of the individual properties of both conductive and polymer materials. Van de Ven et al. proposed the concept of ionic liquid H-3-methylimidazolium bis(tri-fluoromethanesulfonyl) imide ([h-mim] Ntf2) embedded into porous non-conductive PBI polymer matrix with tailored morphology as the membrane for high temperature ($> 100\text{ }^{\circ}\text{C}$) fuel cell applications. The resulting membrane showed a proton conductivity of 1.86 mS cm^{-1} at $190\text{ }^{\circ}\text{C}$. A peak power density of 0.039 W cm^{-2} was observed at $150\text{ }^{\circ}\text{C}$, which proved that the developed PBI/IL membrane can be considered as a candidate for high-temperature fuel cell applications[26].

There are substantial attempt to fabricate polymer electrolyte membranes having electrically aligned nanostructure along with the direction of electric field. Lee and his co-workers demonstrated the effect of alignment technique by DC electric field in continuous and scale up modes[27]. Four series of aligned sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) polymer filled porous polyethylene membranes were prepared in accordance with different IEC values and varying intensity of applied electric field. The optimized aligned composite membrane showed the highest maximum power density than other fabricated composite membranes and Nafion-115. The morphology of the membranes was also studied under the influence of the electric field.

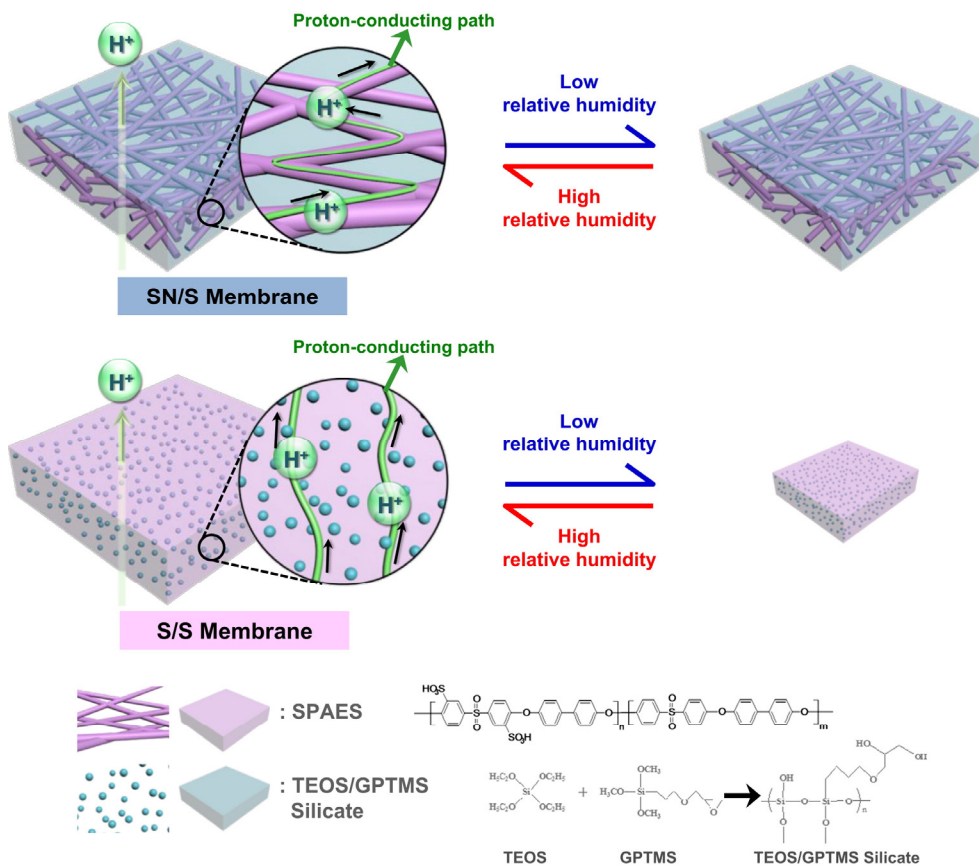


Figure 2. Schematic illustration of phase morphology and the relative humidity variation driven dimensional change of SN/S and S/S membranes (Reproduced with permission from Elsevier)[19].

2.2. Nano fibrous composite membrane

Recently, the method of building the proton transfer channel based on nanofibers has drawn considerable interest from researchers. Electrospun nanofiber mat provides high porosity and a three-dimensional network structure. Unlike conventional fiber production method such as extrusion, electrospinning form long strands of nanofibers and subsequently mat with better interconnectivity and uniformity[28]. Nanostructured composites can be prepared either by embedding electrospun fibers of proton conducting polymer in an inert polymer matrix or by filling matrix ionomer in a nanofiber mat. Proper selection of matrices can improve swelling as well as mechanical and conductivity behaviour of the composite membrane. For example, Nafion filled electrospun nanofibrous sulfonated poly(aryl ether sulfone) (CSPES) composite membranes reported by Wang et al. showed improved proton conductivity, mechanical and methanol barrier properties as well as the reduction in swelling ratio[29].

Gao and his co-workers reported a novel approach to enhance the performance of PEMs by filling sulfonated poly(ether ether ketone) (SPEEK) into the pores in the sulfonated pre-oxidized polyacrylonitrile (SONF) fiber web by solution impregnation method. The introduction of nanofiber improved the thermal stability, water absorption, dimensional stability as well as proton conductivity and decreased methanol permeability due to the long and tortuous diffusive pathway in the

presence of nanofibers[10].

