Chapter 14
Fabrication Techniques for the Polymer Electrolyte Membranes for Fuel Cells

Aniruddha Chatterjee and D.P. Hansora

Abstract In this chapter, we summarize the various fabrication techniques for the development of polymer electrolyte membrane fuel cells (PEMFC). The purpose is to present a brief overview about different fabrication techniques such as plasma method, phase inversion method, sol–gel method, direct copolymerization, ultrasonic coating technique, ultraviolet polymerization, phase inversion method, in situ reduction, decal transfer method, and catalyst-coated membrane method. After reviewing the above all methods, cost-effective and simple fabrication technique would be useful in the synthesis of PEM depending on the applicability in FC.

Keywords Fabrication · Polymer electrolyte membrane · Fuel cells · Nanocomposites

1 Introduction

Polymer electrolyte membrane (PEM) fuel cells are energy devices, which can convert the chemical energy stored in hydrogen fuel, directly and efficiently, to the electrical energy with water as the only byproduct. These fuel cells are capable to reduce our energy consumptions, pollutant emissions, and dependence on fossil fuels. During the last couple of decades, great covenant of efforts has been made to advance the PEM fuel cell (PEMFC) technology and their fundamental research. Factors, such as durability and cost, are still the major barriers for commercialization of the FCs. Various fabrication methods for the development of PEMFC are

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summarized here for identifying a proper, cost-effective, and simple fabrication technique that would be useful while selecting the materials depending on the applicability of FCs. PEMFCs, made from sulfonated polystyrene-divinyl benzene copolymer, were first deployed in the Gemini space program during early 1960s. But, at that time, PEMFCs were extremely expensive and had had short lifetimes due to the oxidative degradation. DuPont commercialized Nafion by chloralkali processes and also demonstrated its potential interest in FC application. PEMFCs are generally found in three main applications: automotive, stationary, and portable power generation equipment. Later on, direct methanol fuel cells (DMFCs) came into the market because of their longer operating lifetimes and the ability of refueling versus the recharging the batteries [1–5].

Polymeric PEMs are the most widely used membranes for FC applications. Proton-conductive groups containing sulfonic acids are generally introduced into the main side chains of the polymer which can give thermal and chemical stability. Most newly developed polymeric PEMs are capable to work at an elevated temperature (>100 °C). Many polymeric PEMs can be operated at low relative humidity (<40%). But high cost associated with their synthetic processes is the biggest setback.

Different organic–inorganic hybrid nanocomposites have been prepared for PEMFC applications, which include organic materials with tin phosphate, silica, cerium phosphate, heteropoly acid, polyantimonic acid, titanium phosphate, titanium dioxide, zirconia and sulfated zirconia, zirconium phosphate, palladium, montmorillonite, zeolites, tungsten dioxide, phosphorous hydride-silicon dioxide, anhydrous phosphoric acid, inorganic/membrane impregnated with ionic liquids and heterocyclic solvents. On the other hand, polymer composites such as sulfonated poly(aryl ether ketone)s containing the hexafluoroisopropylidene diphenyl moiety, sulfonated poly(ether ether ketone)/polyaniline blends, cross-linked polyvinyl alcohol-silicon dioxide hybrids containing sulfonic acid groups, polyethelene oxide–potassium bicarbonate composites, nanosilica-polyethoxysiloxane within a sulfonated poly(ether ether ketone) matrix, titanium NP self-assembled aromatic polyamide thin films have also been used for PEM in FC application.

