Chapter 4
Organic/Zeolites Nanocomposite Membranes

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Abstract There are different types of fuel cells, but Polymer Electrolyte Membrane (PEM) Fuel Cells are one of the most promising because they are low-temperature fuel cells. The solid polymer electrolyte has to present transport selectivity, besides the ion conductivity; thus in case of using in fuel cells, the membrane must let the hydrogen ions pass easily and block the passage of fuel (methanol or hydrogen) as

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well as oxidant molecules (oxygen) which have to be kept separated from each other. In addition to these properties, list other important properties that PEMs must show for high performance: low electronic conductivity, low water transport through diffusion and electro-osmosis, oxidative and hydrolytic stability, good mechanical stability in both dry and hydrated states, low cost, and capability for fabrication into membrane electrode assembly (MEA). This chapter is divided into seven sections. The first section presents some statistical data of publications concerning fuel cell, PEM fuel cells (PEMFC) and PEMFC with zeolites. The second section exhibits some concepts about zeolites types, structure, properties and industrials applications. The third section presents the role of the zeolite properties on the performance of the PEMFC. The fourth section describes the main technique used for producing zeolite/polymer nanocomposite membrane for PEMFCs. The two following sections outline the state of the art of using the zeolite for PEMFC applications, being the fifth and sixth sections dedicated to the synthetic and natural polymers, respectively.

Keywords Fuel cells · Zeolites · Nanocomposites · Polymorphs · Nanostructures

Abbreviations

APTS	3-Aminopropyltrimethoxysilane
DMFC	Direct methanol fuel cells
IZA-SC	International Zeolite Association Structure Commission
MEA	Membrane electrode assembly
MPD	Maximum power density
OCV	Open circuit voltage
PEEK	Poly(ether ether ketone) or nafion
PEM	Polymer electrolyte membrane
PEMFC	Polymer electrolyte membrane fuel cells
PES	Polyethersulfone
PFSA	Perfluorosulfonic acid
PTCS	Phenyltrichrolosilane
PTFE	Polytetrafluoroethylene
SPAES	Poly(arylene ether sulfone)
S-PEKES	Sulfonated poly(ether ketone ether sulfone)
SPK-ZrP	Sulfonated poly(ether ketone)-zeolite-zirconium hydrogen phosphate
SSM	Stainless steel mesh

1 Introduction

The number of academic papers about fuel cells has increased significantly in recent years. Figure 1 shows the number of scientific articles resulting from searches conducted on the Scopus® that is the most outstanding abstract and citation database of peer-reviewed literature. The search field chosen to obtain the data was article title, abstract, and keywords. We also restricted the search to the scientific journals and conference proceedings in the English language between 1996 and 2015, i.e., during the last 20 years. Moreover, we improved our search by using "*" as a wildcard to find plural and inflected forms of words; then the first search was Fuel Cell* which could be "fuel cell" or "fuel cells." In the last 20 years, the number of papers jumped from 712 in 1996 to 7810 in 2015, i.e., an increasing of more than ten times (Fig. 1). The total number of papers was 85607. By refining the search, it was included another term to the search field that was "Fuel Cell* and PEM*". The term PEM refers to the Polymer Electrolyte Membrane, and the "*" was used to increase to find the plural word (PEMs) or even inflected words like PEMFC (Polymer Electrolyte Membrane Fuel Cell). This search presented the same tendency, and the numbers jumped from 19 in 1996 to 1590 in 2015, i.e., an increasing of more than eighty times. On the other hand, the total number of papers in this refining search was 17,871; that is about 21% of the whole papers about Fuel Cells.

The inset Figure shows the last search that was "Fuel Cell* and PEM* and Zeolite*". The number of papers was null between 1996 and 2000; the first paper was just found in 2001. Moreover, there was one record with this search in 2011 that was nine papers. It is important to mention that the USA, China, and Japan, together, have about half of the papers for the first (Fuel Cell) and second search (Fuel Cell and PEM). On the other hand, Italy and South Korea got the first position for the third search when the term zeolite was added. Finally, USA and China got the second and third place, respectively.

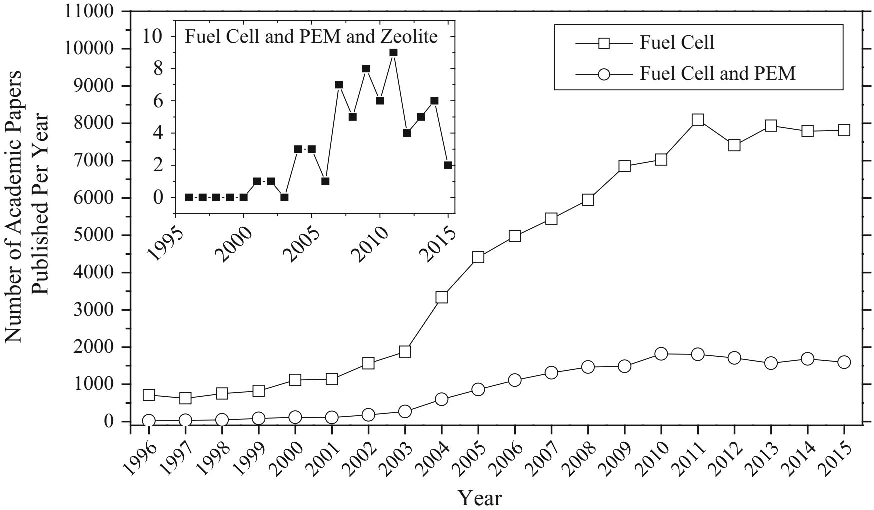


Fig. 1 Number of academic papers published per year according to Scopus database

It is known that fuel cell (PEMFC) works well when hydrogen is used as fuel, producing only electricity and water. However, as it has been presented earlier, it is difficult to store hydrogen, be it as compressed gas, cryogenic liquid, metal hydride, or carbon nanotubes [1]. The construction of a cell that directly uses methanol as organic fuel, instead of previously converting it to hydrogen through industrial reforming, is a very promising alternative compared to the trivial solution. Methanol oxidation potential ($E^{\circ} = 1.21$ V) is comparable to hydrogen potential ($E^{\circ} = 1.23$ V) and methanol volume energy density is 50% higher [2], which consists as a great incentive for researching the so-called DMFCs (Direct Methanol Fuel Cells).

The matrix of PEM membranes is usually composed of solid polymer, known as Nafion, which is an efficient insulating for free electrons, a good proton conductor (1×10^{-1} S cm^{-1}, saturated in water, room temperature) [3], and adaptable and resistant to most chemical products. However, Nafion loses its proton conducting properties when submitted to temperatures over 100 °C, which is the temperature regime that provides the best cathode kinetics. Another significant disadvantage to be overcome is that Nafion membranes used in these DMFCs allow methanol crossover from the anode to cathode. This crossover results in two main effects: first, methanol chemical energy is reduced when it percolates the membrane, drastically reducing its efficiency when used as fuel. Second, the two simultaneous cathode electrochemical reactions directly compete for cathode catalytic sites, reducing the global efficiency of the cell. Currently, methanol crossover limits feed concentration from 0.5 to 1.0 mol L^{-1} of methanol. By increasing methanol feed concentration, it would be possible to enhance methanol oxidation kinetics [4]. In such context, there is a quest for high performance and low-cost polymeric materials that enable high-ionic conductivity and low-methanol crossover.