Phase morphology of the composite membranes has much influence on its proton conductivity and dimensional stability. Sulfonated poly(arylene ether sulfone) (SPAES) nanofiber nonwoven fabric/silicate composite membrane with dual phase co-continuous morphology (SN/S membrane) and conventional SPAES/silicate composite membrane (S/S membrane) was compared by Won and his co-workers. The unique phase morphology and the relative humidity variation driven dimensional change of the membrane has been schematically shown in Figure 2. Dual-phase co-continuous morphology in SN/S membrane exhibited noticeable improvement in dimensional stability (Figure 3). The three-dimensionally interconnected silicate phase acted as an independent inorganic framework which is highly stable against humidity variation, thereby effectively mitigating the dimensional change of the SPAES phase in the SN/S membrane. SN/S membrane exhibited lower activation energy (7.07 KJ mol^{-1}) than that of S/S membrane (8.1 KJ mol^{-1}) illustrated the effect on conductivity[19].

Nanofibrous composite membranes consist of three main parts: nanofiber phase, polymer matrix and interfacial regions among these two phases for proton transfer. It is easy to tune the proton transfer pathway at interfacial region between nanofiber and polymer matrix of composite and there have been lots of attempts to construct efficient pathways at these regions. The functional groups from nanofiber and/or

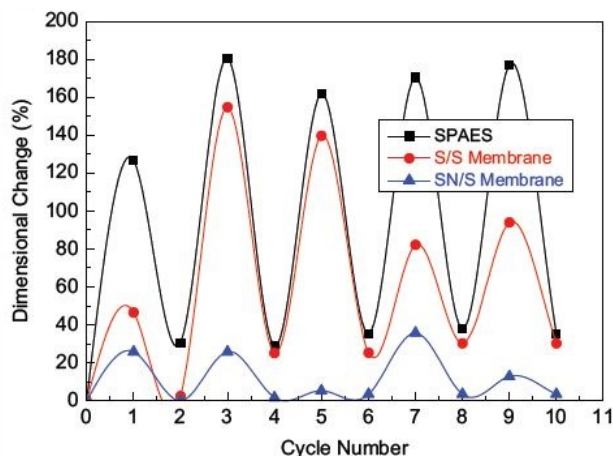


Figure 3. Comparison of dimensional change between SPAES, S/S and SN/S membranes with humidity cycling (repeated hydration-room temperature/100% RH/24 h and dehydration 80 °C/50% RH/3 h) (Reproduced with permission from Elsevier)[19].

incorporated polymer matrix could transport protons along the inter lapped fibers, creating continuous conduction pathways at interfacial regions. Introducing acidic and basic groups can form acid-base pairs, which would work as facile hopping sites for ultrafast proton conduction along the interfacial pathways. Zhang et al. investigated a novel and facile strategy to construct dual interfacial proton conducting pathways in the platform of nanofibrous composite membranes (NFCMs) by incorporating sulfonated halloysite nanotubes (SHNTs) into chitosan (CS) matrix followed by incorporating them into the pores of sulfonated poly(ether ether ketone) (SPEEK) nanofiber mat. Two distinct interfacial pathways are created at SPEEK/CS and CS/SHNTs interfaces, on which ordered acid-base pairs ($-\text{SO}_3\cdots\text{H}_3\text{N}-$) formed reduces the energy barrier for proton conduction. The large surface area and high aspect ratio of nanofillers allowed to form long-range pathways for proton transport. Moreover, the plenty of acid-base pairs formed onto the surface of nanofibers and nanofillers inhibited the movement of polymer chains and improved the thermal and structural stabilities of the membranes[30].

Coupling of different conductive groups could construct different environments, which would significantly modify the proton transferability of the resultant composite proton carriers. In order to study the influence of coupling different functional groups on proton migration, a series of nanofiber mats bearing different functional groups (neutral, acidic, or basic groups) were fabricated. Subsequently, acidic or basic polymer matrix was incorporated into nanofiber mat to obtain nanofiber composite membranes bearing three types of composite proton carriers (I-type: acid-neutral or base-neutral, II-type: acid-acid or base-base, III-type: acid-base or base-acid) at the interfacial domains of nanofiber/matrix. Electrospun nanofiber bearing lots of $-\text{OH}$ (neutral groups) (NF-OH) was prepared using PVA/TEOS. Then, NF-OH was facilely modified with two kinds of silane coupling agents to introduce $-\text{SO}_3\text{H}$ groups (NF- SO_3H) and $-\text{NH}_2$ groups (NF- NH_2). SPEEK and chitosan (CS) respectively, were chosen as the acidic and basic poly-

mer matrices for pore filling. The proton conductivity was found to be increased in the order of I < II < III. The highest hydrated conductivity of 93.8 mS cm^{-1} at 65°C was exhibited by acid-base paired SP/NF- NH_2 . The electrostatic interactions within type III proton carriers facilitated protonation and deprotonation process and providing low energy barrier proton hopping sites as well as admirable thermal, mechanical and oxidative stability by inhibiting polymer chain mobility. SP/NF- NH_2 displayed a 49% increase in maximum current density (475.8 mA cm^{-2}) coupled with a 63% increase in maximum power density (143.4 mW cm^{-2}) compared to SPEEK cast membrane[4].