2 Recent Developments of PEM-Based on Organic–Inorganic Nanocomposites

Organic–inorganic nanocomposites based PEM have attracted a lot of attention during the last decade. Disparate characteristics of the two components can provide potential barriers for strategical preparation of convenient membrane, but simple processes were also reported for developing the highly efficient nanocomposite-based PEMs [1–4]. Wanga et al. [5] reviewed the technology, applications, and needs of fundamental research on PEMFCs [5]. PEMFCs based on ionomers were also developed [6]. Similarly, polyvinyl alcohol (PVA)/SiO_2 hybrid based PEMs, containing sulfonic acid groups, were also developed for direct methanol FC applications [7]. Organic–inorganic material based membranes were also prepared using polyether diamine and epoxy silane based composites [8]. Costamagn et al. [9] discussed about the fundamental and scientific aspects, including science and technology, related to PEMFC from the 1960s to the year 2000. Similarly, non-precious metal catalysts and self-supported electrocatalysts such as metal, metal alloys are another important supporting part of FC membranes [10–16]. PEMs are required for efficient FC performance due to their characteristics properties such as ionic conductivity, fuel permeation, mechanical stability, thermal stability, durability, and low fabrication cost [17]. Support materials for PEMFC and DMFC electrocatalysts [18], phosphotungstic acid doped catalysts [19], and microstructural pore analysis of the catalyst layer [20] have been also reviewed. Catalyst-coated membranes, prepared by screen printing method, were used in a PEMFC [21], while PEMFC catalysts can be electrodeposited by the use of a hydrogen depolarized anode [22]. Thin films of tungsten selenides were developed for electrocatalytic hydrogen evolution reaction using FC [23]. Various polymers and their nanocomposites are presently in use for industrial FC applications [17]. PEMFC composite comprising of triblock copolymer and heteropolyacid can also be used for FC applications [24]. Zaidi et al. [25] reported about research trends in PEMFCs. Various materials such as thin films of tungsten selenides [23] and phosphide-based materials [26] were used for electrocatalytic hydrogen evolution using FC. Organic–inorganic hybrid materials were also reported as PEMs for separation processes [27]. Carmo et al. [28] reviewed water electrolysis by PEMs. There are some alternatives toward proton-conductive anhydrous membranes for FC applications, such as heterocyclic protogenic solvents comprising polymer electrolytes. Anhydrous PEMs have almost no dependence on humidity, and they are able to maintain high proton conductivity at elevated temperature. Azole-based water-free polymer systems enable the formation of protonic defects and provide strongly labile proton donor–acceptor functions [29, 30]. Anion exchange membranes are also important for alkaline FCs. Merle et al. [31] reviewed and summarized various PEMs for alkaline FCs. These PEMs are made of heterogeneous and homogenous materials, IPN polymer based materials, and ion solvating polymer based materials. Degradation mechanisms and mitigation strategies of PEMFC durability were reviewed [32, 33], similarly, test protocols, [34] stack testing [35] and bipolar plates [36] related to PEMFC were also reviewed. PEMs for DMFCs have been also studied by Neburchilov et al. [37]. Polymer nanocomposites (e.g., PEO + $KHCO_3$) were used for PEMFC applications [38]. Approaches and recent developments of PEMFC operating above 100 °C were also studied [39, 40]. Silica nanocomposite based PEMFC systems, made of polyethoxysiloxane within a sulfonated PEEK matrices prepared by using the sol gel process, were also studied [41]. Various polymer systems were studied for the applications of proton exchange membranes [42, 43]. Various characteristics, of PEMFC such as electrical properties [38], surface morphology, proton mobility [41], effective transport properties with a focus on the gas diffusion layer [44], interfacial properties [45], and bactericidal anti-fouling [46], have been examined. Various models related to PEMFC were also studied [47, 48]. Sulfonated polymers such as polyaniline [3] poly(aryl ether ketone)s containing the hexafluoroisopropylidene diphenyl [49] moiety and factors affecting [50] the life of PEMFC were also investigated for PEMFC applications. Novel polyvinyl butyl based PEMs and their application in gel polymer electrolytes for lithium-ion batteries were reported [51]. Various polymeric nanocomposites based membranes were studied by several workers [52–58] for PEMFC applications. Most of proton exchange membranes [59, 60] were designed indicating their unit operation modeling [61–64], computational study [65], efficiency enhancement and cost reduction [66], self-passivating carbon film as bipolar plate based protective coating [67, 68], cooling flow designs [69], numerical study investigation of the effects of GDL compression and intrusion [70], PEM degradation modeling [71], improving gas diffusivity with bi-porous flow-field [72], and the properties effect on gas diffusivity [73] for PEMFC applications. Effects of idling temperature on high-temperature PEMFC degradation have been studied under simulated start/stop cycling conditions [74]. Hybrid inorganic–organic nanocomposites, made from polymeric nanocomposite based electrolytes, such as PVA/SiO_2 [7], sulfonated PEEK/silica nanocomposites [46], TiO_2 nanoparticle self-assembled aromatic polyamide [46], Nafion and fluorinated TiO_2 for PEMFCs [75], Nafion/inorganic nanocomposites [76], graphene supported platinum nanoparticles (NPs) [77], sulfonated PEEK/sulfonated NPs composite [78], UV polymerized 1-H-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide [79], Nafion, [(ZrO_2)(HfO_2)0.25] and [(SiO_2)(HfO_2)0.28] NPs [80, 81], Nafion and fluorinated TiO_2 NPs [82], novel polymer-coated nanoparticles dispersed-carbon micro-nanofibers-based air-cathode [83], functionalized Al_2O_3 particles as additives in proton-conducting polymer [84], poly (ether-imide) [85], polytetrafluoroethylene (PTFE) [86] and high performance polymer based [87], metal-supported tubular solid oxide [88], SiO_2-ceramic nanoporous substrate-reinforced sulfonated poly (arylene ether sulfone) composite [89], poly(2,5-benzimidazole) (ABPBI)-based MEA assembly [90], poly(vinyl alcohol) (PVA) [91–93], partly fluorinated poly (arylene ether ketone sulfone) hydrophilicehydrophobic multiblock copolymers [94], multilayer-structured, SiO_2/sulfonated poly(phenylsulfone) composite [95], sulfonated bisphenol-A-polysulfone based composite PEMs containing tungstophosphoric acid [96], aligned polyaniline nanorods in situ grown on gas diffusion layer [97] were used for PEMFC applications. Feasibility of combining electrochemical impedance spectroscopy and synchrotron X-ray radiography was used to determine the influence of liquid water on PEMFC performance [98]. Detailed analysis of integrated steam ethanol reformer and different high temperature effects on PEMFC were studied by George et al. [99, 100]. Hydrogen generation from aluminum hydride for wearable PEMFC was studied [101]. Various selective membranes, made from polymer nanocomposites, were studied for hydrogen purification [102–105]. A galvanostatic analysis technique was developed by Lee et al. [103] as an in situ diagnostic tool for PEMFC single cells and stacks. Several polymer nanocomposites based PEMs, such as sulfonated poly(ether ether ketone) (PEEK)/polyaniline composites [3, 103–105] were also studied.

For efficient FC performance, PEMs are required having characteristics properties such as chemical and electrochemical stability, ionic conductivity, fuel permeation or low permeability, mechanical stability, thermal and hydrolytic stability, high durability, flexibility to operate with different fuels, fabrication and production cost. Criteria for selecting the inorganic NPs include hygroscopic characteristics, ceramic property, surface area, porosity, and pore connectivity [17, 24, 25, 29].

3 Fabrication Techniques for the Preparation of PEM

Organic–inorganic nanocomposite systems can be prepared by different synthesis routes, shimmering the various methods available to introduce each phase. During preparation of organic–inorganic nanocomposites, the organic component can be introduced as: (i) a precursor (monomer or oligomer), (ii) a preformed linear polymer (in molten, solution, or emulsion states), or (iii) a polymer network, physically (e.g., semicrystalline linear polymer) or chemically (e.g., thermosets, elastomers) cross-linked. The inorganic part can be introduced as: (i) a precursor (e.g., TEOS) or (ii) preformed NPs. Organic or inorganic polymerization generally becomes necessary if at least one of the starting moieties is a precursor [1–3]. Significant progress has been made in the current decade for the development of new organic–inorganic hybrid nanocomposite based membranes, depending on fundamental understanding of their preparation techniques, and applications in diversified areas.

