# Chapter 11
# Methods for the Preparation of Organic–Inorganic Nanocomposite Polymer Electrolyte Membranes for Fuel Cells

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**Abstract** In the last decade, the organic–inorganic nanocomposite polymer electrolyte membranes (PEM) have gained high technical relevance in a wide range of fuel cells applications. The significance of nanocomposite membranes fabrication is particularly highlighted by the fact that one of the major challenges of this century is to provide well-performing and cost-effective membrane materials for fuel cells applications. Many efforts have been made in the development of advanced membranes with the aim to outperform the most commonly used polymer membranes. With the advances in nanomaterials and polymer chemistry, the innovative nanocomposite membranes with superior properties can be designed by various techniques including blending of nanoparticles in a polymer matrix, doping, or infiltration and precipitation of nanoparticles and precursors, self-assembly of nanoparticles, layer-by-layer fabrication method, and nonequilibrium impregnation

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reduction. This study presents a brief overview of these techniques and discusses the encountered challenges, the problems to be overcome, the major findings and guidance for future developments.

**Keywords** Nanocomposite · Synthesis · Membrane · Preparation · Fuel cell

# 1   Introduction

A significant amount of research and development is currently underway throughout the world to protect environment via development of green power technology such as fuel cells (FCs). A fuel cell is an electrochemical device that converts chemical energy into an electrical energy by using various types of fuels such as hydrogen, methanol, ethanol, methylene blue, glucose, natural gas, etc., through a reaction with an oxidant (mainly oxygen). There are five different types of FCs that are primarily classified based on the nature of the polymer electrolyte in the FC: (1) alkaline fuel cells (AFCs) (alkaline solution), (2) phosphoric acid fuel cells (PAFCs) (acidic solution), (3) solid proton exchange membrane fuel cells (PEMFCs) (polymer electrolyte), (4) molten carbonate fuel cells (MCFCs) (molten carbonate salt electrolyte), and (5) solid oxide fuel cells (SOFCs) (ceramic ion conducting electrolyte) [1]. Among them, PEMFC is the most promising one since it can be applied to small-scale products such as automotive, portable power generation, and stationary equipment [1, 2].

The key component of the PEMFCs is the polymer electrolyte membrane (PEM), which facilitates transport of protons from the anode to the cathode and prevents the passage of the electrons and fuel. Ideal membranes for the PEMFCs should have high proton conductivity and oxidative stability, low fuel permeability, reasonable mechanical stability, adequate water transport (diffusion and electro-osmotic) properties, and low cost of fabrication [1, 3]. The widely applied Nafion membranes possess high thermal and chemical stability as well as high ionic conductivity. However, a decrease in ionic conductivity and relative humidity by increasing temperature limits the commercialization of FCs [1]. Hence, numerous research works have been conducted to synthesize high-performance PEMs.

Membrane for FC applications can be prepared from either neat polymer membranes or from nanocomposite membranes where other materials such as inorganic nanoparticles including silica, titania, tin phosphate, cerium phosphate, titanium phosphate, zirconia, sulfated zirconia, palladium, montmorillonite, zeolite, etc., are incorporated in a polymer matrix. Application of high-performance polymers, other than poly (perfluorosulfonic acid) (Nafion), for the synthesis of PEMs, have been widely investigated [1]. These polymers including polystyrenes, polyimides, polyphosphazenes, polybenzimidazoles, poly(arylene ether), polysulfones, and their derivatives are typically sulfonated to achieve conductivities higher than Nafion. High degree of sulfonation causes excessive membrane swelling and subsequently decreases mechanical stability and durability during operation.

In order to overcome this drawback, nanocomposite membranes are developed to provide a unique combination of polymers (high processability and electrical conductivity) and inorganic materials (high thermal and chemical stability, high mechanical strength, and low fuel permeability through the membrane) [1].

During the past few years, several advances on the fabrication of nanocomposite membranes have been made [4]. The general idea is to induce the thermal, electrical, mechanical properties of these nanomaterials to the base membrane. However, the incorporation of nanomaterials into a polymer, with the aim of fabricating a robust hybrid membrane, may not induce the desired functionality to the polymer and even deteriorate its properties. The major challenges to this are the severe aggregation of the nanomaterials in monomer containing solutions and the weak compatibility of encapsulated nanomaterials with polymers. The nonuniform dispersion of nanomaterials within the host polymer forms nonselective voids at the interface of the polymer and nanomaterials, reducing the permeation properties significantly. Furthermore, the desired thermal stability is not achieved, since the predicted reduction in chain mobility by the addition of nanomaterials is mitigated by the formation of these voids. This article aims to (i) present various techniques that have been used for fabrication of nanocomposite membranes for FC application, (ii) discuss the challenges encountered for each technique, (iii) provide guidelines for overcoming the challenges, and (iv) assess the future trend in the fabrication of high-performance nanocomposite membranes.