Liao et al. prepared a highly conductive quasi-coaxial quaternized polyvinyl alcohol (Q-PVA) nanofibers via the electrospinning process. Potassium hydroxide doped nanofiber mat demonstrated a 36.4% increase in peak power density compared with a cell employing a pristine Q-PVA membrane. They ascribed both high conductivity and suppressed methanol permeability obtained are attributed to the quasi-coaxial structure of the electrospun nanofibers. The more amorphous core region forms highly conductive paths, while the outer shell of the nanofibers contains more polymer crystals serve as a hard sheath surrounding the softcore. The mass transfer resistance and tortuous fuel pathway formed by the outer shell suppressed the methanol permeation[31]. Nanocomposite membranes made from nanofiber mats of sulfonated PEEK-polyvinyl butyral (SPEEK-30%PVB) filled with a blend of SPEEK and polyvinyl alcohol (SPEEK-35%PVA) provided mechanical stability, methanol barrier properties and certain proton conductivity up to a crosslinking temperature of 120°C . DMFC performance experiments concluded promising results for this new low-cost type of membranes[18]. The electrospun fiber mats made up of non-charged polymeric materials such as PVDF and PSF fused to one another form a welded porous mat, which is filled with perfluorosulfonic acid (PFSA) polymer generate a proton conducting composite polymeric electrolyte. The membrane exhibited lower water uptake and higher mechanical stability[32].

As the electrolyte with high molecular weight polymer tends not to be completely embedded in the substrate, the pore-filling method conventionally used to fabricate reinforced composite membranes exhibits limited reliability. This can be solved by the use of electrospun substrates with desired pore size and porosity. In view of that, Jang and his co-workers introduced a reinforced micro-composite polymer electrolyte membrane by simultaneous electrospinning/spraying process. A diluted polysulfone (PSf) solution was sprayed on to a thin layer of sPAES electrospun fiber and vice versa to form PSf (SP) + sPAES (ES) and PSf (ES) + sPAES (SP) membranes. The PSf (ES) + sPAES (SP) membrane exhibited the highest durability with slightly lower cell performance. The CV curves of PSf (ES) + sPAES (SP) showed little fuel cross-over induced changes up to 300 cycles, with significant changes observed between 300 and 600 cycles due to progressing membrane degradation[20].

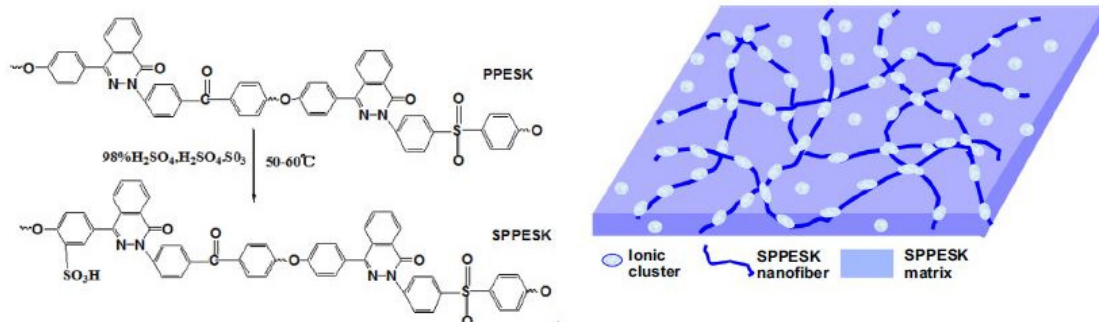


Figure 4. Schematic structure of electro spun nano fiber enhanced SPPEEK composite PEM (Reproduced with permission from Elsevier)[38].

3. Proton Exchange Membrane Fuel Cells

Maximizing the proton conduction, while keeping sufficient mechanical strength and reduced dimensional swelling is a key challenge for the development of PEMFC membranes. Much research approaches in this domain have been devoted to the use of perfluorosulfonic acid (PFSA) ionomers. sPEEK/Aquivion® composite membranes prepared by casting the PFSA ionomer dispersion (Aquivion®) onto cross-linked sPEEK electrospun mats showed improvement in mechanical strength and dimensional stability than pristine® membrane ascribed to the high stiffness of the porous substrate. However, the proton conductivity values are comparatively lower due to the relatively lower conductivity of sPEEK[1]. Nafion-impregnated SiO_2 /sPEEK composite nanofiber membranes were prepared by electrospinning of mixed solutions of silica precursor (tetraethylorthosilicate) and SPEEK followed by impregnating Nafion inside the pores. Nafion impregnated SiO_2 /SPEEK nanofiber composite showed a maximum power density of 170 mW cm^{-2} at 120°C and 40% RH, which was more than doubled the power density for the recast Nafion (71 mW cm^{-2}) membrane[33]. Acid doping can provide polymer electrolyte a better proton conductivity. N, N-dimethylhexadecylamine partially quaternized poly(vinyl benzyl chloride) (qPVBzCl) ionomer filled porous polytetrafluoroethylene (PTFE) film treated with phosphoric acid gives a composite membrane with improved conductivity and a peak power density of 360 mW cm^{-2} at 175°C under low humidity conditions (< 1%)[34]. Incorporating chitosan (CS) matrix into electrospun sulfonated poly(ether ether ketone) (SPEEK) nanofiber mats exhibited electrostatic interaction within acid-base pairs and more proton hopping sites in the perpendicular direction of the nanofiber composite membranes[35].

The durability of membranes are normally affected by two different sources: hydroxide radicals generated as byproducts of the electrochemical reactions during PEFC operation attack the main or side chains of ionomers which lead to its decomposition, swelling-induced mechanical stresses lead to pinhole formation, delamination, and creep. In an effort to address the durability demands, PFSA membranes with reinforcement have become of great interest as they have demonstrated superior durability in PEMFCs compared to their unreinforced analogues. Shi et al. explored how reinforcement could impact the overall structure-property relationship and anisotropy of ionomers which could potentially benefit the development of alternative hybrid

ion-conductive polymers. Nafion XL composed of 10% PTFE, 75-90% PFSA/TFE copolymer and up to 5% proprietary additive was subjected to different pretreatment and conditioning to elucidate the impact of reinforcement on its anisotropic properties and structure/property relationship. Heating of the membranes in water at different temperatures showed significant impacts on its structure/property relationship, in particular, the mechanical stability, conductivity, and their anisotropy, which were related to the morphological changes observed from microscopy studies[6].