There has been a significant contribution of research in the quest for incorporating inorganic materials to the polymeric membrane to overcome such difficulties. This organic/inorganic composite material must have the double function of blocking most of the methanol crossover and keeping high-proton conductivity [5]. Some inorganic materials have already been combined with conductive polymers, such as calcium phosphate [6], montmorillonite [7, 8], zeolites [9] and TiO_2 nanoparticles [10], in order to make use of their particular properties.

Zeolites, with their structural properties, shape selectivity and framework composition, are attractive inorganic fillers for DMFC membranes. Such inorganic microporous materials may be incorporated into the polymer matrices producing organic/inorganic composite membranes with the desired properties. Polymer-zeolite membranes have shown good performance in reverse osmosis processes and PEMs due to the synergy of the system [11]. Zeolite has evaluated as filler for polymers electrolyte membrane fuel cell to reduce the methanol permeability and enhance the thermal stability.

2 Basic Concepts About Zeolites

The term “zeolite” was originally used to designate a family of natural minerals which had ion exchange properties and reversible water desorption. This last property originated the word zeolite, which is derived from the Greek words: *zeo* = “to boil” and *lithos* = “stone” [12].

Zeolites are crystalline aluminosilicates with well-defined structures formed by the combination of three-dimensional tetrahedral TO_4 (SiO_4 or AlO_4^-), linked by oxygen atoms to form subunits and vast networks of identical blocks. Aluminum or silicon atoms (T-atoms) occupy the center of the tetrahedron, and the oxygen atoms occupy the vértices [12, 13]. Zeolites are microporous materials that typically present a high specific surface area (>350 m^2/g), variable diameter of micropores (2 and 12 Å), high-thermal stability (200 and 1000 °C) and high-chemical stability [12, 14].

The tetrahedrons may be connected to form a structure containing regular and uniform channels and cavities, with dimensions of the order of a few angstroms, which allow the passage of a particular size and shape molecules. This characteristic has given rise to the name “molecular sieves,” which applies to zeolites and other similar structure materials like pillared clays and carbon polymers. More recently, the name zeolite was limited to only aluminosilicates, using the name Molecular Sieves when there are other structural atoms.

Zeolites can be natural, found directly in nature, or synthesized in the laboratory or industrially. Natural zeolites were initially considered as impurities of volcanic or basaltic rocks, limiting their commercial use. Only later, starting at 50s was discovered large sedimentary deposits, such as those located in the Western of the United States, which allowed their exploitation and marketing [15].

There are about 40 naturally occurring zeolites, which formed through slow hydrothermal reactions of volcanic lava deposited over thousands of years, under the influence of high temperatures in the presence of water or saline and alkaline solutions. The first attempts to obtain synthetic zeolites in laboratory imitate the natural conditions (high temperature and pressure and an extended period of synthesis). Mild conditions and shorter synthesis times were only obtained after using reagents that were more reactive. The synthetic zeolites obtained in the laboratory have several advantages over the natural, such as high-purity and well-defined chemical composition, because their composition did not vary according to the deposit of origin that had been extracted.

As the aluminum oxidation number is +3 and it is coordinated by four oxygen atoms, the tetrahedral $(AlO_4)^-$ induce the formation of negative charges in the zeolite structure. This negative charge is counterbalanced by a cation, called compensation cation, which is located in the zeolite cavities and channels without belonging to the crystalline structure [12].

In natural zeolites, the compensation cations can be sodium, potassium, calcium, magnesium, or barium. In synthetic zeolites, these can be Na^+, K^+, H^+, NH_4^+, La^{+3}, and several organic cations used as structure-directing agents from the synthesis of zeolite or ion exchange processes. It can be performed an isomorphic substitution of Si and Al by other atoms such as Ge, P, Ga, and B. In addition to the cations, water molecules can also be contained within the channels and cavities of the zeolites, giving properties of ion exchange and reversible dehydration without disruption of the framework.

The structural formula of a zeolite can be written as (Eq. 1) [13]:

$$M_{x/n}\left[(\mathrm{AlO_2})_x(\mathrm{SiO_2})_y\right]\cdot w\mathrm{H_2O} \tag{1}$$

where M is the compensation cation with valence n, w is the number of water molecules, and the ratio y/x usually has values of 1–5 depending on the structure. The sum $(x + y)$ is the total number of tetrahedra per unit cell.

According to the Atlas of Zeolite Framework Types (6th Edition, 2007), 176 distinct types of zeolite framework have been approved by Commission of the International Zeolite Association (IZA-SC). To the present day, 231 structures have been approved by IZA-SC [16]. Such structures can be visualized at the database (http://www.iza-structure.org/databases/) of zeolite that provides structural information on all of the zeolite framework types that have been approved by the Structure Commission of the International Zeolite Association (IZA-SC).

3 Polymer-Zeolite Composite Membranes: The Role of the Zeolite

The use of zeolites as an inorganic component in DMFC composite membranes reflects some important aspects that must be observed during the preparation of membrane [17–19]. Hereafter, a brief discussion on the parameters related to zeolites that directly influence the polymer-zeolite performance will be presented.

3.1 Influence of Si/Al Ratio

Zeolites are aluminum silicates on which Si/Al molar ratio intensely modifies the microporous structure properties. Each structural aluminum atom generates a negative charge on the solid structure that must be compensated by an exchangeable cation. Thus, the concentration of ion exchange sites is proportional to the content of aluminum in the framework. These compensating charge cations in aqueous or ammoniacal medium suffer solvation, which is directly related to proton conductivity. Since the purpose is the maximization of this conductivity, the lower the Si/Al ratio, the higher the hydrophilic character of zeolite, which permits preferential adsorption of water or ammonia and, as a result, preferred proton transference.

It is important to consider that the distance among the exchange sites is directly related to the Si/Al ratio: more the aluminum content, the greater is the proximity among them in this framework and, therefore, to its compensating charge cations. The mobility provided by the compensating charge cations is responsible for the ionic conductivity exhibited by zeolites.

3.2 Proton Mobility in Zeolites

It has been observed in several works that solvated zeolites which contain NH_3 and H_2O molecules enabled faster proton transport and lesser activation energy compared to unsolvated zeolites. It is believed that protons are moving along the channels where solvated molecules are encapsulated within these channels, according to *Grotthuss* transport mechanism [20, 21]. In hydrated zeolites, the proton moves from oxonium ion to the neighboring H_2O molecule that is present in the zeolite channel. This process occurs through tunneling with H_2O molecule reorientation to accommodate proton movement. *Grotthuss* proton transport mechanism is the principal mechanism observed in PFSA (perfluorosulfonic acid) and liquid electrolytes.

Simon et al. [22], in their study on the construction of zeolite-based sensors, observed through the use of impedance measurements that the presence of NH_3 in the pores influences the proton mobility through H-Beta zeolite channels, which was adequately observed by conductivity measurements. However, by using the Na-β zeolite, it was found that the conductivity is not affected by the presence of NH_3. The authors concluded that NH_3 predominantly influences the mobility of Brønsted protons. β-zeolite (or BEA structure), used in this study, is formed by the intergrowth of two polymorphs (A and B) closely related to each other. Polymorphs consist of a three-way system of channels delimited by 12-membered rings which are interconnected, forming channels. There is a high incidence of stacking faults in this zeolite, due to successive interconnection on the plane [001] creating an intersection of two systems of linear channels, according to Fig. 2.