## 2   Methods for Preparation of Nanocomposite Polymer Electrolyte Membranes

Remarkable advancements have been recently performed in the preparation of organic–inorganic nanocomposite PEM materials, development of basic principles for the synthesis processes, and application of PEMs in various industries. The nanocomposite membranes can be synthesized by various techniques through physical blending (mixing) of inorganic nanoparticle or precursor (oligomer and monomer) in the three-dimensional (3D) network or linear polymer structure (Fig. 1) [5]. In the case of incorporating pre-synthesized nanoparticles into the polymer matrices, the main challenge is proper dispersion and distribution of nanoparticles in the membrane. Hence, strategies must be developed for surface functionalization of nanoparticles to improve their dispersion in both aqueous and organic solvents. In the case of using inorganic precursors and monomers, crosslinking and polymerization of inorganic or organic monomers is needed. Inspired by the mechanism of mineralization, NPs can be self-assembled via a hydrolysis and condensation reaction of inorganic precursors within the polymer matrix during membrane formation [6]. In this technique, the formation of membrane and nanoparticles could occur at the same time when the membrane is synthesized by the in situ polymerization reaction of two reactive monomers. Upon
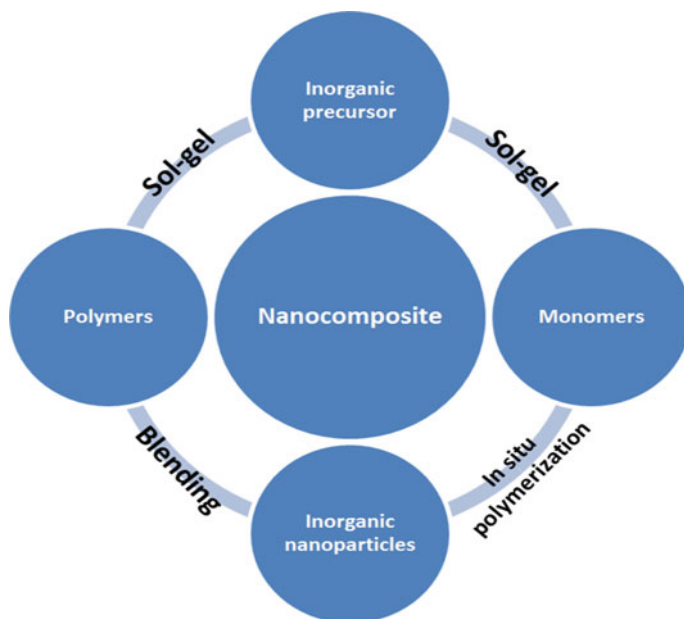
**Fig. 1** Representative of various synthesis routes of nanocomposite membranes

contact of solutions containing inorganic precursors and monomers, the monomers will react to form the polymer, and simultaneously, the nanoparticles will be synthesized and entrapped in the polymer matrix. The main challenge is the timing of the polymerization reaction and hydrolysis/condensation reaction to ensure the incorporation of nanoparticles inside the polymer matrix. The techniques used to prepare organic–inorganic membranes are explained in the following.

## 2.1 Blending of Nanoparticles in Polymer Matrix

Physical blending of nanoparticles into the polymer structure is the simplest way to synthesize nanocomposite PEMs. Physical blending can be accomplished by either melt mixing or dissolution in a solvent, where inorganic nanoparticles are uniformly dispersed in the molten or dissolved polymer. The melt mixing is more favorable owing its environmentally friendly nature and efficiency. One major challenge is the uniform dispersion of nanoparticles in the polymer since the nanoparticles tend to minimize their surface energy by aggregation. Tuning the surface chemistry of nanoparticles by modifying their surface with proper functional groups that have a better interaction with the polymer yields defect-free nanocomposite membranes. Surface treatment such as "*Whisker*" surface modification, irradiation, Grignard

reagents treatment, grafting, ion-exchange treatment, etc., have been widely used to change the surface chemistry of nanoparticles and break down its agglomerates in preparing hybrid inorganic–organic nanocomposite electrolyte membrane [7].