Solution blowing has been reported as a new process for nanofiber preparation because of its significant advantages such as high productivity due to its high solution feed rate, easy accessibility and low energy consumption due to the absence of high voltage equipment over electrospinning. The fibers are also commonly curled in three dimensions. Solution blown sulfonated poly(ether ether ketone) (SPEEK) nanofibers after impregnation into Nafion form pore filled nanofiber composite membranes with suppressed in-plane swelling and improved conductivity. The absence of any significant cracks indicated good compatibility among nanofiber and Nafion. Generally, high water uptake also leads to high swelling of the membrane. However, the prepared membranes possessed both high water uptake and low swelling ratio. The tortuous and anfractuous channels developed by nanofibers prevented methanol cross-over and achieved good selectivity to the membranes[36].

Most non-fluorinated membranes possess aromatic polymer chains with sulfonic acid functional groups connecting to the backbones, which lead to narrow, tortuous and dead-end proton conductive channels and low proton conductivity. Hence interconnecting proton channels are essential to get high conductivity and mechanical stability in non-fluorinated membranes. Gong and his co-workers proposed a novel approach of using thickness aligned nano-size proton conductive channels by means of electrospinning process for high-performance fuel cells. Sulfonated poly(phthalazinone ether sulfone ketone) (SPPEEK) was electrospun into aligned nanofibers and then arranged through the plane in the membranes to induce straight nano-scale proton conductive channels. The negatively charged sulfonic acid groups were aggregate towards the surface of the fibers and then on inter-fiber voids. The long-range ionic clusters formed along the aligned electrospun nanofibers in the thickness direction resulted in much higher through-plane conductivity, nearly twice the conductivity of SPPEEK

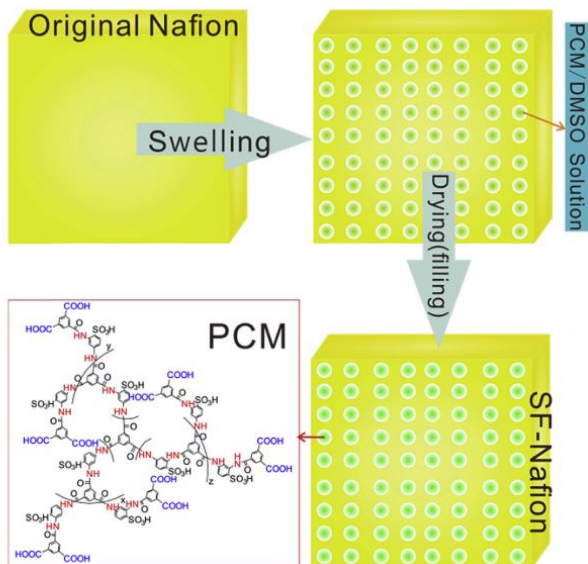


Figure 5. Schematic diagram of in-situ nano scale SF strategy (Reproduced with permission from Elsevier)[40].

membrane. The membranes exhibited higher single cell power density (1.2 fold), lower hydrogen crossover (33%) and higher tensile strength (1.5 fold) as compared with that of Nafion 115[37]. The interfacial compatibility between electrospun fiber and inter fiber voids filler affects the proton conductivity and mechanical stability. The strategy of higher ion exchange capacity (IEC) electrospun fiber mats with lower IEC inter-fiber voids filler matrix improved the contribution of electrospun fiber mats embedded in the SPPEK matrix (Figure 4). Larger and ordered ionic clusters aggregated along the interfaces between SPPEK nanofibers and matrix exhibited a high proton conductivity of 186.4 mS cm^{-1} and controlled swelling of 30% at 80°C [38].

Integrating proton conductive sulfonated poly(ether ketone) (SPEK) nanofibers as reinforcement into a Nafion membrane by direct electrospinning and membrane deposition was reported. The proton conductivity of the fiber reinforcement led to a reduced membrane resistance and higher power density compared to a similarly fabricated composite membrane with inert reinforcement, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) material. The chemical accelerated stress test (100 h OCV hold at 90°C , 30% RH, H_2/air , 50/50 kPa) revealed a degradation rate of about 0.8 mV/h for the fuel cell with SPEK reinforced membrane, compared to 1.0 mV/h for the PVDF-HFP reinforced membrane[39].

Significant efforts have been made to reduce the methanol permeability through Nafion membranes by adopting different strategies of modifying surface and composition. Unfortunately, negative impacts on the remaining properties were observed. In the work of Li et al., they have developed an in-situ nanoscale swelling-filling (SF) strategy to improve the performance of Nafion membranes. Nafion membrane was filled in-situ with proton conductive macromolecules (PCMs) of the structure, shown in Figure 5 which are capable of physically blocking the fuel molecules during fuel cell operation. The DMFC equipped with the membrane yielded 33% higher power density than the original

Nafion DMFC and these notable advantages demonstrated the significance of SF strategy in the performance of DMFCs[40]. Xu et al. were also boosted methanol permeation resistivity and proton conductivity of Nafion by structural architecture modification of PCM filler using $-\text{COOH}$ as end capping groups[41].