Research on NH_4-chabazite and NH_4-clinoptilolite zeolites demonstrates that proton transport occurred via NH_4^+ cations with conducting properties present in ammoniated zeolites. Krever et al. [23] proposed the *vehicle transport mechanism*, where the proton is bonded to the “vehicle” solvate, i.e., H_2O or NH_3, generating H_3O^+ or NH_4^+ species carriers. “Uncharged” vehicles move in the opposite direction, and the conduction of the proton is determined by the diffusion rate of the vehicle solvate. For clarity, Fig. 3 shows the representation of the CHA structure which presents selectivity shape and large diameter of micropores ($0.6 \text{ nm} < d_p < 0.8 \text{ nm}$) and its framework composition is $[Ca^{2+}{}_6(H_2O)_{40}][Al_{12}Si_{24}O_{72}]$ (CHA structure) [16]. These characteristics allow adsorption of molecules with an average kinetic diameter and also provide increased mobility of proton due to the structural flexibility of the framework.

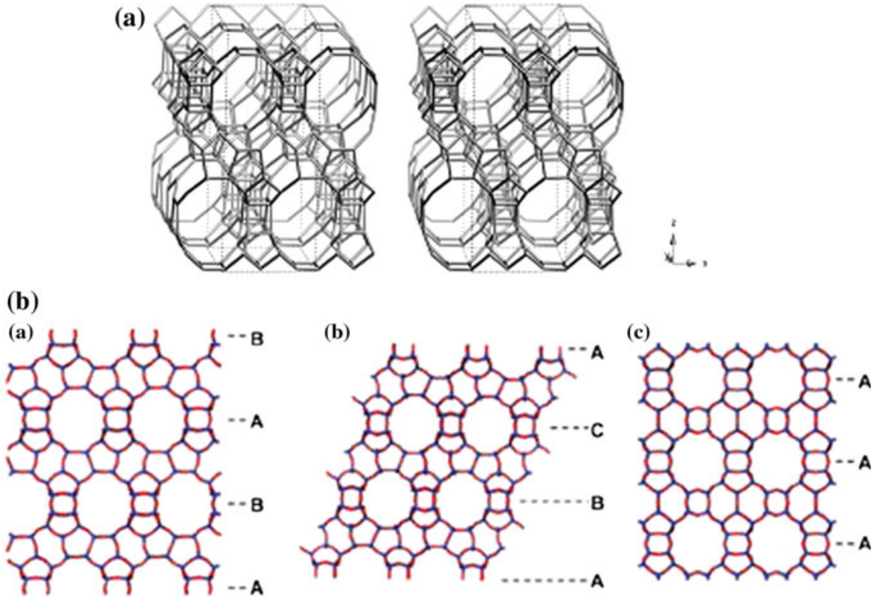
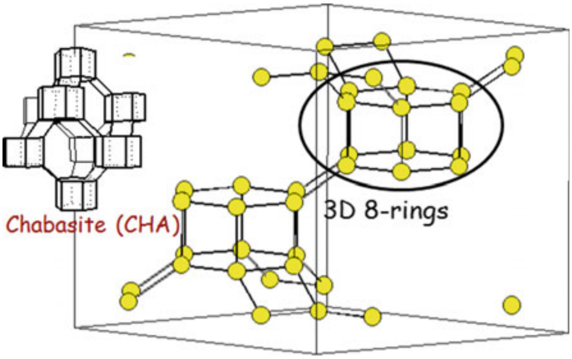


Fig. 2 **a** Beta zeolite structure. **b** Polymorphs *A*, *B* and *C*

Fig. 3 Scheme for CHA structure



Franke and Simon reported that the proton transport in solvated H-ZSM-5 zeolite (Si/Al $\leq$ 40) might present both kinds of mechanisms [24]: *Grotthuss* type and vehicle transport. *Grotthuss transport mechanism* is predominant in temperatures under 120 °C, whereas *vehicle transport mechanism* occurs at higher temperatures.

Experiments and calculations based on theoretical models demonstrate that the activation energy range for conducting ions in zeolites is between 40 and 130 kJ mol^{-1}, which is lower than the deprotonation energy (1300 kJ mol^{-1}). The data suggest that the proton transport in zeolites in mild temperatures follow

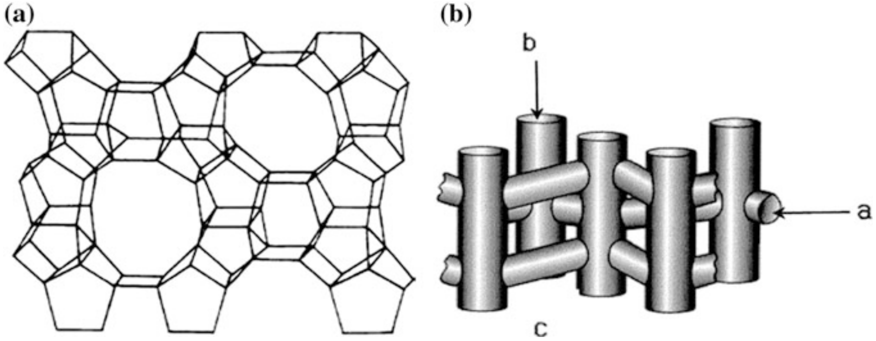


Fig. 4 Scheme for MFI structure (**a**) and interconnected channel system (**b**)

different mechanisms that are related to the zeolite framework composition and the metal cation present in the cavities [25].

Franke and Simon have studied the proton mobility in H-ZSM-5 zeolite and found that the proton movement in zeolites with adsorbed water and ammonia vapor showed proton movement activation energy dependent on the temperature [26]. The H-ZSM-5 zeolite shows medium-sized micropore diameter ($0.5 \text{ nm} < d_p < 0.6 \text{ nm}$), as shown in Fig. 4. ZSM-5 zeolite (MFI structure), whose composition is $Ca_2\ [(AlO_2)_4(SiO_2)_8]\cdot H_2O$ presents ion exchange capacity, a structure that allows adsorption of molecules with an average kinetic diameter and framework aluminum content that makes it moderately hydrophilic. H-ZSM-5 has Brønsted acidity similar to sulfuric acid due to the presence of H^+ protons in its framework.

Franke and Simon also found that zeolites in conditions of low temperature and high ammonia and water loads have their surface covered by a condensed phase of solvate molecules weakly bonded (called solvent molecule chains) among adjacent Brønsted sites, which permit *Grotthuss* proton type transport [26]. The presence of a significant amount of adsorbed solvated molecules may induce the formation of solvent complexes attached to acid protons of Brønsted sites. Thus, the proton transfer takes place with a relatively small activation energy (Fig. 5a). By gradually elevating the temperature, a growing desorption of the adsorbed weakly bonded molecules takes place, dismounting the complex solvate chains and opening larger space among them. As a consequence, the proton transport activation energy among groups becomes higher, resulting in more difficulties for the occurrence of the *Grotthuss*-type mechanism.