Organic–inorganic hybrid nanocomposites can be prepared in different ways of blending the inorganic precursor (monomer and oligomer) and organic linear/network polymer matrix. With a monomer precursor, both polymerization and cross-linking of organic or inorganic segments are necessary. However, blending, sol–gel, and in situ polymerization techniques are important preparative methodologies (Fig. 1). The sol–gel process is used for the preparation of inorganic

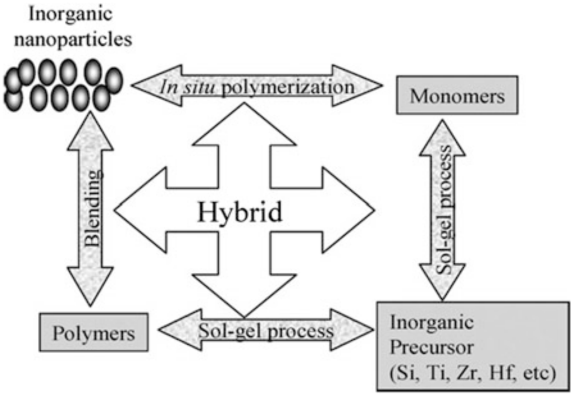


Fig. 1 Schematic representation of different routes for the preparation of organic–inorganic hybrid materials and PEMs (reprinted with permission of Ref. [4])

materials such as glasses and ceramics, and it is based on inorganic polymerization. The low temperature processing of a sol–gel technique provides a unique opportunity for tailoring well-controlled organic–inorganic hybrid materials [4–6]. Organic–inorganic polymer nanocomposites have been reported as an effective PEMs and also the significant improvements have been made on the PEM to empower the FC applications at high temperature and low humidity, for better water adsorption and retention, ionic conductivity, fuel crossover, thermo and mechanical properties, for better FC performance, durability, for ease of fabrication techniques [17, 30]. Lee et al. [56] reported various polymer membranes for high-temperature PEMFC applications. He also reported their synthesis and fabrication procedures for preparation of the membranes such as sulfonated aromatic hydrocarbon membranes, organic–inorganic composite membranes, polymer blend membranes, and PBI-based acid–base membranes [56]. In general the materials, used in synthesis of the PEMs, can be classified into three major groups: (a) perfluorinated ionomers (or partially perfluorinated), (b) nonfluorinated hydrocarbons (including aliphatic or aromatic structures), and (c) acid–base complexes. Mendes et al. [58] reviewed relevant literatures related to segmented PEMs published since 1998 focusing on the SFC design techniques: such as (i) printed circuit board, (ii) resistors network, and (iii) Hall effect sensors. Three techniques were described and their fundamental considerations for design, construction and electrochemical characterization were also provided. The effect of most important parameters on the current density distribution was also highlighted [58]. Rowshanzamir et al. [60] reviewed and summarized three types of membranes along with their preparation and modification methods. He also discussed about new materials, technologies, and research directions being pursued to meet the demanding performance and durability needs of the PEMFC industries. Several methods, which have been used to prepare PEM for FC applications, are described as follows.

3.1 Different Polymerization Routes

Polymerization routes such as in situ polymerization, UV polymerization, chemical polymerizations, and atom transfer radical polymerization (ATRP) are most widely used techniques for the preparation of PEM materials for FC applications. Sulfonated poly(ether ether ketone) (PEEK)/polyaniline (PAni) composite membranes, in order to prevent methanol crossover, were prepared by chemical polymerization of a thin layer of PAni in the presence of a high oxidant concentration on a single face modification. This cost-effective and simple fabrication technique can be used for the synthesis of such composite membranes [3, 4]. Infiltration techniques or doping routes have been used by introducing the inorganic nanoparticles (NPs) or precursors to modify PEM for better transport properties. Preformed membranes were swelled in solvent to increase the pore or void volume before doping or infiltration of inorganic NPs. After infiltration, the polymer nanocomposites were cured by heat, radiation or chemical grafting of inorganic precursor, to obtain covalent bonding inside the polymer matrix. Organic–inorganic nanocomposites can be obtained by infiltration of polymerizable organic monomers with oxide gels or by the mixing of polymers with a single or mixed metal alkoxides. Impregnation of porous oxide gels with organics followed by thermal or irradiation in situ polymerization has resulted in stable PEM for FC applications. Polymers can be trapped within the oxide gel network if the hydrolysis and condensation of metal alkoxide are carried out in the presence of preformed polymers [4, 6]. For the ideal ionic membrane, hierarchically ordered ionic channels/particles should orient vertical to the membrane surface. This can be achieved only via surface-initiated ATRP. Ordered two-dimensional macroporous silicon renders proton-conducting membrane by growing a thick uniform polyelectrolyte brush using surface-initiated atom transfer radical polymerization throughout the porous matrix [17, 24]. Hybrid organic/inorganic composite based PEM consisting of a triblock copolymer (tBC) and varying concentrations of heteropolyacid (HPA) were investigated for application in PEMFCs. An ABC triblock copolymer, that is, polystyrene-b-poly (hydroxyethyl acrylate)-b-poly (styrene sulfonic acid), PS-b-PHEA-b-PSSA, at 28:21:51 wt%, was synthesized via atom transfer radical polymerization (ATRP) and solution-blended with a commercial HPA [24]. Neburchilov et al. [37] reviewed various PEMs for DMFC applications, according to one report, chemical membranes were prepared by the copolymerization of tetrafluoroethylene with a vinylene monomer. Nafion-polyfurfural alcohol (PFA) nanocomposites membranes have been synthesized [37] by in situ polymerization with varying different wt% of PFA. Nafion-polypyrrole based membranes had been prepared by two methods: (i) the impregnation of polypyrrole by in situ polymerization and (ii) polymerization in hydrogen peroxide with Fe(III) as the oxidizing agent. A novel asymmetric membrane composed of a three-component acrylic polymer blend (TCPB) was reported to be prepared by polymerization of an acrylic polymer blend consisting of 4-vinylphenol-*co*-methyl methacrylate (P(4-VP-MMA)), poly(butyl methacrylate) (PBMA) and Paraloid B-82 acrylic copolymer resin [37]. Zhang et al. [43] also reviewed and reported about partially fluorinated acid ionomer membranes prepared via radiation-grafting polymerization, as shown in Fig. 2 [43].