Some progress has been made recently on nanofiber based bilayer membranes to improve the methanol barrier properties. Nanofiber-based bilayer membranes by direct electrospinning of sulfonated polyethersulfone (SPES) nanofibers on Nafion112 membrane's surface followed by impregnation of Nafion solution into the pores of electrospun SPES (SPES-N-N112) were compared with Nafion impregnated porous SPES nanofibrous membranes with a uniform top layer of Nafion (SPES-N-N). The proton to methanol selectivity of the SPES nanofiber-based bilayer membranes is about 53,680 and 45,500 S cm^{-3} for SPES-N-N and SPES-N-N112 in comparison with 28,300 and 40,500 S cm^{-3} for Nafion112 and Nafion117, respectively[42].

Membranes with sufficient durability for long-term operation of high-temperature PEMFC is one of the challenges. Two types of porous polybenzimidazole (PBI) membranes with symmetric and asymmetric morphologies were fabricated by template leaching method using different soft templates, DBP and 1-ethyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide ([EMIM] [TFSI]), respectively. Asymmetrically porous PBI exhibited a higher porosity compared to the symmetrical one, which had better tensile properties and oxidative stability. On the other hand, an ultra-high proton conductivity of $2.02 \times 10^{-1} \text{ S cm}^{-1}$ was obtained at 160°C for the symmetrical one. Moreover, significant improvements in the durability of fuel cell operation, fuel crossover and phosphoric acid leakage were observed in symmetrically porous structure[43]. Improvements in electrochemical durability were achieved also by introducing cross-linker with two or more cross-linkable sites. Monomer impregnated porous PE film sandwiched between polyethyleneterephthalate (PET) films after simultaneous polymerization and cross-linking using UV radiation forming a three-dimensional polymer network with long-term durability[44]. Phosphoric acid doped track-etched polybenzimidazole (PBI) membranes, formed by energetic heavy ion irradiation followed by a selective chemical etching of these tracks into pores exhibited a conductivity of more than 15 mS cm^{-1} even after 250 h of operation at 150°C [45]. Silica nanofiber biofunctionalized with four kinds of amino acids (including cysteine, serine, lysine, and glycine) impregnated into Nafion matrix obtained composites (Figure 6 (a)) with dimensional and thermal stability as well as continuous pathways for proton conduction. The molecular structure of modifiers are given in Figure 6 (b). Bio- SiO_2 nanofiber-grafted cysteine, serine, lysine, and glycine were designated as $\text{SiO}_2\text{-Cys}$, $\text{SiO}_2\text{-Ser}$, $\text{SiO}_2\text{-Lys}$, and $\text{SiO}_2\text{-Gly}$, respectively. Nafion-Cys presented the best proton conductivity and Nafion-Gly demonstrated the best dimensional stability and methanol permeability[46].

Table 1. Summary of Composite Membranes

Membrane designation	Modification	Ion conductivity, σ (S cm ⁻¹)	Methanol permeability (cm ² s ⁻¹)	Peak power density (mW cm ⁻²)	Reference
UHMWPE porous substrate (6 μ m)/low equivalent weight perfluorosulfonic acid (PFSA)	Pore filling	0.1 (80 °C, 90% RH)		1,000 (100 °C, 30% RH)	[2]
SP/NF-NH ₂	Porefilling/ nanofibrous	0.09 (65 °C)	-	143.4 (120 °C)	[4]
SPEEK/SONF	Porefilling/ nanofibrous	0.11 (60 °C)	6.39×10^{-7} (RT)	-	[10]
PVDF-CSPS	Pore filling	0.21 (90 °C, 90% RH)	-	-	[12]
(SPEEK-30%PVB)/(SPEEK-35%PVA)	Porefilling/ nanofibrous	0.01 (60 °C)	3.82×10^{-6} (2 M, 60 °C)	100 (DMFC) 120 °C	[18]
SPAES/silicate (SN/S)	Porefilling/ nanofibrous	0.06 (30 °C)	-	-	[18]
PTFE/sEBS	Pore filling	0.02 (60 °C)	3.78×10^{-6} (1 M, 60 °C)	91.4 (DMFC) 70 °C 16.5 (DEFC) 81.5 (DFAFC)	[22]
PAEK (f = 5%)-SPAEC (DS = 80%)	Porefilling	0.12 (90 °C)	0.5×10^{-5} (2 M)	-	[24]
PBI/IL	Porefilling	0.002 (190 °C)	-	39 (150 °C)	[26]
SPPO/PE (ASPFM-2-0.8V)	Porefilling	0.048 (RT)	-	280 (30 °C)	[27]
CSPEs-70-3	Porefilling/ nanofibrous	0.06 (20 °C)	1.02×10^{-7} (2 M, 20 °C)		[29]
CS/SPNF/SHNTs	Porefilling/ nanofibrous	0.12 (90 °C, 100% RH)	-	-	[30]
QPVA/KOH	Porefilling/ nanofibrous	0.04 (60 °C)	5.27×10^{-6} (2 M, 30 °C)	54 (DMFC) 60 °C	[31]
H ₃ PO ₄ @PTFE/qPVBzCl ⁻	Porefilling	0.11 (180 °C)	-	360 (175 °C, < 1% RH)	[34]
SPEEK/CS	Porefilling/ nanofibrous	0.12 (30 °C)	-	-	[35]
Sulfonated poly(phthalazinone ether sulfone ketone) (SPPEsk)	Porefilling/ nanofibrous	0.04 (80 °C, 100% RH)	--	300 (50 °C, water saturated H ₂ and O ₂)	[37]
SPPEsk	Porefilling/ nanofibrous	0.19 (80 °C)	-	350 (50 °C, 60% RH)	[38]
poly(ether ketone) (SPEK)/Nafion	Porefilling/ nanofibrous			2040 (80 °C, 100% RH)	[39]
SF-Nafion	Porefilling (nano-scale swelling-filling)	0.23 (80 °C)	10×10^{-7}	4.8 (DMFC)	[40]
PBI					
Symmetrically porous	Porefilling	0.20 (160 °C)	-	838 (160 °C)	[43]
Asymmetrically porous		0.08 (160 °C)		835 (160 °C)	