Physical blending at liquid state is extensively used to synthesize nanocomposite membranes due to its relatively simple synthesis route accomplished mainly through well-known phase inversion and solution casting methods [8, 9]. Such nanocomposite films have been widely applied for ultrafiltration [2, 3], pervaporation [10–12], gas separation [13, 14], and PEMs for fuel cell applications [6–9].

The blending of nanoparticles into the polymer matrix technique is typically conducted by phase inversion and hot press techniques, which are discussed in the following sections [15–17].

### 2.1.1  Phase Inversion Method for Preparation of PEMs

During the phase inversion process, a thermodynamically stable polymer solution is subjected to a liquid–liquid demixing during which the cast polymer film separates into a polymer-rich (membrane matrix) and a polymer lean phase (membrane pores). Polymeric membranes can be prepared by means of phase inversion from virtually all polymers that are soluble at a certain temperature in an appropriate solvent. Based on the way the polymer solution is solidified, phase separation technique can be distinguished into four techniques [18, 19]:

1. **Thermally induced phase separation (TIPS)**. In this method, a low molecular weight liquid that acts as solvent at high temperature and as nonsolvent at low temperature is required. A system of polymer and solvent is used which has a high critical solution temperature. The solution is cast at high temperature and cooling leads to demixing/precipitation [18]. Evaporation of the solvent often leads to the formation a skinned microfiltration membrane [20].
2. **Nonsolvent-induced phase separation (NIPS)**. This method is also called immersion precipitation or wet method. Most commercially available membranes are prepared by this technique. A polymer solution is cast on a suitable support and is subsequently immersed in a coagulation bath containing a nonsolvent (typically water). Demixing and precipitation occur due to the exchange of solvent and non-solvent, that is, the solvent and non-solvent must be miscible [18, 20, 21].
3. **Vapor-induced phase separation (VIPS)**. This technique is based on the fact that absorption of nonsolvent from vapor can also cause phase separation of a polymer solution. The polymer solution is exposed to a vapor atmosphere containing a nonsolvent (typically water), saturated with the same solvent. The high solvent concentration prevents the evaporation of solvent from the cast film. Diffusion of nonsolvent into the cast film causes demixing/precipitation [18, 20].

4. **Evaporation-induced phase separation (EIPS)**. The polymer in this method is dissolved in a volatile solvent and nonsolvent mixture. The evaporation of the solvent causes a higher concentration of nonsolvent in the casting solution that eventually results in precipitation of polymer and formation a skinned membrane [18, 20].

The TIPS and the NIPS process are most widely used to prepare all membrane geometries because of the compatibility with very short residence times between formation of the liquid polymer films and the onset of phase separation. The slower VIPS and EIPS processes are much less frequently used, but they can also be used in combination with the NIPS process [18].

A few studies have been conducted on the synthesis of PEMFC using phase inversion technique [10, 11]. The main challenge that limits the application of phase inversion membranes for proton exchanging in FCs is the high porosity of the synthesized membranes. Phase inversion process typically results in porous membranes that possess poor separation properties. However, dense structures can also be obtained by smart control of the kinetics of the solvent–nonsolvent demixing process [12]. Hence, in order to yield suitable phase inversion membranes for FC application, synthesis parameters must be adjusted to levels that slow down the precipitation of polymer. In addition, selection of slower phase inversion techniques (e.g., EIPS) is critical to obtain dense membranes.

Synthesis of mixed matrix phase inversion membranes is also more complicated than it sounds. Due to the good interaction of most nanoparticles with the nonsolvent, a considerable amount of them are leached out of the polymer matrix to the nonsolvent during phase separation process, thereby reducing the real loading of nanoparticles in the membrane. Hence, the surface of nanoparticles must be modified with proper functional groups that have good interaction with the polymer to reduce their tendency toward nonsolvent.

### 2.1.2   Solution Casting Method

The solution casting method is the simplest technique of synthesizing inorganic–organic hybrid PEMs. In this method, the following general stages are involved to fabricate reproducible and homogenous cast PEMs:

(a) Homogeneous dispersion of nanofillers in the solvent.
(b) Incorporation of a certain amount of polymer to the mixtures.
(c) Mixing the mixtures by ultrasonic equipment or stirrer.
(d) Casting the mixture uniformly on an appropriate substrate.
(e) Drying in an inert or in a vacuum environment.

