



An Overview of Organic/Inorganic Membranes Based on Sulfonated Poly Ether Ether Ketone for Application in Proton Exchange Membrane Fuel Cells

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ABSTRACT

Nowadays, proton exchange membrane fuel cells (PEMFCs) are the most promising green energy conversion devices for portable and stationary applications. Traditionally, these devices were based on perfluoro-sulfonic acid electrolytes membranes, given the commercial name Nafion. Nafion is the most used electrolyte membrane till now; because of its high electrochemical properties such as high proton conductivity, good mechanical and chemical stability at fuel cell conditions, and However, its high cost, reducing the performance at temperature higher than 80°C, and low humidity are the major problems. Hydrocarbon polymers are encouraging alternative to Nafion, since they show the same or even superior performance than Nafion at high temperature and low humidity by some modifications. Numerous researches confirmed that Sulfonated poly ether ether ketone (SPEEK) is a promising PEM because of its low-cost, low fuel cross over, and acceptable thermo-mechanical stabilities. However, suitable proton conductivity in SPEEKs is depending on the high degree of sulfonation (DS), which could deteriorate the mechanical properties of SPEEK membranes progressively at the high level. To overcome this dilemma, various SPEEK-based hybrid/blend membranes are synthesized, and the effects of the introduced fillers on their performance are investigated. The introduced inorganic particles to the polymer membranes might be silica, zirconia, titania, heteropolyacids, carbon nanotubes, and.... Enhanced proton conductivity, water retention at high temperatures, and higher electrochemical properties are mentioned as some advantages of incorporating inorganic material into the polymer matrix. High thermo-mechanical resistance and electrochemical activities are supplied by inorganic moieties, while the organic parts supply plasticity and easier ductility at the low temperature. Indeed, SPEEK blends have a good potential to alter Nafion at the high temperature and/or relatively low humidity. In this paper, the last advances in progress of SPEEK-based organic/inorganic composite membranes that perform truly under fuel cell conditions are discussed.

1. INTRODUCTION

Nowadays, proton exchange membrane fuel cells (PEMFC) are at the center of concern, due to their eco-friendly energy conversion system, high efficiency, potential of usage at portable and stationary power, and adjustable output power from a simple cell stacking for various applications requiring different power outputs [1, 2]. In a PEMFC, the electrolyte membrane has a key role, which is conduction of protons from anode to cathode selectively and act as a barrier between the electrodes. Perfluorinated polymers such as Nafion have been widely used since 1970s, due to their reliable proton conduction, excellent chemical and dimensional stability. However, their performance is still not satisfactory at the temperature above 80°C and partially

humidified conditions; since the protons are transported through the hydrated ionic clusters formed by the hydrophilic sulfonic groups attached to the polymer backbone. These limitations and its high-cost stimulating cause to find alternative polymer electrolytes [3-6].

Various type of investigated materials are classified as: blend of polymers [7], cross-linked membranes [8], ionic liquids [9], block-copolymers [10], and organic/inorganic hybrids/ blends membranes [4]. Usage of organic/inorganic hybrid/blend membranes has a lot of advantages in the field of fuel cell materials. Their main characteristics are the combination of the inorganic material properties (e.g., high strength, thermo-chemical stability) and the organic material characteristics (e.g., flexibility, dielectric, ductility, and process-ability). The main specification of nanocomposite membranes is that the fine size of inorganic fillers significantly increases at the interfacial

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area as compared with conventional materials. Even at low loadings, the inorganic nano fillers create a significant volume fraction of interfacial polymer with different properties from the bulk polymer [4]. One of the most important effects of the introduced additives is reducing fuel crossover [11], especially, in direct methanol fuel cells [12].

Different class of membranes like non-fluorinated hydrocarbon membranes and acid-base complexes are the most investigated alternative materials. Aromatic hydrocarbon polymers by polar pendent acidic groups have gained the most attention over the last decade. Polysulfones, poly arylene ether, sulfonated poly ether ether ketone (SPEEK), and polybenzimidazole (PBI) are some of the alternative polymers, which have been widely investigated. Several studies have indicated that

SPEEK can be an alternative to commercial Nafion due to its comparable (or more) electrochemical activities, excellence in physicochemical properties, lower fuel crossover and peculiarly lower costs to Nafion in some cases [7]. As shown in Fig. 1, this polymer has the composition of hydrophilic part of sulfonic acid groups and hydrophobic part of polymer backbone. In the humidified condition, condensation of sulfonic acid groups causes separate hydrophilic/hydrophobic domains. Hydrophobic domains keep the polymer morphological structure and hydrophilic part prepare water and proton transport routes [13]. Despite, the necessity of high DS for acceptable proton transportation is accompanied by undesirable swelling and loss of mechanical strength [14].