Franke and Simon observed that the continuous increasing of temperature leads to complete desorption of the weakly bonded molecules, and the proton transport may occur only by *vehicle* mechanism. NH_4^+ cations or H_3O^+ group enable proton transport that moves among neighboring Brønsted sites [26]. However, when comparing proton mobility, the movement of these vehicle species presents lower activation energy [27]. In mild to higher temperatures, proton mobility increases

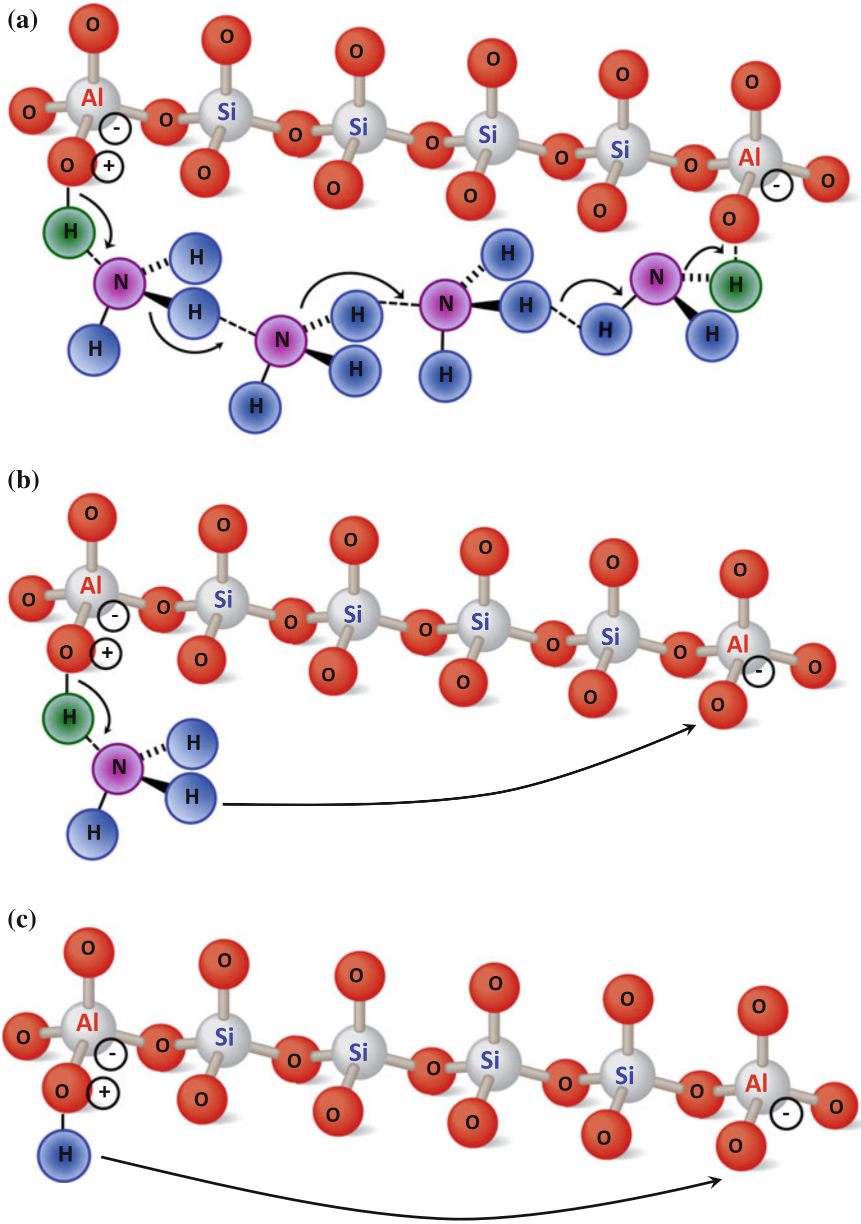


Fig. 5 **a** *Grotthuss* transport mechanism in low temperatures; **b** vehicle transport mechanism: NH_4^+ works as proton transport vehicle; **c** submitted to high temperatures, the elimination of adsorbed molecules presents the same observed conductivity for unsolvated zeolite

Fig. 6 Scheme for X and Y zeolites (FAU structure)

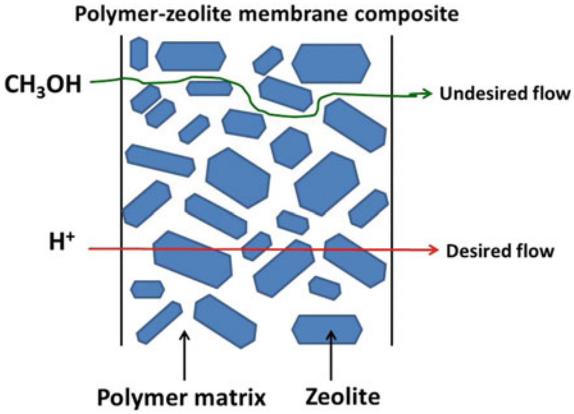


Fig. 7 Methanol and H^+ diffusion by using a polymer matrix containing zeolite

and, as a consequence, zeolite proton conductivity increases as well (Fig. 5b). The complete elimination of solvates in high temperatures leads to almost constant conductance and this conductance, as well as the activation energy, gets close to the values observed in the unsolvated zeolite (Fig. 5c) [27].

These differences found in proton mobility mechanisms may explain that typical zeolites, such as H-ZSM-5 (Fig. 4), HY (Fig. 6), and mordenite presented ionic conductivity no higher than 10^{-4} S cm^{-1}. However, some hydrated zeolites, such as Sn–Mordenite, present high-ionic conductivity closer to the one shown by PFSA polymer, around 0.1 S cm^{-1} [28]. Now Fig. 7 illustrates the FAU structure, with large-sized micropore diameter (0.6 nm $< d_p <$ 0.8 nm), suitable for shape selectivity of larger molecules. Depending on the Si/Al ratio, i.e., on the composition of its framework, the zeolite will be named Y or X. The zeolite with FAU structure and Si/Al ratio in the range from 1.0 to 1.5 is called X. The zeolite with Si/Al ratio above 1.5 is named Y, and its composition is $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\cdot H_2O$. Such characteristics enable them to adsorb molecules which have average kinetic diameter and hydrophilic ion exchange.

3.3 Internal and External Surface Area

The number of available active sites in a zeolite is proportional to its high microporous surface area. The availability and accessibility of the active sites of the solid (functionalized or nonfunctionalized) directly influence proton transport. It must be taken into account the fact that the reduction in the size of the zeolite crystallites leads to the increase of the external surface area. This contributes to the reduction of the molecules or ions diffusion path and as a consequence, there is an increase of the accessibility to solvated sites.

It has already been shown that large zeolite crystallites form composite membranes with interconnecting defects between the zeolite and the polymer due to the small external contact surface area [11]. Such defects may transform the membrane into a barrier for proton conduction and an open door for methanol diffusion. It would be possible to produce membranes with good zeolite-polymer compatibility making use of the size of functionalized zeolite nanocrystals, such as the sulfonic acid [9], promoting good contact due to the high external surface area.

3.4 Configurational Diffusion

It is known that microporous materials have high resistance to chemical species diffusion. Since micropores are approximately of the same size of the kinetic diameter of the molecules, the diffusion coefficient will be between 10^{-14} and 10^{-5} cm^2 s^{-1}, i.e., the diffusion will depend strongly on this parameter [27]. Due to its small size, the proton will not suffer much effect of the constraint of the mean free path internally available in the zeolites. However, partial blocking of the pores may constraint proton conductivity in functionalized surfaces.

3.5 Crystallite Size [17, 18]

The crystallite size of the zeolite used in the construction of the membrane is critical to DMFC performance. Crystallite size and surface area are deeply connected. As said before, large crystallites do not enable good connectivity to polymer matrix [29–33]. A good polymer-zeolite membrane depends on the incorporation technique of the zeolite nanocrystallites to the composite membrane because the agglomeration of these nanocrystallites, when removed from the solution, must be avoided so that good dispersion must be kept during simultaneous synthesis of the polymer [18, 34].