Both phase separation and solution casting methods require a coating of a polymer film on a suitable substrate. The coating is conducted by film applicators, roll-coaters and spin-coaters. Applying manual film applicators, the homogenous polymer solutions are cast by adjusting the clearance gap at a specific thickness.

Casting speed can be adjusted by a motorized film applicator [12]. In roll-coating polymer solution is poured into a feed tank, which is placed under a roller, and then roll-coated on the surface of a suitable support (e.g., polyester fabric) [13]. In spin-coating, the polymer solution is poured drop by drop on an appropriate surface and housed in a spin coater, which is then rotated at a specified speed. The speed of the rotation and the concentration of the solution affect the membrane thickness. This technique is, however, only applicable for the low-to-medium viscosity of the polymer solution and would not be useful for a sol–gel like a mixture since the rotation of spin coater is not sufficient to distribute the mixture droplet radially on the substrate surface to make a thin membrane.

### 2.1.3   Hot Press

The hot press device for fabrication of PEMFC is shown in Fig. 2. A certain amount of polymer, nanofillers, and salt are poured into the mortar and blended for an hour. The sample is then pressed between two Mylar sheets and is placed into a



**Fig. 2** Representation of hot press device: **a** weighing cylinder, **b** heater, **c** base, and *T* temperature controller [22]
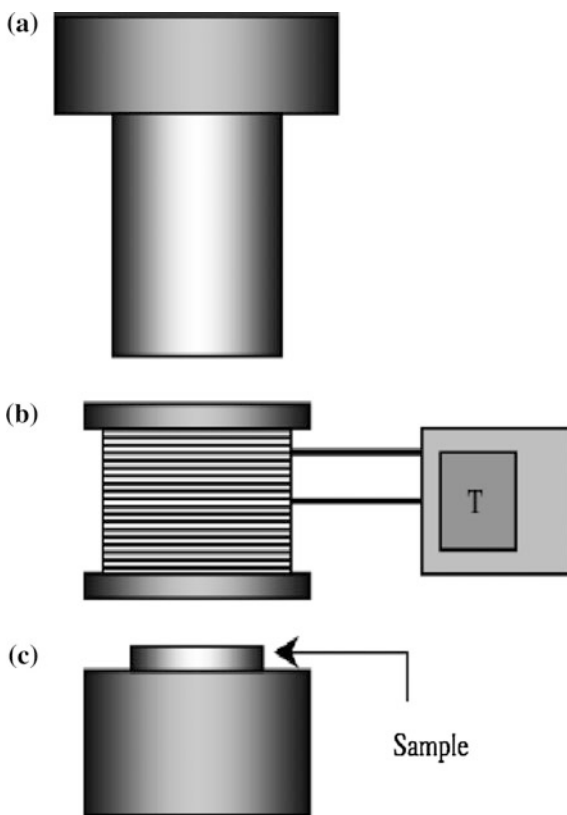
box. Afterward, the box is heated at temperatures higher than the melting point of the polymer. Subsequently, the mixture is pressed for a certain time at an adjustable pressure, which is set by weighing cylinder. After heating and pressing processes, the film is naturally cooled down to ambient temperature. Finally, the film is detached from the Mylar sheets and kept in a glove box. This method is promising since it can provide robust membranes with the repeatable fabrication process. However, there are a few records in literature for the synthesis of nanocomposite membranes by hot press method. The main challenges are the preparation of monodispersed mixtures of polymer and nanoparticles at such a high viscosity and unknown/noncontrollable behavior of the nanoparticles at high temperatures [22].

## 2.2 Doping or Infiltration and Precipitation of Nanoparticles and Precursors

Infiltration or doping method and precipitation of nanoparticles and precursors have generally been used to prepare polymer electrolyte membranes to change the separation performance by incorporating precursors or nanofillers. In this method, the preformed film is swelled in a suitable organic solvent to enhance the free volume before infiltration or doping of precursor or nanofiller. After infiltration process, the hybrid nanocomposites must be cured by radiation, thermal annealing or chemical grafting of precursor/nanoparticles, to achieve covalent bonding within the nanocomposite networks. This technique suffers extremely from the leaching of precursor/nanoparticles from the polymer network. However, the hybrid polymer membranes can be achieved by mixing single or mixed metal alkoxides with polymers or by infiltration of oxide gels with polymerized monomers. Impregnation of porous oxide gels with polymers through the in situ irradiation or thermal polymerization forms stable nanocomposite membranes [5, 23].