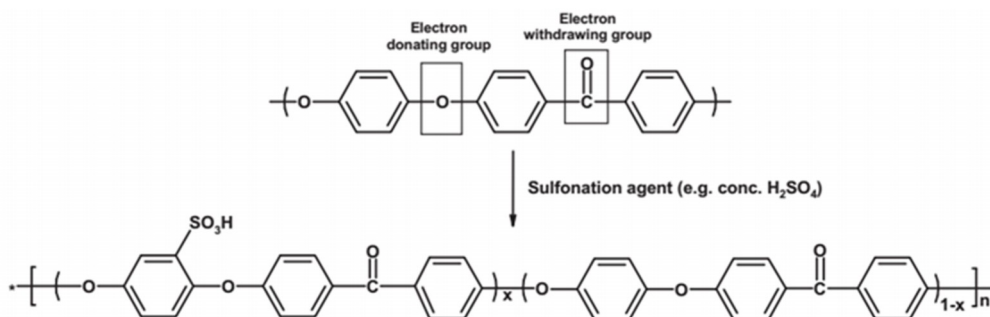


Figure 1. Sulfonation of poly(ether ether ketone) (PEEK) [6]

Proton conductivity is strongly influenced by water uptake. For example, it was shown that conductivity increased non-linearly from 1×10^{-2} to 1×10^{-1} S.cm⁻¹, as the water uptake was increased from 33 to 115% [7]. In fact, the membranes hydration number (λ , nH₂O/nSO₃H) depends on water activity and temperature; which, strongly influences the proton conductivity and dimensional stability. At the beginning of the swelling process, the softening effect occurs in the membrane that makes it mechanically weak. Finally, at high λ values, the hydrophilic regions of the polymer would be irreversibly swollen and deformed that causes degradation of the membrane. This is one of the major problems accompanied with the membrane in fuel cell operations [15]. To solve this problem, hybrid membranes (organic/inorganic composite) with hygroscopic specific additives (e.g., SiO₂ [1, 16], ZrO₂ [17, 18], TiO₂ [19], heteropolyacid (HPA) [20, 21], carbonaceous material [22-25] and ...) have been suggested. Such composite membranes have shown improved thermo-mechanical stability and hygroscopic properties.

This study focuses on the recent advanced hybrid SPEEK-based membranes as alternative PEMs for fuel cell applications.

2. APPLICATION OF HYBRID SPEEK-BASED MEMBRANES IN PROTON EXCHANGE MEMBRANE FUEL CELLS

Adding hygroscopic particles to a polymer matrix improves the water retention at high temperature and it causes various benefits such as (1) improving the thermochemical properties and mechanical stabilities by the inorganic-organic interfacial interactions, (2) enhancing proton conductivity by additional sites of acid on the surface of inorganic fillers, (3) increasing reactants permeation resistance by blocking the permeation pathways [26-28]. Incorporating of the fillers into the polymer matrix is in two ways: the insertion of an inorganic compound into the polymeric matrix or in situ formation of an inorganic network in the preformed membranes. These composites can be configured in different ways [15]:

- Polymer and inorganic components can be conductive ionically;
- No conductive inorganic fillers could be introduced in ionic conductive polymers as a mechanical supporter;
- Hygroscopic fillers could modify ionic conductive polymers;
- An ionically conductive inorganic additive can be introduced to an insulating supporting polymer.

In the following, the most effective fillers, which used in SPEEK polymer matrix and their effect on the fuel cell performance, are discussed.