3.6 Functionalization of Zeolite Surface

A different way to partially solve the problems related to the proton conductivity is the surface functionalization with organosilanes or by modifying functional groups attached to polymer backbone chain. Functional groups attached to zeolite surface, such as sulfonic acid, considerably enhance proton conductivity. The handling of the inorganic surface by functionalization or incorporation of heteropolyacids in the molecular sieve pores provides higher proton conductivity [18]. There is lots of space for innovation and development in this field of research.

3.7 Selectivity, Proton Conductivity, and Permeability

Hereafter, some important aspects for understanding DMFC membranes will be discussed. The selectivity of the organic/inorganic composite membrane (β, in S s cm^{-3}) is defined as a relation between proton conductivity (σ, in S cm^{-1}) and the membrane methanol permeability (P, in cm^{2} s^{-1}), that is, $\beta = \sigma/P$ [35, 36].

When developing a DMFC membrane, high selectivity is sought, resulting in high-proton conductivity and low permeability (Fig. 7). In the past, this objective was thought only by obtaining high-proton conductivity. However, while the current membrane of a standard Nafion fuel cell presents very high conductivity, its selectivity is compromised due to high-methanol permeability. If another membrane shows highest selectivity, albeit lowest conductivity, its conductance could be enhanced by making a thinner membrane.

Composites with zeolite particles in hydrophobic polymer have been under study to make it possible to discover membranes with higher selectivity. As it is shown in Fig. 8, membrane components were chosen in a way that protons are transported through the dispersing phase and polymer matrix. If the dispersed material is impermeable to methanol, protons will follow a more direct and shorter path compared to methanol [35].

Another important aspect that must be taken into consideration when preparing polymer-zeolite membranes is the choice of polymers to be employed. Initially, the polymer matrix used to develop these polymer-zeolite membranes was PTFE (polytetrafluoroethylene), inert and nonconductive [37]. Conductivity would be attributed solely to zeolite phase. PTFE-zeolite X or PTFE-zeolite Y composites presented better conductivity compared to similar PTFE-NaA, PTFE–Na–ZSM-5, and PTFE-Na-mordenite membranes. PTFE-LiY membrane reached conductivity of 2×10^{-3} S cm^{-1} (348 K), and PTFE-Na-mordenite was stable at 623 K. PFSA-zeolite membrane (PFSA: perfluorosulfonic acid) is one of the most studied zeolite composite membranes.

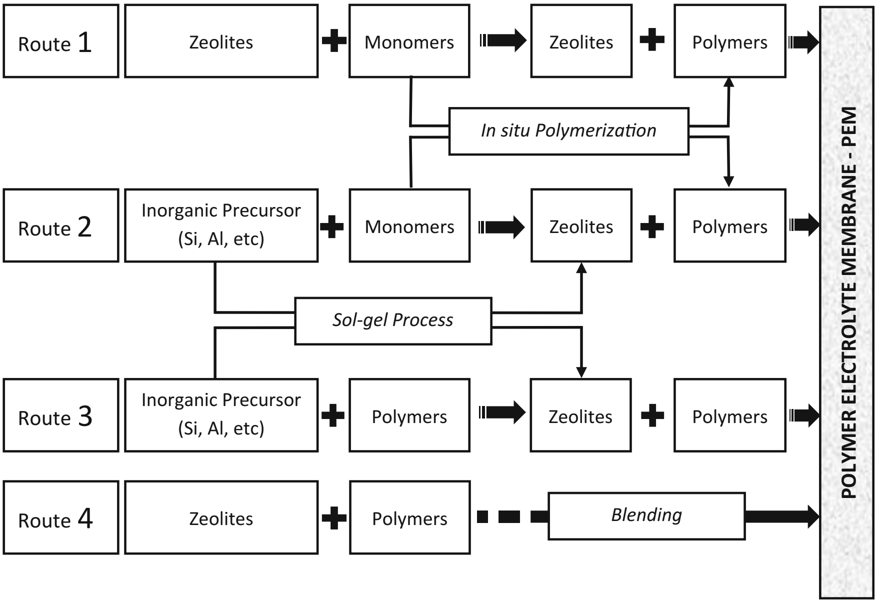


Fig. 8 Schematic routes for the preparation of polymers electrolyte membranes

4 Techniques for Producing Organic/Zeolite Nanocomposite Membranes

To better understand the different routes for producing organic/inorganic nanocomposite membranes, it is important to think about zeolite as being crystalline inorganic polymer that is formed by repeated tetrahedral units. In this sense, it is possible to combine at four raw materials for producing organic/zeolite nanocomposite membranes:

(1) organic monomers;
(2) "inorganic monomers" (AlO_4 and SiO_4 tetrahedra) of zeolite structure. In truth, they are inorganic precursors that are alkoxide precursors $M(OR)_n$, where M is Si or Al in the zeolite structure and R is an alkyl group;
(3) organic polymers;
(4) inorganic polymers (zeolites).

All the above raw materials can be combined according to Fig. 8.

When the monomers are provided to the composite membrane preparation, it is imperative to conduct the polymerization during composite membrane formation. Thus, classical techniques like radical or addition polymerization are employed to yield the organic polymer, as well as, the sol–gel process for the inorganic polymer (zeolite). The combination of those raw materials allows to design four routes according to Fig. 8.

The Route 4 (Fig. 8) would be the simplest route to produce the organic–inorganic hybrid PEM using both organic and inorganic polymers. In this route, the zeolite can be dispersed into the organic polymer that was previously melted (melt blending) or was solubilized in an appropriate solvent (liquid-state blending). As both polymers are blended, this could also be called Blending Process. Needless to say that the melt blending is a more environmentally friendly process because no organic solvent is used. The interaction between zeolite and organic matrix polymer impact on the performance of nanocomposite membrane because the dispersion of zeolite may lead to undesirable agglomeration, then sometimes surface modification techniques are carried out to enhance the interaction between the organic and inorganic phases. Such surface modification may be irradiation grafting or functionalization of zeolite. Additionally, in another version, the zeolite is previously synthesized on a support surface and then polymer solution is casted on this support.

On the opposite side, the Route 2 would be the most complicated because both the raw materials are monomers (organic monomers and inorganic precursors monomers), such route will require the inorganic polymerization (sol–gel process) to yield the inorganic polymer (zeolite) and the classical polymerization for the organic polymer. That is why this route could not be found in the literature. There are also intermediates routes when just the organic polymer is formed during the PEM preparation (Route 1), or just the inorganic polymer (zeolite) is formed (Route 3).

However, there are also variations of Routes 3 and 4 which are called doping or infiltration technique. In this technique, the preformed membrane is swelled in a solvent to enlarge the pore before the doping or the infiltration of the zeolite nanoparticles or inorganic precursors. Then the composite is cured, and covalent bonds are carried out inside the polymer matrix. The curing process can be carried out by heat, radiation, or chemical grafting of the inorganic precursor. The leaching of the zeolite from the membrane is one of the challenges to be overcome.

Finally, layer-by-layer is one of the newest techniques to produce self-assembled hybrid membrane. The organic and inorganic components are organized in a nanoscale by electrostatic interactions. Every oppositely charged component is deposited alternately on each other.