And also this radiation-grafting polymerization method involves a cost-competitive option because of the use of inexpensive commercial materials.

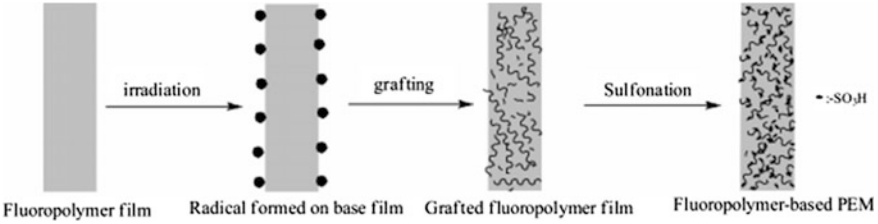


Fig. 2 Process for the preparation of PEMs by the radiation-grafting method (reprinted with permission of Ref. [43])

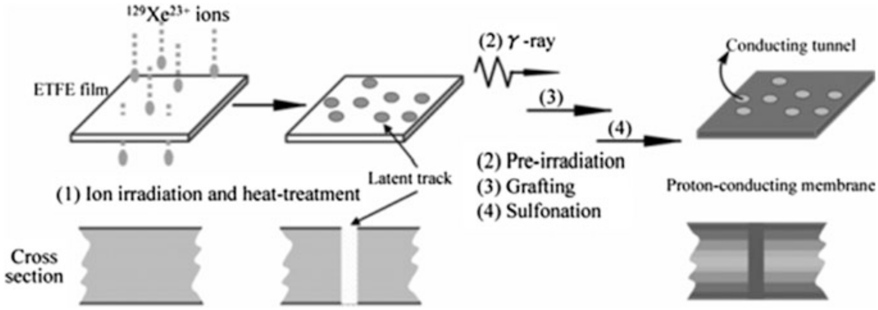


Fig. 3 Schematic diagram for the preparation process of Xe-irradiated ETFE-based proton-conducting membranes (reprinted with permission of Ref. [107])

There are three steps involved during the preparation procedure: (i) the pre-irradiation of the base matrix by ionizing sources, (ii) the grafting of a versatile monomer such as styrene onto the matrix, and (iii) the sulfonation of the grafted membrane (Fig. 2) [43]. The ETFE is widely used as base matrix for radiation-induced grafting PEM because of its high radiation stability and superior mechanical properties. Two modified radiation-induced grafting techniques were used to enhance the performance of ETFE-g-PSSA membranes [43, 106, 107].

In the first initial steps of these techniques, the ETFE film was pretreated by swift heavy ion-beams of Xe^{23+} to create latent tracks extending fully through the ETFE film (Fig. 3) followed by γ-ray pre-irradiation grafting of styrene. The ETFE-g-PSSA membrane exhibits highly anisotropic proton conductivity, with proton conductivity in the thickness direction 3 times greater than that in the surface direction because the styrene is readily grafted in the latent track region [43, 106, 107].

Kim and co-workers [108] explored the single-step synthesis of grafted fluoropolymer films via ATRP. However, the characteristics of their studies depend on the further modified technique to these grafted fluoropolymer films prepared through ATRP. P(VDF-co-CTFE)-g-PSSS films can be synthesized using ATRP, the terminal chlorine atoms on them are converted to end-functional azide groups and sequentially cross-linked by UV irradiation (Fig. 4) [43, 108].

The hybrid membranes composed of inorganic Si–O–Si linkages and organic polymer chains covalently immobilized with phosphonic acid (Fig. 5a) possess good thermal stability up to 200 °C [43, 109]. Saxena and co-workers [110] prepared highly conductive and stable organic–inorganic nanocomposites PEMs with controlled spacing between the inorganic segment and covalently bound sulfonic acid functional groups (Fig. 5b) through a more ingenious method. The resulting PEMs exhibited obvious improvement over the Nafion membrane as evidenced by the higher ratio of proton conductivity to methanol permeability (β-value), which is caused by the lower methanol permeability [43, 110]. Jiang et al. [111] reviewed the work appeared on the use of the sulfonic acid functionalized plasma polymerization techniques for the preparation of PEM for FC applications. These plasma polymerization techniques include glow discharge plasma polymerization, ion beam assisted