4. Summary and Conclusions

An extensive research on the preparation and characterization of polymer electrolyte membranes are performed aiming at improving the mechanical, chemical and electrochemical stability. Ionically conductive polymer gel with porous matrix or electrospun mat support may efficiently overcome the limitations associated with the state of the art perfluorosulfonic acid based membranes and enhance mechanical strength,

conductivity, stability, selectivity and durability. This review gives an overview of various efforts that have been made during the last five years on porous supported polymer electrolyte membranes. Table 1 shows a summarized report on the work performed on various membranes.

Isotropic porous matrices have been most common for preparing pore-filling composites. Membranes composed of supporting PTFE matrix filled with Nafion were extensively studied and demonstrated significant benefits. Reinforced composite membranes based on

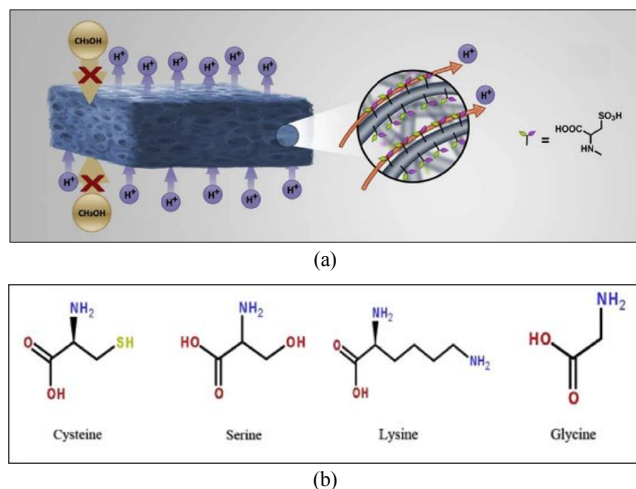


Figure 6. (a) Schematic diagram of Nafion membrane with biofunctional SiO₂ nanofiber (cysteine) and (b) molecular structures of cysteine, serine, lysine and glycine (Reproduced with permission from Elsevier)[46].

cross-linked polymers embedded porous substrate demonstrated dimensional stability, high-temperature applicability and durability. The use of similarly structured substrate and filling material leads to enhanced interfacial compatibility and hence proton conductivity. Dual interfacial proton conducting pathways by implementing acid-base interaction reduces the energy barrier for conduction. Enhanced mechanical properties and selectivity were achieved by the use of bilayer membranes. Further improvements in performance, especially conductivity, may be achieved in anisotropic matrices through the alignment of ionic channels. In-situ nanoscale swelling-filling strategy significantly affected the DMFC performance by blocking the fuel molecules.

The past investigations have laid a solid foundation for the basic understanding of how the performances of polymer electrolyte membranes been affected the structure of the membranes.

Acknowledgment

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the ministry of science and ICI (NRF-2015 M1A2A2058028).

References

1. C. Boaretti, L. Pasquini, R. Sood, S. Giancola, A. Donnadio, M. Roso, M. Modesti, and S. Cavaliere, Mechanically stable nanofibrous sPEEK/Aquivion® composite membranes for fuel cell applications, *J. Membr. Sci.*, **545**, 66-74 (2018).
2. Y. Oshiba, J. Tomatsu, and T. Yamaguchi, Thin pore-filling membrane with highly packed-acid structure for high temperature and low humidity operating polymer electrolyte fuel cells, *J. Power Sources*, **394**, 67-73 (2018).
3. G. C. Abuin, E. A. Franceschini, P. Nonjola, M. K. Mathe, M. Modibedi, and H. R. Corti, A high selectivity quaternized poly-

sulfone membrane for alkaline direct methanol fuel cells, *J. Power Sources*, **279**, 450-459 (2015).