## 2.3 Self-assembly of Nanoparticles

The sol–gel technique for the synthesis of hybrid materials has been widely investigated due to its environmental containment and low-temperature process. In this method, the functional groups of polymer matrix enhance bonding of two phases, followed by a sol–gel reaction, and form a ceramic like phase.

It is vital to gain fundamental sciences of the physical and chemical properties of the nanocomposites synthesized by sol–gel technique. Numerous efforts have been recently accomplished on sol–gel process to understand the chemistry and mechanism of sol–gel reaction. The "sol" in general is a dispersion of colloidal particles in a liquid. The "gel" can be categorized into four groups:

(i)   The polymer matrix shaped by physical aggregation;
(ii)  The covalent disordered polymer matrix;
(iii) The disordered buildings of organic and inorganic materials; and
(iv)  The well-ordered lamellar structures of nanoparticles/precursor with poly-
      mers, e.g., organopolysilsesquioxanes.

The well-known chemistry of the sol–gel reactions contain two serial phases:
(I) the hydrolysis of single or mixed metal alkoxides to form hydroxyl functional
groups, (II) the polycondensation of the hydroxyl functional groups to produce a
3D structure (Fig. 3).

A typical sol–gel reactions commonly initiates in an organic solvent with low
molecular weight in the presence of metal alkoxide precursors $M(OR)_n$, where M is
the element in the structure which can be Zr, Al, Ti, B, Si, etc., and R can be water
or an alkyl group. When the hydrolysis and polycondensation reactions are
accomplished, some undesirable byproducts such as water or alcohol are produced
that must be removed, otherwise cause shrinkage during the formation of the
nanocomposites [5].

The hydrolysis and polycondensation reactions are classified as "nucleophilic
substitution" methods having three stages: (1) nucleophilic incorporation,
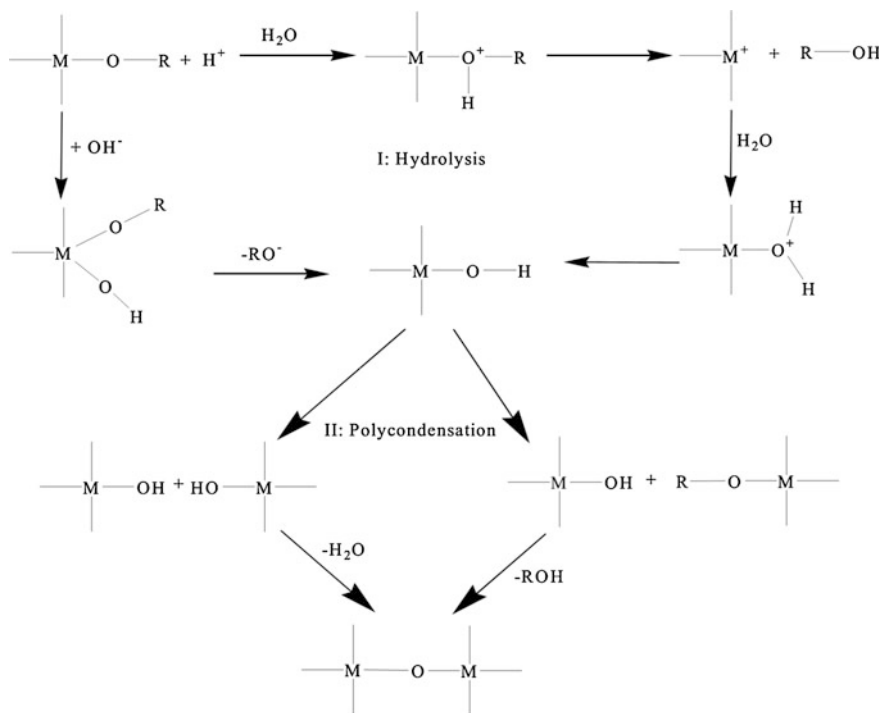(2) transferring proton in the transition modes, and (3) exclusion of the protonated



Fig. 3  Schematic representation of the sol–gel mechanism for metal alkoxide [24]

components. The hydrolysis and polycondensation reactions can be accomplished without the addition of a catalyst particularly for non-silicate-based metal alkoxides, whereas for silicon metal alkoxides base or acidic catalysts are needed. When a catalyst is used, the morphology and structure changes severely which is related to the nature of the catalyst [5].