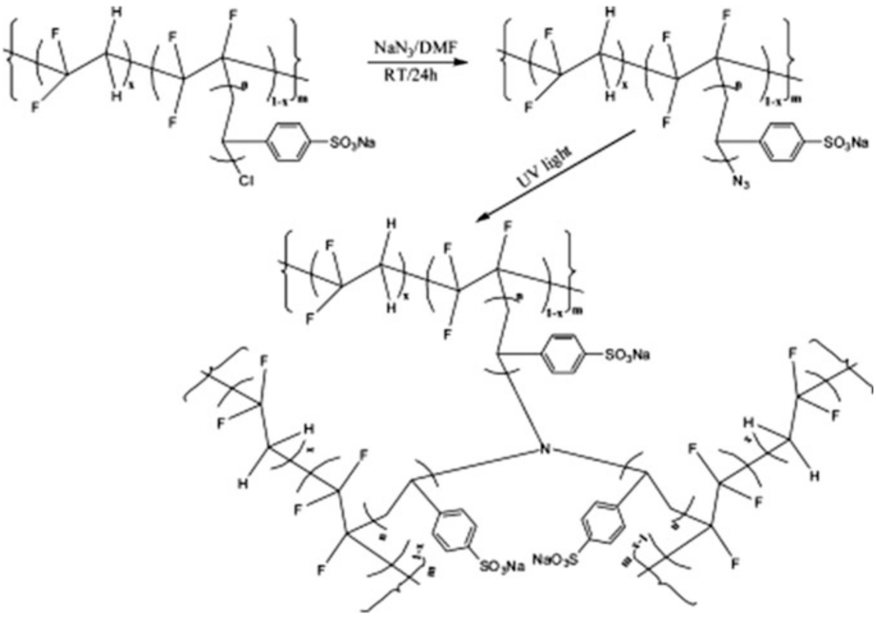
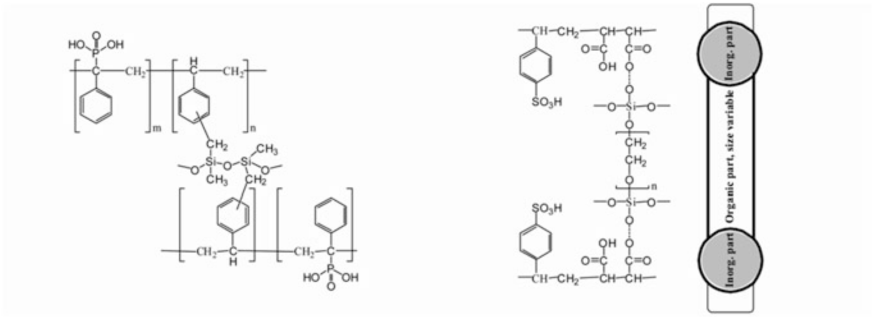


Fig. 4 Schematic procedure for the preparation of cross-linked P(VdF-co-CTFE)-g-PSSA membranes (reprinted with permission of Ref. [108])



a) Chemical structure of inorganic-organic hybrid membrane based on Si-O networks with phosphonic acid groups

b) Chemical structure and schematic representation of inorganic-organic hybrid membrane with controlled spacing between inorganic segment and covalently bound sulfonic acid groups

Fig. 5 Structures of two inorganic–organic hybrid membranes (**a**, **b**) (reprinted with permission from Refs. [109, 110])

plasma polymerization, low frequency after-glow capacitive coupled plasma discharge, pulsed plasma discharge polymerization, etc. [111]. The after-glow plasma discharge process used to prepare AEMFCs involved three steps, (i) plasma polymerization of 4-vinylbenzyl chloride (VBC) monomer into poly(vinylbenzyl chloride); (ii) quaternization of benzyl chloride groups into –$N^+(CH_3)_3Cl^-$ groups; and

(iii) alkalization of $–N^+(CH_3)_3Cl^−$ groups into $–N^+(CH_3)_3OH^−$ groups. The obtained plasma-polymerized AEMFCs exhibited a satisfactory thermal stability, chemical stability, and ionic exchange capacity [111]. Sulfonated poly(aryl ether ketone)s containing the hexafluoroisopropylidene diphenyl moiety were prepared by direct copolymerization using aromatic nucleophilic polycondensation of hexafluoroisopropylidene diphenol with 5,5′-carbonylbis(2-fluorobenzenesulfonate) and 4,4′-difluorobenzophenone (DFBP) at various molar ratios [49]. Pina et al. [79] represented the enhancement of durability of polymeric ionic liquid (PIL) membranes, prepared by ultraviolet (UV) radiation-induced polymerization, for high-temperature PEMFC applications. In particular, the copolymerization of 1-H-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide [HVIm][TFSI] with divinylbenzene used as crosslinker (CL) or prepared by the “in situ” UV polymerization on a preexisting randomly porous polybenzimidazole (PBI) matrix as novel preparation methods, has been fully studied and compared as endurance strategies [79].

3.2 Plasma Methods

ETFE-SA based PEM can be prepared by plasma irradiation (with a total dose of 500 kGy and dose rate of 2.7 kGy s^{-1}) followed by sulfonation without grafts of other polymers. These PEMs were semicrystalline and the cross-linking effects of the crystallites result in the low swelling of the sulfonated PEMs [37]. Jiang et al. [111] reviewed in his paper about applications of the plasma technique for the preparation of PEM for FC applications. He reported that the PEM modified or directly synthesized by the plasma technique exhibited superior properties, such as higher ion conductivity, low fuel permeability, high thermal and chemical stability, which made them promising PEM for FC applications. However, the plasma polymerization is a very complicated process which involves the degradation of monomers and the formation of polymers. Therefore, the conditions used for the membrane modification and preparation must be well controlled to obtain membranes with desirable properties. The various plasma techniques, which have been used for the modification and for the preparation of PEM, are reviewed and along with their associated advantages and disadvantages. These include plasma reactors for surface modification, plasma depositing a polymer layer on the surface of PEM, modification of PEM by gas plasma, and plasma grafting techniques [111].