4. Y. He, H. Zhang, Y. Li, J. Wang, L. Ma, W. Zhang, and J. Liu, Synergistic proton transfer through nanofibrous composite membranes by suitably combining proton carriers from the nanofiber mat and pore-filling matrix, *J. Mater. Chem. A*, **3**, 21832-21841 (2015).
5. D. J. Kim and S. Y. Nam, Research trend of organic/inorganic composite membrane for polymer electrolyte membrane fuel cell, *Membr. J.*, **22**, 155-170 (2012).
6. S. Shi, A. Z. Weber, and A. Kusoglu, Structure/property relationship of Nafion XL composite membranes, *J. Membr. Sci.*, **516**, 123-134 (2016).
7. H. W. Zhang, D. Z. Chen, Y. Xianze, and S. B. Yin, Anion exchange membranes for fuel cells: Synthesis strategies, properties and perspectives, *Fuel Cells*, **15**, 761-780 (2015).
8. Z. Zakaria, S. K. Kamarudin, and S. N. Timmiati, Membranes for direct ethanol fuel cells: An overview, *Appl. Energy*, **163**, 334-342 (2016).
9. C. H. Park, S. Y. Nam, and Y. T. Hong, Molecular dynamics (MD) study of proton exchange membranes for fuel cells, *Membr. J.*, **26**, 329-336 (2016).
10. Z. Gao, G. Jiang, and P. Ma, Preparation and performance as PEM of sulfonated pre-oxidized nanofiber/SPEEK composite membrane, *Fibers Polym.*, **18**, 1025-1030 (2017).
11. S. Y. Lee, H. Kim, S. Y. Nam, and C. H. Park, Synthetic strategies for high performance hydrocarbon polymer electrolyte membranes (PEMs) for fuel cells, *Membr. J.*, **26**, 1-13 (2016).
12. N. Kang, J. Shin, T. S. Hwang, and Y. S. Lee, A facile method for the preparation of poly(vinylidene fluoride) membranes filled with cross-linked sulfonated polystyrene, *React. Funct. Polym.*, **99**, 42-48 (2016).
13. D. J. Kim, H. Y. Hwang, H. J. Kim, and S. Y. Nam, Preparation and characterization of polysulfone substrate for reinforced composite membrane fuel cell membrane, *Membr. J.*, **19**, 63-71 (2009).
14. D. J. Kim, H. Y. Hwang, and S. Y. Nam, Characterization of composite membranes made from sulfonated poly(arylene ether sulfone) and vermiculite with high cation exchange capacity for DMFC applications, *Membr. J.*, **21**, 389-397 (2011).
15. T. Y. Son, T. H. Ko, J. H. Kim, J. U. Hong, and S. Y. Nam, Preparation and characterization of chitosan membranes cross-linked using poly(2,6-dimethyl-1,4-phenylene oxide) polymer and chitosan, *Membr. J.*, **28**, 205-213 (2018).
16. T. Y. Son, J. W. Jo, J. H. Kim, T. H. Kim, E. Tocci, and S. Y. Nam, Preparation and gas characterization of poly(phenylene oxide) containing imidazolium, *Membr. J.*, **27**, 528-535 (2017).
17. M. S. Lee, H. G. Kang, J. D. Jeon, Y. W. Choi, and Y. G. Yoon, A novel amphoteric ion-exchange membrane prepared by the pore-filling technique for vanadium redox flow batteries, *RSC Adv.*, **6**, 63023-63029 (2016).
18. S. Molla and V. Compan, Nanocomposite SPEEK-based membranes for Direct Methanol Fuel Cells at intermediate temperatures, *J. Membr. Sci.*, **492**, 123-136 (2015).
19. J. H. Won, H. J. Lee, J. M. Lim, J. H. Kim, Y. T. Hong, and S. Y. Lee, Anomalous behavior of proton transport and dimensional stability of sulfonated poly(arylene ether sulfone) nonwoven/silicate composite proton exchange membrane with dual phase co-continuous morphology, *J. Membr. Sci.*, **450**, 235-241 (2014).
20. S. Jang, Y. G. Yoon, Y. S. Lee, and Y. W. Choi, One-step fab-