The casting or recasting techniques are included in all routes. The casting consists in using solubilizing the organic polymer in an appropriated solvent and then the dispersion is cast in molds like Petri dish (in a lab version) before drying the solvent. On the other hand, the recasting technique starts with the commercial solution of the polymer; the solvent of this solution is evaporated to get a dry residue which is solubilized again in an appropriate solvent and concentration usually different from those of the commercial one.

5 Synthetic Polymers/Zeolite Nanocomposite Membranes for PEMFCs

The Route 2 has not been found in literature because once both monomers are used, synthesis become more difficult.

5.1 Route 1: Zeolite + Organic Monomers

Nur et al. synthesized zeolite ZSM-5 and compared two silylation processes of zeolite. One process was carried out by reaction of ZSM-5 with 3-mercaptopropyltrimethoxysilane, this sample was labeled as ZSM-5-SH [38]. This zeolite was followed by grafting polymerization of styrene and divinylbenzene, and afterward, the sulfonation reaction was performed by pouring the acetyl sulfate solution into the polystyrene-zeolite composite. The obtained zeolite was labeled as ZSM-5-SH-PS-SO_3H. The ZSM-5-SH was also oxidized with hydrogen peroxide to obtain propylsulfonic acid functionalized zeolite, which was labeled as ZSM-5-SH-SO_3H. The other silylation process was carried out by reaction of ZSM-5 with phenyltrichrolosilane (PTCS) and then was sulfonated with sulfuric acid, the zeolites were denominated ZSM-5-PTCS and ZSM-5-PTCS-SO_3H, respectively. It was observed that the higher the amount of sulfonic groups in the sample, the greater the sample hydrophilicity, and consequently, the higher the water uptake capacity and ion exchange. The water molecules may interact with the polymeric matrix by hydrophilic interaction with –SO_3H and the ZSM-5 zeolite may retain water molecules at the channels and cavities especially at high temperatures. The ZSM-5-SH-PS-SO_3H sample had the greatest amount of the functional group on the ZSM-5 surface (65 wt%), that is, a highest carrier (proton) concentration of sulfonic acid groups, consequently, this sample showed the highest proton conductivity, followed by ZSM-5-SH-SO_3H > ZSM-5-PTCS-SO_3H samples.

5.2 Route 3: Inorganic Precursor + Organic Polymer

Nafion/acid functionalized zeolite Beta (NAFB) nanocomposite membranes were prepared by Chen et al. using in situ hydrothermal crystallization technique. A precursor solution of organically functionalized zeolite beta was prepared, and the crystallization of the zeolite was conducted in situ in the swollen Nafion 115 membrane. According to Chen et al., the micrometer-sized particles usually have low-proton conductivity, but the performance can be improved by using nanometer-sized particles once those smaller particles are crucial to the compatibility between the inorganic filler and Nafion [39]. Moreover, the compatibility has a significant effect on the proton conductivity and methanol permeability of the membranes. Acid functionalized zeolite nanocrystals were produced to minimize the loss of proton conductivity and reduce the methanol permeability. Such nanocrystals presented aggregation during the membrane casting. To circumvent the problem, Chen et al. developed an in situ crystallization process to fabricate nanocomposite membranes [39]. Firstly, the Nafion membrane was impregnated in the precursor solution for the organically functionalized Beta synthesis, followed by the hydrothermal treatment of the impregnated membrane in the synthesis solution to grow organic functionalized Beta nanocrystals inside the Nafion membrane. The hydrophilic ionic clusters of the Nafion membrane could be considered one nanoreactor for the formation of the zeolite. Finally, concentrated sulfuric acid was used to remove the template in the zeolite pores and also sulfonate the organic functional groups. They prepared Nafion/acid functionalized zeolite Beta using the technique as mentioned above, and the zeolite loading was 5%. They compared the composite membrane with the commercial Nafion membrane, although the proton conductivity was similar, the composite membrane presented lower methanol permeability (40% reduction). The composite membrane was tested in a Direct Methanol Fuel Cells (DMFC) with two methanol concentrations (1 and 5 M). The composite membrane presented higher open-circuit voltage (OCV) and maximum power density than the commercial membrane; the differences were even bigger for the 5 M methanol.

5.3 Route 4: Zeolite + Organic Polymer

Han et al. prepared microfabricated zeolite proton conducting membrane and structured zeolite-PFSA composite membrane [19]. The first consists of an array of self-supported zeolite micromembranes fabricated on a silicon wafer. The second were built on stainless steel mesh (SSM) with 110 μm diameter holes and Nafion resin was casted on the zeolite-coated SSM. In both methods, they previously synthesized the zeolite on the support material (silicon wafer or SSM). The Nafion solution was casted just to the SSM systems and compared to the silicon wafer with zeolite. The zeolite in a general way acts as an electric insulating, and was used to retain water in the structured zeolite-PFSA composite membrane, improving membrane thermomechanical properties and enhanced PEMFC performance. The purpose of the second study by the same research group was to improve the properties of confined PFSA-zeolite structured composite membrane using bi-layered zeolites [40]. The zeolite served as a protective barrier against corrosion for the stainless support. Interactions between zeolite surface and PFSA polymer chain resulted in higher glass transition temperature and increased proton conductivity. Despite the better mechanical properties, composite membranes presented better performance than the Nafion membrane, an order of magnitude higher MPD (maximum power density) was obtained for hydrogen PEMFC and a substancial increase was observed for passive DMFC.

Han et al. studied supported and self-supporting ZSM-5 membranes (Si/Al = 25) [41]. The supported ZSM-5 membrane was synthesized by seeding as well as by secondary regrowth method on cellulose paper (the polymer). The self-supporting ZSM-5 membrane was prepared by microfabrication method that consists of an array of micromembranes on a silicon substrate. To evaluate the performance of the PEMFC, they previously coated the anode and cathode electrodes with the catalyst and Nafion solution was used to glue every of the membranes mentioned above, as a "membrane sandwich." Due to the contact between the electrode, catalyst and membrane layers in the assembly, the self-supporting H-ZSM-5 membrane showed the values: an open-circuit voltage (OCV) (0.77 V), supported H-ZSM-5 (0.90 V) and Nafion 117 (0.98).

Reference [42] evaluated the effect of the Si/Al ratio of H-ZSM-5 zeolite incorporated in various loadings (1, 3, and 5 wt%) into Nafion membranes. The researchers found that the lowest methanol permeability was obtained using composite membranes with 5 wt% of zeolite with Si/Al ratio 25. This result may be due the induration of a polymer layer around the aggregate zeolite particles. This membrane also showed a high power density and stable performance in time. The highest proton conductivity was obtained using 1 wt% of zeolites with Si/Al ratio 50.

Changkhamchom and Sirivat synthesized composite ZSM-5/sulfonated poly (ether ketone ether sulfone) (S-PEKES) membranes [43]. The ZSM-5 zeolites with different Si/Al ratios (23, 50, 80, and 180) were tested as the inorganic fillers at various volume percentages (2–10% v/v). They observed that the Si/Al ratio directly influence the increase of the sample hydrophilicity, which is inversely proportional to the proton conductivity. In other words, the more is the hydrophilic character of the membrane, the higher is the amount of water molecules retained and better is the protons transport capacity. All composite membranes showed lower methanol permeability than the pristine S-PEKES and Nafion 117 membranes. The methanol permeability decreases with the increasing of Si/Al ratio and with the amount of zeolite added to the membrane. As the methanol molecules are preferentially adsorbed and trapped within the zeolites, the trapped molecules induce the delay in the methanol diffusion, considerably decreasing methanol permeability.