Won et al. [112] developed a selective thin layer on the top of polystyrene-block-poly(ethyleneran-butylene)-block-polystyrene (sSEBS) copolymer PEMs by simple plasma treatment in the presence of maleic anhydride (MA). The hydrophobic anhydride properties on the top of sSEBS membrane acted as a barrier for methanol permeability. Both the methanol permeability and the proton conductivity of the membrane, therefore, were observed to be decreasing gradually with increasing loading amounts of MA, due to the lack of proton exchange groups on the deposited layer. The recovery of the proton conductivity of the membrane was achieved

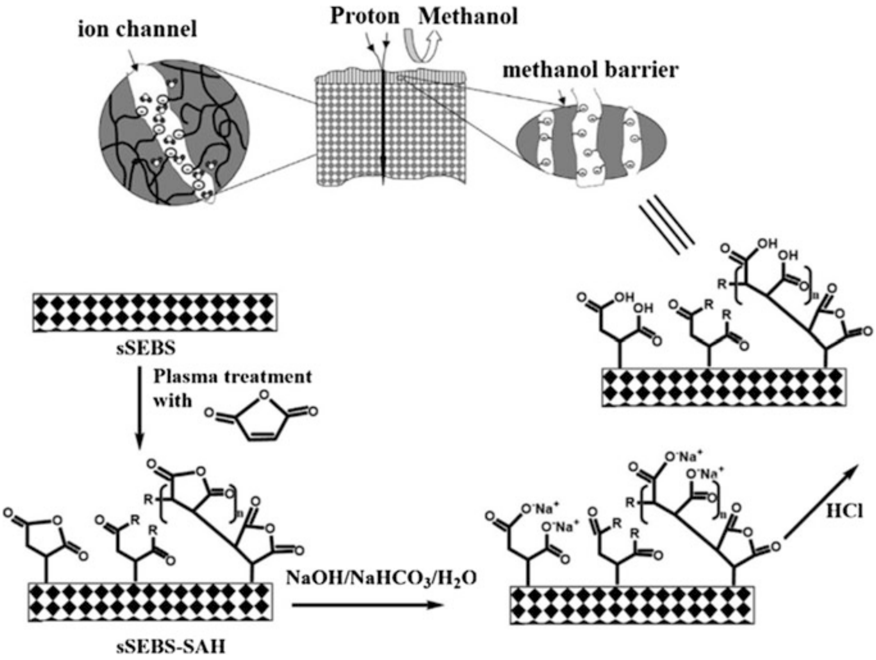


Fig. 6 Modification of the sSEBS membrane through the plasma treatment in the presence of MA and subsequent hydrolysis of anhydride groups to form the PEMs with high conductivity (reprinted with permission from Ref. [112])

through the hydrolysis of anhydride groups, which produced carboxylic acid groups, providing a facilitated transport site for the proton, as shown in Fig. 6.

3.3 Sol–Gel Method

The sol–gel method has been extensively used for the preparation of organic–inorganic nanocomposites as PEM in FC applications and also this method is environmentally friendly because of being low temperature process. Several comprehensive reviews are available on the sol–gel approach to prepare organic–inorganic hybrid materials. Sol–gel method includes mixing of organic polymer solution with organometallic precursors such as tetramethoxysilane (TMOS), tetraethyl orthosilicate (TEOS), Zr(IV)-propoxide, Ti(IV)- butoxide, etc., by hydrolysis and condensation in the presence of suitable catalysts, acid, or base [4–7, 17]. Synthetic techniques used in the sol–gel process to develop polymer/silica hybrid materials include in situ formation of an inorganic network in the presence of an organic polymer and the simultaneous formation of organic polymer and MO$_2$, forming polymer networks [4, 41]. The organic–inorganic nanocomposites made by sol–gel are known as “creamers/ormosils/ormocers” [4]. According to literature [4, 37], organic–inorganic nanocomposites prepared by sol–gel for PEM, include perfluorinated organic–inorganic nanocomposites (Nafion with modifiers such as Nafion-silica NPs, Nafion-ZrP, Nafion, Nafion-titanium dioxide, Nafion-thiophene, Nafion-metal oxides, Nafion-zeolite, Nafion-silica-PWA, Nafion-PAni nanocomposites), partially perfluorinated organic–inorganic nanocomposites (sulfonated styrene with PTFE backbone, functionalized PVDF-silica NPs), and styrene-based nanocomposites (PSMA-silica hybrid material prepared using styrene–maleic anhydride copolymer in the presence of TEOS as a coupling agent, TEOS grafted polystyrene-blocks in polystyrene-b-isobutylene-bstyrene block copolymers, TEOS grafted PSMA-PEG composites, sulfonated PTFE and grafted with TEOS). It has been reported [4] that hybrid materials can also be prepared by nonhydrolytic sol–gel method and because this method involves the reaction of a “metal” halide with an oxygen donor, such as an alkoxide, ether, alcohol, under nonaqueous conditions to form an inorganic oxide and alkyl halide byproducts. One important consideration in this process is the difference in reactivity of metals, such as silicon and transition metals. It was also reported [4] that conversions of polyethoxysilane into SPEEK-silica nanocomposite SPEEK-silica, SPEEK-BPO_4 and PEEK-TiO_2 nanocomposites based membranes, were prepared by sol–gel method. Similarly, polyamideimide/silica composite membrane compatibilized by sol–gel and thermal imidization was reported [4–6, 37, 41]. Organic–inorganic hybrids based on poly (vinyl alcohol) (PVA)/SiO_2 hybrid membranes containing sulfonic acid groups were prepared using the sol–gel process under acidic conditions. The PVA/sulfosuccinic acid (SSA)/silica hybrid membranes were fabricated from different SSA contents [7]. In this sol–gel method, aqueous 10 wt% PVA solutions were prepared by dissolving dry PVA in water and then allowed to reflux at 90 °C for 6 h followed by the addition of a TEOS mixture to the solution. The TEOS mixture was prepared by mixing H_2O, HCl, and TEOS in the molar ratio of 4:0.1:1, which was stirred at room temperature for 2 h. The 5 wt% of TEOS was added to the polymer weight. Then, the PVA/TEOS solutions were mixed together and then stirred at room temperature for 12 h. The solutions were poured onto a plexiglass plate, and casted by using the doctor blade process. The cast solutions were dried in the presence of air at room temperature. The fully dried membranes were peeled away from the glass plate, and then heated in a thermosetting oven at 120 °C for 1 h to induce the cross-linking reaction [7, 37].