2.1. Silica

The extensive investigation of silica-based nanoparticles is due to their lower cost, more negligible electrical conductivity, and higher water retention properties than other inorganic fillers. However, SiO_2 particles aggregate in the polymeric matrix by poor organic compatibility and non-conductive properties and reduce the conductivity of PEMs [29]. Phase incompatibility between the organic polymer membrane and inorganic silicate was circumvented by modifying the silicate surfaces using different modifiers. The precise choice of reactants and reaction procedures can lead to sulfonated silica particles with high ion exchange capacities (IECs) [15, 30]. Nanocomposite membranes based on silica are more strengthened than the plain one due to fortifying effects of silica nanoparticles. The prerequisite conditions for achieving optimum properties are a high degree of nanomaterial distribution in the polymer matrix and enhanced phase compatibility between the inorganic silica and an organic polymer. The higher silica content in the matrix is harmful for the mechanical properties of the polymer due to increased filler–filler interaction compared to filler–polymer interaction. A high degree of sulfonation in either the membrane or the filler can be resulted a reduction in membrane properties due to the increased swelling. Hence, a perfect combination of inorganic material and membrane can lead to an improved mechanical property of the resulting nanocomposites [29].

For instance, Lee et al. [1] investigated a composite SPEEK-based membrane of silica nanofiber mat. The composite had been impregnated by Nafion, for achieving a compact membrane. The resulted membrane showed the maximum power density of 170 mW.cm^{-2} which was 2.4-fold higher than recast Nafion (71 mW.cm^{-2}) at temperature of 120°C and relative humidity of 40%.

Moreover, Sivasankaran et al. [31] prepared modified nanocomposite membranes based on SPEEK and sulfonated silica ($\text{SiO}_2\text{-SO}_3\text{H}$) to apply in a microbial fuel cell. Fig. 2 shows the SEM images of the samples. It was found that the SPEEK (Fig. 2a) membrane showed a smooth, uniform and defect free surface. The mixing of the polymer and filler was checked by noticing the homogeneity of the films. The composite membranes (Fig. 2c–d) exhibited high clarity and transparency and no phase separation. The composite membrane surface with up to 7.5 wt% of sulfonated SiO_2 showed a uniform distribution of the filler without the formation of cracks. However, agglomeration of the fillers was observed at the concentration beyond 7.5 wt% (Fig. 2f).

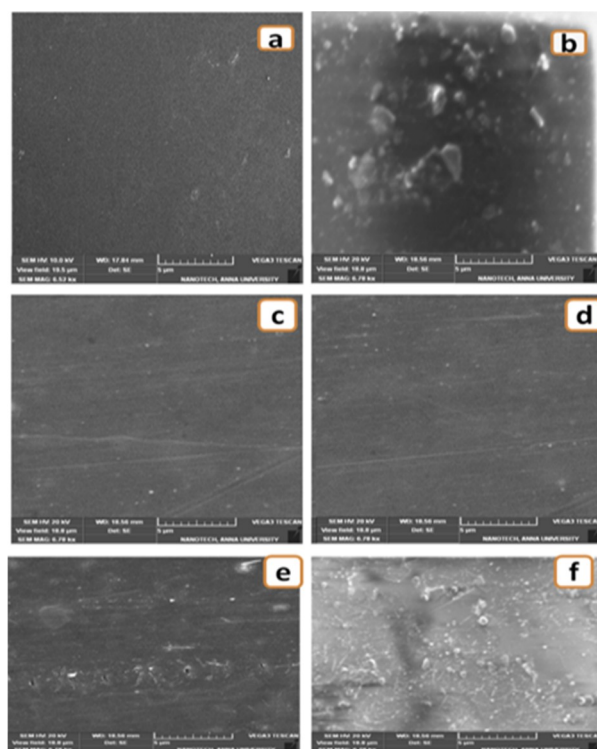


Figure 2. SEM images of (a) SPEEK (b) SPEEK/ SiO_2 (c) S-2.5% (d) S-5% (e) S-7.5% and (f) S-10% [31]

As expected, incorporating the $\text{SiO}_2\text{-SO}_3\text{H}$ particles (up to 7.5 wt%) into the polymer matrix improved the proton conductivity and the highest peak power density of 1008 mW.m^{-2} was exhibited in a single chambered microbial fuel cell (SCMFC), while peak power density of 680 mW.m^{-2} and 802 mW.m^{-2} was obtained for SPEEK and SPEEK- SiO_2 membranes, respectively in the same conditions. Also, the composite membrane delivered more than 3 times higher power density compared to Nafion 115 (320 mW.m^{-2}) in the same MFC setup (Fig. 3).