Yu et al. used 1,3-propane sultone (5, 10, and 15%) to functionalize ZSM-5 zeolites and then incorporated them to the sulfonated poly(arylene ether sulfone) (SPAES) copolymers using the blending technique [44]. As reported by Nur et al. [38], the proton conductivity of the functionalized zeolite increases due to the high amount of sulfonic acid groups. However, the amount of zeolite was found to directly influence this parameter. The addition of 5 wt% of sulfonated zeolite resulted in the increase of proton conductivity up to 0.030 cm^{-1} (120 °C and 50% RH) compared to the pristine membrane (0.022 S cm^{-1}). This result was attributed to the dispersion of zeolite in the membrane and generation of the hydrophilic channel networks by the sulfonic acid groups, increasing the movement of protons and resulting in high conductivity proton. However, increasing the amount of sulfonated zeolite (10 or 15 wt%), sulfonated zeolite aggregated and acted as a barrier for proton conducting channels and networks, decreasing proton conductivity.

Sancho et al. studied four different materials, namely, NaA zeolite, mordenite, umbite, and ETS-10 [45, 46]. The materials were prepared by pressing (7 ton/5 min), to obtain pellets of 13 mm of diameter, using the polymer PVDF (10 wt%) as a binder, and not as material to composite membrane production. Nafion membrane showed the best results of conductivity up to 100 °C, and after, progressively declined due to degradation process. However, zeolite-polymer composites were shown to be more stable at high temperature. NaA zeolite increased the proton conductivity up to 120 °C and ETS-10 up to 150 °C. The ionic conductivity of the zeolites increases with temperature mainly due to high ion mobility and the large quantity of adsorbed water inside the pores. ETS-10 pellet presented values in the same order of magnitude as Nafion membrane (40 °C/70 RH). ETS-10 (1.97 mS s cm^{-3}) also showed the best selectivity, with the same order of magnitude as Nafion membrane (5.84 mS s cm^{-3}) at 40 °C.

In another work, the functionalized zeolite was previously synthesized and mixed with the Nafion solution, then was cast, and the solvent was evaporated [18]. Zeolite loading was evaluated in the 2.5–20 wt% range, demonstrating that zeolite nanocrystals were homogenously dispersed within the polymer matrix for 2.5 and 5.0 wt%. But the dispersion was heterogeneous for 10, and 20 wt% zeolite membrane was overloaded and brittle. The selectivity decreased when the temperature increased for all the membranes. The selectivity was evaluated ex situ and in situ (in a Membrane Electrode Assemblies). The results ex situ showed that incorporation of 10 wt% of zeolite impaired the selectivity, although the 5 wt% showed better results than 10 wt% of zeolite. Moreover, similar results were verified for in situ configuration when 2.5 and 5.0 wt% were tested, and the first presented best results.

Li et al. prepared Nafion/Zeolite A composite membranes. Zeolite NaA has low Si/Al ratio which offers a hydrophilic character and preferential adsorption of water; thus, proton transfer can be improved [17]. Moreover, zeolite NaA could exclude methanol from the zeolite channels which could provide low-methanol permeability. The poor interfacial compatibility between the organic polymer matrix and zeolite crystals promotes pinholes between them, which favor the methanol transport; therefore, the functionalization of the zeolite surface can be carried out to overcome the poor compatibility between zeolite and the organic polymer. The organic polymeric chains were grafted onto the inorganic zeolite surface using 3-aminopropyltrimethoxysilane (APTS) as silane coupling agent. Functionalization could improve the interface compatibility between zeolite crystals and Nafion, resulting in a decrease of methanol permeability, which could be attributed to the inhibition of pinhole formation. On the other hand, a noticeable reduction in the proton conductivity of functionalized composite membrane has also been verified. The decrease was attributed to the alkaline nature of NH_2-groups of the APTS, a large molecule that is unable to get into the NaA porous; thus modifying only the external surface of the zeolite.

On the other hand, Tripathi et al. studied sulfonated poly (ether ether ketone) (SPK)-zeolite-zirconium hydrogen phosphate (ZrP) nanocomposite PEM prepared by in situ infiltration and precipitation [47]. The authors had already verified promising results with SPK-ZrP composite membranes. First, SPK membranes doped with surfactant (cetylpyridinium chloride) were prepared. The surfactant was used to form pores. Secondly, the surfactant was leached out with HCl solution, and fine zeolite particles were infiltrated in the swelled SPK membrane for developing SPK-zeolite composite, and finally ZrP was precipitated in the SPK-zeolite composite membrane. Although the thermal, mechanical strengths, oxidative and dimensional stabilities, these nanocomposite membranes offered no significant advantages over SPK or Nafion (N117) membrane for proton conductivity at 30 °C. However, SPK-zeolite-ZrP nanocomposite membranes showed improvement over SPK or N117 membrane at 70 °C due to their high selectivity index, which indicates that nanocomposite PEMs was a suitable candidate for DMFC applications at moderate temperatures (between 60 and 150 °C).

Micro and nano-sized NaX zeolites were prepared by Cui et al. using the sol–gel process. Then, the sodium ion was exchanged by ammonium to form the NH_4X zeolite [48]. According to the authors, the ammonium ions would establish a chemical equilibrium with protons and ammonia, which could prevent the methanol permeability and supply further protons and increase the ionic conductivity. Zeolite (5 and 10 wt%) and Nafion solution were blended, and the composite membranes were prepared by the recasting method. Concerning the zeolite loading, the membranes with 10 wt% loading of zeolite presented microcracking and segregation for both nano and micro-sized, but with 5 wt% loading the membranes showed uniform distribution. They also verified that the selectivity of NH_4X/Nafion micro-sized 5 wt% composite membrane was more than twice that of pristine Nafion. Moreover, DMFC cell tests at 60 °C showed that peak power density for this NH_4X/Nafion was threefold higher than the value for pristine Nafion membrane.

Kongkachuichay et al. incorporated two types of natural zeolite (Analcime and Faujasite) into Nafion membranes using the blending technique [49]. The water uptake, ion exchange capacity, and proton conductivity were higher for composite membranes than for Nafion membranes. Moreover, the authors also found that Analcime/Nafion nanocomposite membranes exhibited better properties than Faujasite. Based on this results, Intaraprasit and Kongkachuichay selected Analcime to study the effect of sulfonation on poly(ether ether ketone) (PEEK or Nafion) [50]. First, sulfonation of PEEK was carried out using concentrated sulfuric acid and different zeolite content was evaluated in nanocomposite membranes prepared by blending technique. The increasing amount of added Analcime decreased the ion exchange capacity and water uptake of the membranes. The proton conductivity was enhanced up to 10 wt% of Anacilme, but the agglomeration of zeolite particles led a decrease above this value, being even lower than that of the SPEEK. The improvement of conductivity was attributed to the hydrophilicity and protons inside the connected channels of Analcime.

Devrim and Albostan evaluated the preparation of Nafion/Beta zeolite composite membranes with different zeolite loading [51]. The authors also used the recasting method and the maximum zeolite loading was 12.5% because the membrane cracked above this value. The proton conductivity increased as the temperature increased. Moreover, the growth of zeolite loading with the decrease of proton conductivity may be attributed to barrier properties of nonhomogenously dispersed zeolite particles. The Nafion/zeolite membrane with 10 wt% zeolite loading showed the best performance for single cell PEMFC tests, although all the Nafion/zeolite membrane performed better than Nafion membrane.