Tang et al. [106] reported that a Nafion/SiO_2 composite membrane based on self-assembled Nafion–SiO_2 NPs (Fig. 7) can be formed through a reformative sol–gel process. The self-assembled Nafion–SiO_2 NPs are uniformly distributed in the Nafion/SiO_2 composite membrane and have an average particle size of 2.8 ± 0.5 nm. With the addition of 5 wt% SiO_2 NPs, the Nafion/SiO_2 composite membrane showed significantly improved performance in terms of stability and durability at cell/humidifying temperature of 60 °C [42, 43, 106].

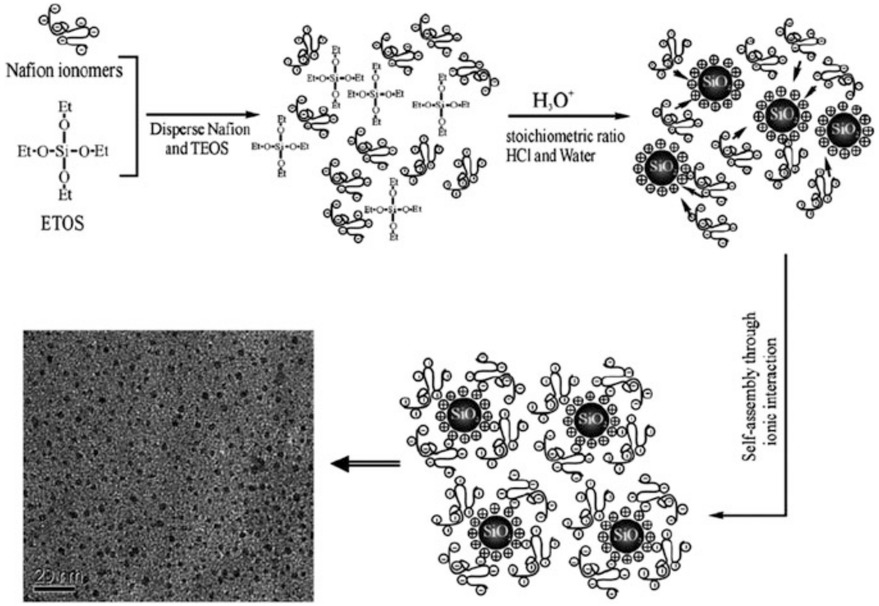


Fig. 7 Scheme for the formation of the Nafion–SiO_2 nanoparticles by self-assembly method. The inset shows the transmission electron microscopy (TEM) micrograph of the self-assembled Nafion–SiO_2 nanoparticles (reprinted with permission from Ref. [106])

3.4 Ultrasonic Coating Technique

Membrane electrode assemblies with Nafion/nanosize titanium silicon dioxide ($TiSiO_4$) composite membranes were developed by a novel ultrasonic spray technique and tested in PEMFC. Nafion/TiO_2 and Nafion/SiO_2 nanocomposite membranes were also fabricated by these technique and their characteristics and performances in PEMFC were compared with Nafion/$TiSiO_4$ mixed oxide membrane [76]. Nam et al. [78] also used ultrasound-assisted solution casting method for the preparation of sulfonated PEEK/sulfonated NPs composite for the FC application.

A modified catalyst-coated membrane (CCM), containing with phosphotungstic acid (PTA) in catalyst layer, can be fabricated using a heated ultrasonic spray method, reported by Wang et al. [19].

3.5 Phase Inversion Method

Partially perfluorinated organic–inorganic nanocomposites (PVDF-HFP-Nafion and PVDF-HFP-Al_2O_3) were prepared by a phase inversion method [4]. The polyvinyl acetal based polymer membranes were prepared by a phase inversion method using synthetic polyvinyl butyral (PVB) from polyvinyl alcohol (PVA) as the polymer matrix. The proportion of hydroxyl group in PVB was controlled by acid modification, and then appropriate polyurethane reaction occured between the residual hydroxyl groups of PVB and the 4,40-diphenylmethane diisocyanate (MDI) as cross-linking agent. As a result, three-dimensional network structures were obtained, which contributed to the chemical stability of PVB-based membrane in LiFP6-based liquid electrolyte [51].

3.6 In Situ Reduction

In situ impregnation process is a versatile technique for the preparation of low cost proton-conducting nanocomposite materials. The homogeneous membranes obtained at lower temperature following this technique influence their potential applications. The membranes were impregnated in the inorganic material's precursor solution and the process begins with its incorporation. The nucleophilic attack of the water, present in the membrane on the inorganic atoms, leads to the hydrolysis of the infiltrated inorganic precursor and as a result membranes have to be treated with necessary reactants for the condensation process

3.7 Catalyst-Coated Membrane by Screen Printing Method

Wang et al. reported [21] a new PEMFC catalyst paste based on direct screen printing (Fig. 8) method and developed a membrane electrode assembly (MEA) by catalyst-coated membrane (CCM) technique. A mixture of cyclohexanol and ethylene glycol was found to be the best solvent for the screen printed catalyst paste in terms of avoiding the swelling of K^+ form Nafion® membrane and mud-cracking in the catalyst layer during the CCM-MEA fabrication process and improving adhesion between the Nafion membrane and catalyst layers was also observed [21].