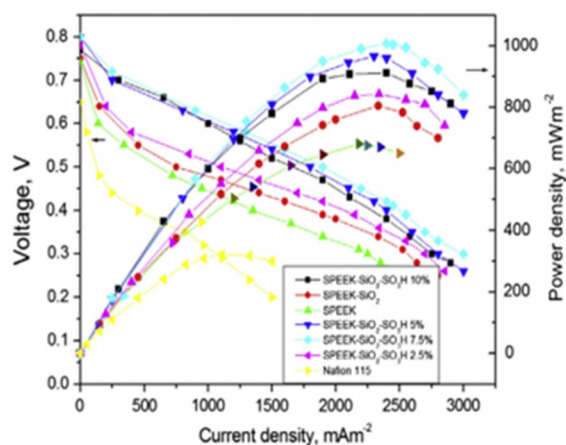


Figure 3. MFC performance of Nafion 115, SPEEK, SPEEK- SiO_2 and sulfonated composite membranes [31]

At a molecular level, the proton transport in hydrated polymeric matrices was in general described on the basis of either of the two principal mechanisms: “proton hopping” or “Grotthus mechanism” and “diffusion or vehicular mechanism” which was the movement of the hydrated protons) in the PEM [32]. In the case of metal oxide based polymer composites, the hydroxyl groups of metal oxides improved the proton conductivity of the membrane at high temperatures by proton hopping mechanism. In humidified conditions, water molecules effectively facilitated proton transportation by hopping mechanism rather than metal oxides. Therefore, the presence of metal oxides was not so important in humidified conditions. But, in the case of composite membranes containing sulfonated metal oxides, the presence of $-SO_3H$ group preferentially pull out the protons rather than $-OH$ groups of SiO_2 in humidified conditions. Indeed, SO_3H groups of sulfonated nanoparticles would act as a vehicle for proton transportation, while the $-OH$ groups prepared the route for proton transportation in the polymer matrix. The increased density of sulfonic acid sites in such composite membranes formed the ionic cluster channels with better connectivity for the transport of protons [31].

2.2. Montmorillonite clay

Clay or layered silicate is an attractive type of fillers, due to their hygroscopic nature, good proton conductivity, and acceptable thermal stability. The most commonly used clay minerals for PEMFCs are montmorillonite (MMT), which are composed of silica tetrahedral and alumina octahedral sheets. Like the most of inorganic fillers, presence of nanoclay in the polymer matrixes would improve the barrier properties, thermal, and mechanical characteristics [32-34].

Hasani-Sadrabadi et al. had studied SPEEK-based membrane mixed by MMT clay to prepare an electrolyte membrane that its fuel crossover and cost was reduced [33]. The results showed that by increasing of MMT loading, the proton conductivity of the composites decreased, due to the existence of silicate plates of MMT in the membrane. Also, methanol crossover was reduced by MMT increasing, since presence of MMT fillers, resulted in tortuous routes for fuel across the membrane. Membranes selectivity, which defined as the ratio of proton conductivity to methanol permeability is shown in Fig. 4. The ideal electrolyte membrane for a DMFC should have high proton conductivity and low methanol permeability, simultaneously. As presented in Fig. 4 selectivity of SPEEK membrane with DS= 62% and 1.0 wt% MMT content is about 2-fold greater than Nafion 117.

Moreover, Doğan et al. [34] had investigated the effects of incorporation of modified MMT with dimethyl dioctadecylammonium chloride (DMDOC) on SPEEK

polymer matrix as a PEM. The results showed that although thermal stability and proton conductivity of SPEEK-based composites were improved, oxidative stability did not change and even at high loadings of filler (above 15%) was decreased.

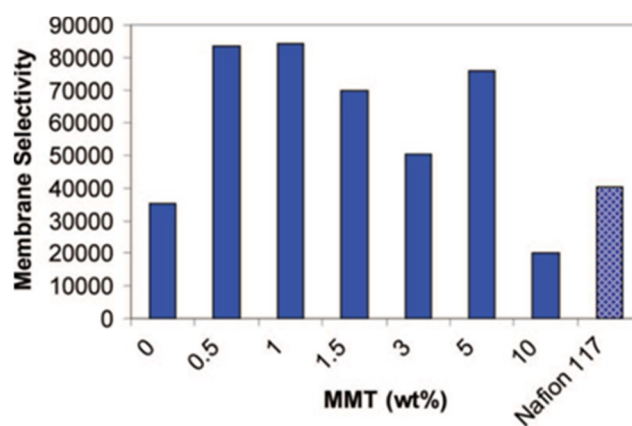


Figure 4. Membrane selectivity of nanocomposite membranes as a function of MMT loading [33]