Mecheri et al. compared the recasting method to the hot pressing method with different faujasite zeolite loading [52]. For the hot pressing method, membrane and zeolite were hot pressed at 140 °C under a pressure of 227 kg/cm^2 for 40 s. The water uptake and the proton conductivity of nanocomposite membranes increased with increasing zeolite loading. The recasting method presented higher values than hot pressing. The decrease of the membranes porosity could explain the lower water uptake of hot pressing. The surface composition of the zeolite, as well as the introduction of porosity at the polymer/filler interface could account for the enhancement of the water mobility degree in the membrane.

Patet et al. used the atom transfer radical polymerization to synthesize poly (vinylidene fluoride-co-chlorotrifluoroethylene)-g-poly(styrene sulfonic acid) (graft copolymer) with 47 wt% of poly(styrene sulfonic acid) and posteriorly blended with zeolite type A (3–10 wt%) [53]. The authors found that the zeolite particles strongly interact with the sulfonic acid groups of the graft copolymer matrix. Both the proton conductivities and water uptake decreased with the increase of both zeolites (3A and 5A).

Zeolites beta crystals with various SiO_2/Al_2O_3 ratios were added to SPES-SPEEK blend membranes [54]. Sulfonation of poly (ether ether ketone) (PEEK) and polyethersulfone (PES) was carried out to enhance the proton conductivity of the polymers. The polyethersulfone was used to improve the thermohydrolytic stability of the membrane. The proton conductivity of SPEEK was enhanced by the addition of zeolite beta. Moreover, the thermohydrolytic stability was improved by blending poly-ether-sulfone (PES). The SiO_2/Al_2O_3 ratio of 50 at 10 wt% loading presented the best conductivity results for zeolite Beta/SPEEK composite membranes. On the other hand, SPES/SPEEK membrane was more hydrodynamically stable and also performed better than pristine SPEEK membranes which excessively swell.

Chabazite and Clinoptilolite were used as fillers to Nafion composite membranes. Zeolites presented uniform distribution up to 40 vol%, and although more brittle than Nafion, the composite membranes showed reasonable flexibility below 40 vol% when hydrated. Zeolitic fillers could provide notable changes of conductivity and selectivity with respect to Nafion membranes without fillers [9].

6 Natural Polymers/Zeolite Nanocomposite Membranes for PEMFCs

Natural polymers have shown great promise in the production of devices for generating and storing energy at low cost. Natural polymers are cost-effective and eco-friendly derived from renewable sources and become a promising replacement for synthetic polymers. There are a wide variety of natural polymers present in nature; the main polymer employed for a zeolites incorporation for methanol fuel cell is chitosan [55].

Chitosan has been a promising source because it is abundant in the environment [56], it has hydrophilic character, can be use in high temperature and low humidity environments, it has low-methanol permeability, and certain functional groups that allow chemical modification to adjust its properties [11, 57]. Furthermore, chitosan has high-proton conductivity [11, 58].

Chitosan can be applied in fuel cell electrodes based polymer and in biofuel cells [59]. It is a natural polymer derived from chitin and it is composed of randomly distributed beta (1–4)-linked D-glucosamine (deacetylated unit) and *N*-acetyl-D-glucosamine. It is insoluble in water and in most of the organic solvents and alkali. However, it is soluble in diluted organic acids such as acetic acid, formic acid, and lactic acid. Chitosan contains three different polar functional groups, namely hydroxyl (–OH), primary amine (–NH_2), and ether (C–O–C) groups, and due to the presence of these functional groups, it has a high water attraction ability [56].

Several studies describe the employment of chitosan for the production of hydrogen from methanol [11, 60–62].

The production of natural polymers nanocomposites is based on casting method. This method is based on the solubilisation of chitosan in an aqueous acetic acid solution while stirring by 80 °C. After complete solubilization of the polymer, the desired zeolite in added and homogeneously stirred. Then, bubbles need to be removed, followed by plating and dry at ambient temperature. After drying, the membrane should be crosslinked with H_2SO_4, and subsequently washed with buffer solution and finally, dried [62].

The compatibility between the polymer and inorganic filler surface is a key issue to determine the ownership of the final performance and membrane. To improve the interfacial morphology of the hybrid membrane, a transition will be created between the organic and inorganic phases, mitigate or eliminate nonselective voids [61]. Considering the high selectivity, low cost, and environmentally friendly, as well as easy to manufacture, chitosan offers great promise for the development of Nanocomposites Natural Polymers.

Wang et al. developed chitosan membrane incorporating zeolite beta particles (300–800 nm) [62]. A homogeneous matrix with size larger than 800 nm was shown to be difficult to be produced. The best membrane was obtained by employing zeolite beta-2. To evaluate the performance of membrane, it is important to know the water and methanol crossover and proton conductivity. The authors observed that the increase of zeolite in the membranes decreased the water and methanol uptake. This fact can be explained by the high hydrophobic character of zeolite compared to chitosan.

In another study, Wang et al. developed a chitosan membrane incorporating zeolites (3A, 4A, 5A, 13X, mordenite, and H-ZSM-5) [11]. The diffusion resistance of methanol and methanol permeability were evaluated. The results were dependent on the type of zeolite incorporated in the matrix which influenced the efficiency.

The application of modified chitosan membrane as the electrolyte in fuel cells is aimed for improved chemical, mechanical, and thermal stability, also contributing to the proton conductivity. Transport of protons in the chitosan membrane can occur by two mechanisms, namely, *Grotthuss* mechanism and electrostatic interactions. The *Grotthuss* mechanisms protons can be transferred jumping from functional group to another. In this type of low-temperature ionic conductor, migration of protons occurs mainly by OH^-, which allows jumping through the protons in water molecules together. The electrostatic interactions occur between the amine group (NH_3^+) of the chitosan and sulfate ions (SO_4^{2-}) of crosslinking (crosslinking in the case of sulfuric acid). In this mechanism, protons are transferred along the chains through ionic interactions, facilitated by reducing the energy barrier for transport of protons through ion (SO_4^{2-}) [63].

7 Conclusions

Some promising possibilities related to the use of DMFC composite membranes have been discussed employing a polymer-zeolite system. ZSM-5 and Beta zeolites are produced at extremely low cost in oil refining industry and would not represent extra costs to the production of membranes that include inorganic components. The versatility in the use of zeolites in systems with various temperatures enables the handling of the proton transport mechanism, either of *Grotthuss* type or of vehicle type. In lower operation temperature, the materials used in the fuel cell construction would be less thermally and mechanically demanding, thus making possible a simpler and cheaper technology. Thus, the control of the ionic conductivity properties would lie mainly on the chosen polymers.

The clear advantages in the use of zeolites and the vast knowledge in their application in other technological areas indicate their potential use in these energy generation systems. However, there are inherent disadvantages when using a microporous system, which constraints the transport to the interior of the inorganic structure that must be creatively overcome. Configurational diffusion and shape selectivity must be handled, avoiding the undesired methanol crossover and allowing the proton conductivity, enabling the construction of the cell. The surface functionalization of the zeolites needs to be more carefully studied, but it configures as a good alternative to make zeolite and other inorganic solids viable.

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