- rication and characterization of reinforced microcomposite membranes for polymer electrolyte membrane fuel cells, *J. Membr. Sci.*, **563**, 896-902 (2018).
21. K. Kim, S. W. Choi, J. O. Park, S. K. Kim, M. W. Lim, K. H. Kim, T. Ko, and J. C. Lee, Proton conductive cross-linked benzoxazine-benzimidazole copolymers as novel porous substrates for reinforced pore-filling membranes in fuel cells operating at high temperatures, *J. Membr. Sci.*, **536**, 76-85 (2017).
 22. B. Y. Wang, C. K. Tseng, C. M. Shih, Y. L. Pai, H. P. Kuo, and S. J. Lue, Polytetrafluoroethylene (PTFE)/silane cross-linked sulfonated poly(styrene-ethylene/butylene-styrene) (sSEBS) composite membrane for direct alcohol and formic acid fuel cells, *J. Membr. Sci.*, **464**, 43-54 (2014).
 23. S. Ichimura, Y. Sota, J. Ishikawa, Y. Imanishi, K. Kitamura, S. Tsujii, and T. Yamaguchi, Poly(p-phenylene sulfonic acid-ran-2,5-benzophenone) pore-filling membranes with highly packed acid structure and their polymer electrolyte fuel cell performances, *Int. J. Hydrogen Energy*, **41**, 21461-21469 (2016).
 24. A. Le Mong, S. Yang, and D. Kim, Pore-filling polymer electrolyte membrane based on poly(arylene ether ketone) for enhanced dimensional stability and reduced methanol permeability, *J. Membr. Sci.*, **543**, 133-142 (2017).
 25. K. Kim, S. K. Kim, J. O. Park, S. W. Choi, K. H. Kim, T. Ko, C. Pak, and J. C. Lee, Highly reinforced pore-filling membranes based on sulfonated poly(arylene ether sulfone)s for high-temperature/low-humidity polymer electrolyte membrane fuel cells, *J. Membr. Sci.*, **537**, 11-21 (2017).
 26. E. van de Ven, A. Chairuna, G. Merle, S. P. Benito, Z. Borneman, and K. Nijmeijer, Ionic liquid doped polybenzimidazole membranes for high temperature proton exchange membrane fuel cell applications, *J. Power Sources*, **222**, 202-209 (2013).
 27. J. H. Lee, J. Y. Lee, J. H. Kim, J. Joo, S. Maurya, M. Choun, J. Lee, and S. H. Moon, SPPO pore-filled composite membranes with electrically aligned ion channels via a lab-scale continuous caster for fuel cells: An optimal DC electric field strength-IEC relationship, *J. Membr. Sci.*, **501**, 15-23 (2016).
 28. S. Subianto, M. Pica, M. Casciola, P. Cojocaru, L. Merlo, G. Hards, and D. J. Jones, Physical and chemical modification routes leading to improved mechanical properties of perfluorosulfonic acid membranes for PEM fuel cells, *J. Power Sources*, **233**, 216-230 (2013).
 29. L. Wang, J. Zhu, J. Zheng, S. Zhang, and L. Dou, Nanofiber mats electrospun from composite proton exchange membranes prepared from poly(aryl ether sulfone)s with pendant sulfonated aliphatic side chains, *RSC Adv.*, **4**, 25195-25200 (2014).
 30. H. Zhang, Y. He, J. Zhang, L. Ma, Y. Li, and J. Wang, Constructing dual-interfacial proton-conducting pathways in nanofibrous composite membrane for efficient proton transfer, *J. Membr. Sci.*, **505**, 108-118 (2016).
 31. G. M. Liao, P. C. Li, J. S. Lin, W. T. Ma, B. C. Yu, H. Y. Li, Y. L. Liu, C. C. Yang, C. M. Shih, and S. J. Lue, Highly conductive quasi-coaxial electrospun quaternized polyvinyl alcohol nanofibers and composite as high-performance solid electrolytes, *J. Power Sources*, **304**, 136-145 (2016).
 32. M. Gummalla, Z. Yang, P. Pintauro, K. M. Lee, and R. Wycisk, Porous nanofiber mats to reinforce proton conducting membranes for PEM applications, *U.S. Patent*, 9716285B2 (2017).
 33. C. Lee, S. M. Jo, J. Choi, K. Y. Baek, Y. B. Truong, I. L. Kyratzis, and Y. G. Shul, SiO₂/sulfonated poly ether ether ketone (SPEEK) composite nanofiber mat supported proton exchange membranes for fuel cells, *J. Mater. Sci.*, **48**, 3665-3671 (2013).
 34. Y. C. Cao, C. Xu, L. Zou, K. Scott, and J. Liu, A polytetrafluoroethylene porous membrane and dimethylhexadecylamine quaternized poly(vinyl benzyl chloride) composite membrane for intermediate temperature fuel cells, *J. Power Sources*, **294**, 691-695 (2015).
 35. J. Wang, Y. He, L. Zhao, Y. Li, S. Cao, B. Zhang, and H. Zhang, Enhanced proton conductivities of nanofibrous composite membranes enabled by acid-base pairs under hydrated and anhydrous conditions, *J. Membr. Sci.*, **482**, 1-12 (2015).
 36. X. Xu, L. Li, H. Wang, X. Li, and X. Zhuang, Solution blown sulfonated poly(ether ether ketone) nanofiber-Nafion composite membranes for proton exchange membrane fuel cells, *RSC Adv.*, **5**, 4934-4940 (2015).
 37. X. Gong, G. He, Y. Wu, S. Zhang, B. Chen, Y. Dai, and X. Wu, Aligned electrospun nanofibers as proton conductive channels through thickness of sulfonated poly(phthalazinone ether sulfone ketone) proton exchange membranes, *J. Power Sources*, **358**, 134-141 (2017).
 38. S. Zhang, G. He, X. Gong, X. Zhu, X. Wu, X. Sun, X. Zhao, and H. Li, Electrospun nanofiber enhanced sulfonated poly(phthalazinone ether sulfone ketone) composite proton exchange membranes, *J. Membr. Sci.*, **493**, 58-65 (2015).
 39. C. Klose, M. Breitwieser, S. Vierrath, M. Klingele, H. Cho, A. Büchler, J. Kerres, and S. Thiele, Electrospun sulfonated poly(ether ketone) nanofibers as proton conductive reinforcement for durable Nafion composite membranes, *J. Power Sources*, **361**, 237-242 (2017).
 40. J. Li, K. Fan, W. Cai, L. Ma, G. Xu, S. Xu, L. Ma, and H. Cheng, An in-situ nano-scale swelling-filling strategy to improve overall performance of Nafion membrane for direct methanol fuel cell application, *J. Power Sources*, **332**, 37-41 (2016).
 41. E. L. Cussler, S. E. Hughes, W. J. Ward, and R. Aris, Performance dependence of swelling-filling treated Nafion membrane on nano-structure of macromolecular filler, *J. Membr. Sci.*, **534**, 68-72 (2017).
 42. I. Shabani, M. M. Hasani-Sadrabadi, V. Haddadi-Asl, and M. Soleimani, Nanofiber-based polyelectrolytes as novel membranes for fuel cell applications, *J. Membr. Sci.*, **368**, 233-240 (2011).
 43. L. C. Jheng, W. J. Y. Chang, S. L. C. Hsu, and P. Y. Cheng, Durability of symmetrically and asymmetrically porous polybenzimidazole membranes for high temperature proton exchange membrane fuel cells, *J. Power Sources*, **323**, 57-66 (2016).
 44. H. Kang, M. Lee, W. Sim, T. Yang, and K. Shin, Effect of number of cross-linkable sites on proton conducting, pore-filling membranes, *J. Membr. Sci.*, **460**, 178-184 (2014).
 45. A. Eguizabal, M. Sgroi, D. Pullini, E. Ferain, and M. P. Pina, Nanoporous PBI membranes by track etching for high temperature PEMs, *J. Membr. Sci.*, **454**, 243-252 (2014).
 46. H. Wang, X. Li, X. Zhuang, B. Cheng, W. Wang, W. Kang, L. Shi, and H. Li, Modification of Nafion membrane with biofunctional SiO₂ nanofiber for proton exchange membrane fuel cells, *J. Power Sources*, **340**, 201-209 (2017).