Several parameters affect the kinetics and mechanism of the hydrolysis and the polycondensation reactions such as the solvent, ratio of silane/water, temperature, and the catalyst nature. The preparation approaches used in the sol–gel method to synthesize nanosilica based nanocomposite membranes take account of the in situ establishment of a nanoparticle/precursor in a polymer, and the simultaneous creation of $MO_2$ nanoparticles and polymer, results in the new generation of membranes with interpenetrating networks (IPNs). These nanocomposite membranes have attracted great attentions in different applications that are not well served by conventional membranes. So far, the commercial use of sol–gel based nanocomposite membranes is not practiced yet, but there is a high potential for novel scientific advancement.

## 2.4   Non-hydrolytic Sol–Gel (NHSG) Method

The non-hydrolytic sol–gel (NHSG) method is primarily used to fabricate the organic–inorganic nanocomposite PEMFC [25]. This method provides a water-free way to synthesize nanocomposite membranes by the interaction of an oxygen donor (e.g., ether, alkoxide, alcohol, etc.) with an appropriate metalloid or metal precursor (e.g., metal halide). Using a metal halide as a precursor, an alkyl halide, and inorganic oxide by-products are generated from this nonaqueous process. The electron transfer mechanism which controls the NHSG reactions is different from the hydrolytic sol–gel reactions. In the NHSG method, the reaction progresses through the coordination between the metal halide and the oxygen donor, and consequently, splitting the C–O bond, instead of metal–O bond splitting that takes place through the NHSG reactions. The key factor in the NHSG method is the change in the reactivity of metals, like transition metals and silicon.

## 2.5   Layer-by-Layer Fabrication Method

The layer-by-layer self-assembly of nanosized fillers with polymer forms one type of organic–inorganic nanocomposite membranes which are structured spontaneously with non-covalent interactions. These hybrid membranes show superior properties due to the high interfacial area, nanosized constituent phases, and synergetic interactions [5]. This technique is established according to the electrostatic association between deposited, oppositely charged species.

## 2.6   Nonequilibrium Impregnation Reduction

The nonequilibrium impregnation-reduction (NEIR) method is another encouraging technique to prepare multifunctional nanocomposite PEMs. In this technique, one side of the membrane is faced to an impregnation solution containing proper nanofillers followed by a reduction process. Finally, the organic–inorganic nanocomposite PEM is soaked in an acid solution and is washed with the deionized water. In this method, the loading of nanofillers in the polymer can be controlled by the impregnation time [26].

## 2.7   Surface Patterning Method

The surface patterning method is a facile and low-cost technique to prepare large-scale platforms with well-ordered patterns of a membrane by means of an elastomer mold at room temperature without hot pressing. The property at the interface of membrane and cathode is controlled by a surface patterned structure of the PEM, which affects the electrochemically active surface area (ECSA). This indicates the electrochemical properties develop the membrane electrode assembly performance [27].

Koh et al. [27] used surface patterning method to prepare patterned Nafion membranes by using polydimethylsiloxane (PDMS) mold as shown in Fig. 4. In this method, the patterned PDMS was used as a mold (not as a stamp) to make a pattern on Nafion membranes. A 0.5 mm thick patterned silicon master was used to fabricate the patterned PDMS mold. The prepared Nafion solution was dropped onto the patterned PDMS mold surfaces. For this purpose, the 5 wt% Nafion solution in a mixture of water and lower aliphatic alcohols was used. This low concentration is due to the small size of the pattern on the PDMS mold, and easy penetration of the solution into the micropatterns. Afterward, the Nafion solution can be casted on the surface of the patterned PDMS to create the same thickness of the Nafion on the patterned surface. Then, the sample should be dried overnight at
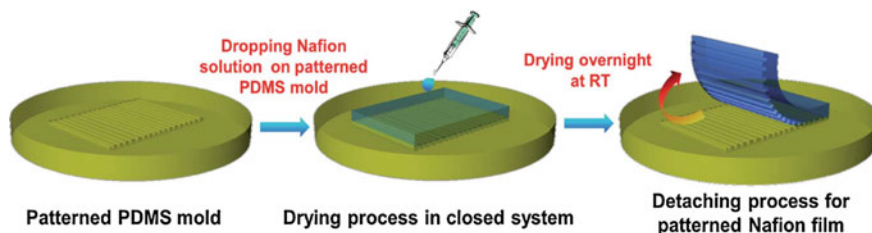


**Fig. 4**   A representation of the preparation process of membranes with surface patterned method [27]

room temperature in a closed system. Subsequently, the patterned membrane must be cautiously detached from the PDMS.