3.8 Solution Casting Method

Organic–inorganic polymer membranes were prepared by reacting 3-glycidoxypropyl trimethoxysilane with diamines containing polyether segments, followed by their hydrolysis and condensation with acid catalysis. Composite membranes were prepared by solution casting on Teflon petri dishes followed by evaporation of solvent and casting (dip-coating) the solution (just after 2 h heating at 80 °C) [8]. Solution casting is another simple method for the preparation of organic–inorganic hybrid nanocomposites. A few microliters of a dilute solution containing

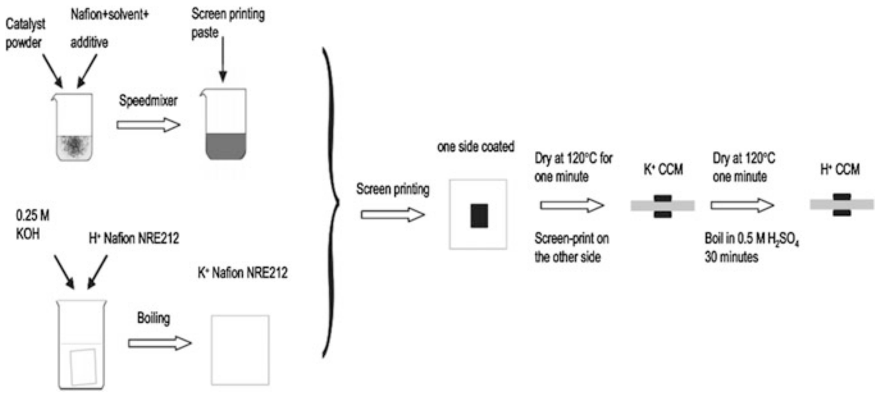


Fig. 8 Schematic of the CCM-MEA preparation procedure using direct screen printing method (reprinted with permission from Ref. [21])

the dissolved polymer and nanofillers can be film casted by mixing with the polymer solution under vigorous stirring followed by the evaporation of a solvent, because this enables direct incorporation of inorganic NPs into a polymer matrix. The thickness of the PEM could be easily controlled [17, 24]. The triblock copolymer composite membranes containing HPA in various weight ratios were prepared using a solution casting method. This method includes washing with water, vacuum drying, solution casting followed by drying [24]. Sulfonated polyphosphazene (sPPZ) membranes were prepared by dissolving benzophenone (a photo-initiator) in the membrane casting solution and then the resulting films, after solvent evaporation, were exposed to UV light. The films of ethane cross-linked polyphosphazene can be sulfonated from the surface inward. This prevents dissolution in water, thus allowing sulfonation to proceed through the material. The sPPZ membrane has the highest thermal and chemical stabilities and low methanol crossover in DMFC operation [37]. Noto et al. [75, 82] reported three hybrid inorganic–organic proton-conducting membranes based on a novel fluorinated titania labeled TiO_2F dispersed in Nafion prepared by solution casting method. Noto et al. [80] also reported the development of the hybrid inorganic–organic membranes, labeled as [Nafion/(ZrHf)x] and [Nafion/(SiHf)x], were prepared by a standard solvent-casting procedure [80].

3.9 Other Methods

Self-assembly structures of organic–inorganic nanocomposites are made of discrete organic and inorganic nanoscale components spontaneously organized with non-covalent interactions. These hybrid nanocomposites exhibit interesting characteristics because of constituent phases at nanoscale, high interfacial area, and synergetic properties. Tripathi et al. [4] reported that layer-by-layer self-assembly technique was remarkably adaptable approach to produce hybrid systems. Sulfonated PEEK-silicon dioxide-zirconium phosphate (ZrP) nanocomposites based PEMs can be prepared by electrochemical method in hydrophilic channels and voids of preformed and swelled membranes. In this technique, $ZrOCl_2$ was infiltered out followed by reaction with phosphoric acid or mesoporous ZrP/SiO_2 was blended after the incorporation of inorganic ZrP components. Polyimide (PI) and polybenzimidazole (PBI) based nanocomposites (PBI-phosphoric acid based composites) can be prepared by solution blending, while PBI-silicon dioxide nanocomposites can be prepared by solvent exchange method [4, 37, 42]. It was reported [4] that designing new PEMs can be done by modifications of aliphatic/aromatic polymers using suitable functionalization and introduction of inorganic NPs to obtain specific characteristics like: (i) mechanical strength and dimensional stability of PEM in hydrated state at intermediate temperatures; and (ii) water retention at higher temperature, to maintain the hydration and conductivity. Well-defined morphology and structure of PEMs with phase separation between hydrophobic as well as hydrophilic ionic domains along with stabilities for organic polymer chain containing sulfonic acid groups must be studied to assess their suitability [4]. Covalently cross-linked ionomer membranes via sulfinate alkylation, ionically cross-linked acid–base blend membranes materials as PEM were also reported [6]. An attempt has been made to develop a new polyethylene oxide (PEO) (PEO + $KHCO_3$) based solid PEM, by isothermal immersion technique. Using this conducting PEM, FC stack was fabricated with the configuration anode/polymer electrolyte/cathode [38]. Hybrid organic/inorganic reverse osmosis (RO) membranes, composed of aromatic polyamide thin films underneath titanium dioxide (TiO_2) nanosized particles, have been fabricated by a self-assembly process, aiming at the breakthrough of bio-fouling problems [46].

Consequently, the important problems in developing optimized organic–inorganic nanocomposite based PEMs are: (i) to identify the appropriate inorganic filler and dispersing conditions for selected polymer matrix; (ii) to optimize the concentration of filler best composite PEMs; (iii) to identify the synthesis and casting conditions; (iv) to acquire the knowledge of interactions between the NP, the polymer matrix and/or solvent.

4 Summary

Organic–inorganic hybrid nanocomposites based PEMs can be prepared in different ways by blending inorganic precursor (monomer and oligomer) and organic linear/network polymer matrix. With a monomer precursor, both polymerization and cross-linking of organic or inorganic segments are necessary. Various techniques for fabrication of PEMs are discussed, which include direct polymerization, plasma method, phase inversion method, sol–gel method, direct copolymerization, ultrasonic coating technique, ultraviolet polymerization, phase inversion method and in situ reduction, decal transfer method, and catalyst-coated membrane method. However, blending, sol–gel and in situ polymerization techniques are important preparative methodologies.

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