There are numerous advantages when the surface patterned method is used: (i) the thickness of the film can be easily controlled; (ii) it is possible to make a large surface patterned area; (iii) many patterned membranes can be fabricated in a short time, repeatedly; (iv) it is probable to fabricate a desired number of films by using only one silicon master, representing excellent processability and reproducibility without any defection in the mold and the membranes; (v) the surface patterned mold can be reused without any treatments or washing, which is very promising for industrial applications.

# 3 Future Directions and Conclusion

The full potential of the synthesis of organic–inorganic nanocomposite PEMs has yet to be assessed. With the developments in nanoscaled materials and polymer chemistry, the advanced nanocomposite membranes with promising performance can be prepared by different methods. Some of the important methods are incorporation of nanoparticles in polymer, doping or infiltration and precipitation of nanoparticles and precursors, self-assembly of nanoparticles, layer-by-layer fabrication method and nonequilibrium impregnation reduction. The main challenge in making hybrid nanocomposite membranes is to enable efficient dispersion and distribution of nanoparticles in the polymer matrix. For this purpose, effective strategies for surface functionalization of nanoparticles should be developed for all above-mentioned methods except for self assembly of nanoparticles. These strategies rely on the balance of intermolecular forces between surface functionalized nanoparticles including attractive forces (e.g., covalent and hydrogen bonding, electrostatic attraction between oppositely charged ligands, and dipole–dipole interactions) and repulsive forces (e.g., steric forces and electrostatic repulsion between ligands of similar charge). Hence, nanoparticles surface modification has become an active research area for the development of nanocomposite membranes. In the self-assembly technique, controlling of the hydrolysis and condensation reactions yields uniform distribution of small size nanoparticles in the polymer. However, the synthesized nanoparticles are not crystallized since the hydrolysis and condensation reactions are typically conducted at room temperature. Although the synthesized membranes by this method cannot be used in some particular membrane processes that require crystallized (e.g., antibacterial properties of $TiO_2$ nanoparticles in the nanofiltration and reverse osmosis membranes), however, the resulting IPNs membranes show a high capacity to develop high flux membranes. Furthermore, the surface patterning method is a simple and fast method to produce a large surface area with desirable thickness in commercial scale within a short time. Other techniques presented in this study are at the early stage of development and their main challenge is finding the pathway for larger scale fabrication and commercialization.

As far as the future directions for fabrication of nanocomposite membranes in fuel cell applications are concerned, the type and characteristics of the utilized nanoparticles are the most important parameters need to be considered. In fact, the incorporation of nanomaterials to a polymer matrix, with the aim of fabricating a robust hybrid membrane, may not induce the desired functionality to the polymer and even deteriorate its permeation properties. The most important factors to select an appropriate functional additive are (1) the hydrophilicity of the inorganic additive; (2) the acid site density on the inorganic nanoparticle surface; (3) the size or the specific surface area of the nanoparticles; and (4) the nanoparticles loading. Hence, a compelling path for future research is to properly utilize advanced nanomaterials, which can primarily enhance the water uptake, proton conductivity, and thermal stability.

Despite the extensive research conducted on nanocomposite membranes, several disadvantages such as removal of inorganic material from the polymer matrix after operation, inefficient dispersion and distribution of inorganic fillers throughout the membrane, and the miscibility with the catalyst layer are the main obstacles in the path of progress toward commercialization. Therefore, the main technical areas where future directions are predicted are as follows:

- Improving the water retention and proton conductivity of the synthesized nanocomposite membranes at higher temperatures.
- Improving the mechanical strength and dimensional stability of hybrid membranes in the hydrated state and at high and medium temperatures ($\sim$80–150 °C).
- Selecting and utilizing suitable inorganic nanofillers and efficient dispersion in the membrane.
- Developing methods for surface modification of nanofillers to obtain the ideal property of these materials.
- Improving the chemical interaction between organic and inorganic phase to enhance the compatibility of these two phases.
- Testing the long term stability of the synthesized nanocomposite membranes by conducting accelerated aging tests or long term exposure in a fuel cell application.

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