2.3. Titania

Nanosized titanium dioxide at the nanosize level (less than 100 nm) is a good candidate for the hydrophilic filler in the polymer matrix, since it provides suitable hydration of the membrane under fuel cell operation conditions. Also, it is stable under strong acidic or basic state. Kalappa and Lee [35] claimed that incorporating of TiO_2 nanoparticle in SPEEK matrix would be decreased the water swelling, methanol crossover, and proton conductivity. Also, various studies have been done on SPEEK/ TiO_2 composite membranes by many other research groups [19, 36-40]. Their results showed that the properties of composites too depended on the structure of fillers especially at the high temperature and/or low humidity conditions. In addition, functionalization of titanium dioxide would improve the proton conductivity and thermo-mechanical properties of membranes.

For example, incorporating of hydrated titanium oxide into the polymer matrix improves proton conduction in low humidity conditions compared to plain SPEEK. The effects of titanium oxide are mainly on the micro-phase structure of polymer rather than water uptake. Indeed, proper routes is prepared for enhancing the proton conductivity by increasing hydrophilic sections agglomeration during film formation [19]. Fig. 5 indicates a schematic illustration of incorporating of hydrated titanium oxide in a polymer matrix.

In addition, the size and shape of nanostructures play an important role in properties of membranes, since electrons interaction with nanostructures is varied in different dimensions. One method of categorizing of nanomaterial is based on their shape, for example, three-dimensional (3-D) spherical particles (i.e. powder

materials), two-dimensional (2-D) lamellae (i.e. exfoliated clay or nano-sheets), one-dimensional (1-D) materials (including nano-fibers or nanotubes, nanowires and nanorods), and (0-D) nanostructures (i.e. nanoparticles) [41].

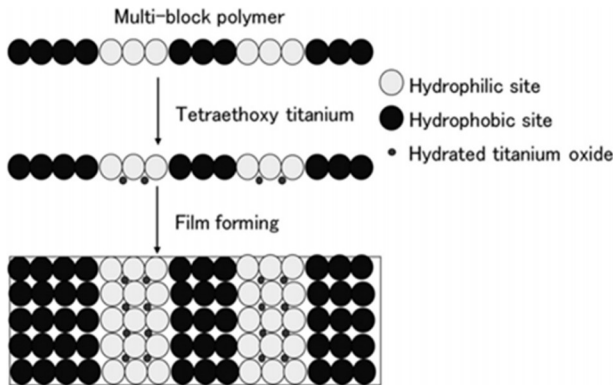


Figure 5. Schematic illustration of the membrane structure composed of a multi-block copolymer with hydrated titanium oxide [19]

Lamellae are at the center of focus, due to their high specific surface area, anisotropic structure and remarkable reducing fuel crossover. Marani et al. [42] had investigated the effects of different loadings of titania nanosheets (TNS) on improvement of the physicochemical properties of PEM. Water uptake of composites is larger than the plain one in any case, as observed in Fig. 6a. Also, volume swelling (VS) (Fig. 6b), have a stable value above 60°C for the composite, while increasing for reference membrane. Hence, the composites dimensional stability is more than the plain one.

Also, incorporating of titanium combinations into SPEEK improve membrane physicochemical properties. For instance, Salarizadeh et al. [43] have synthesized a nanocomposite membranes based on SPEEK and iron titanate, Fe_2TiO_5 , (IT) by solution casting method. As shown in Fig. 7, SPEEK membrane showed an elastic modulus and tensile strength of about 700 and 32.6 MPa, respectively, which increased gradually upon raising IT nanoparticles content up to 1 wt.%. Well distribution of IT fillers through polymer matrix as well as supportive effects of them caused shift of stress from polymer to fillers.

Moreover, there was hydrogen bonding between $-\text{SO}_3\text{H}$ group in SPEEK and $-\text{OH}$ group on IT nanoparticles which increased mechanical strength. Decreasing of the tensile strength at filler concentration above 1% could be attributed to the agglomeration of the nanoparticles. The elongations of SPEEK/IT membranes were lower than SPEEK membrane and decreased with the increasing nanoparticle content which can be due to the restriction of the polymer chains movement and the reinforcing effect of the filler.

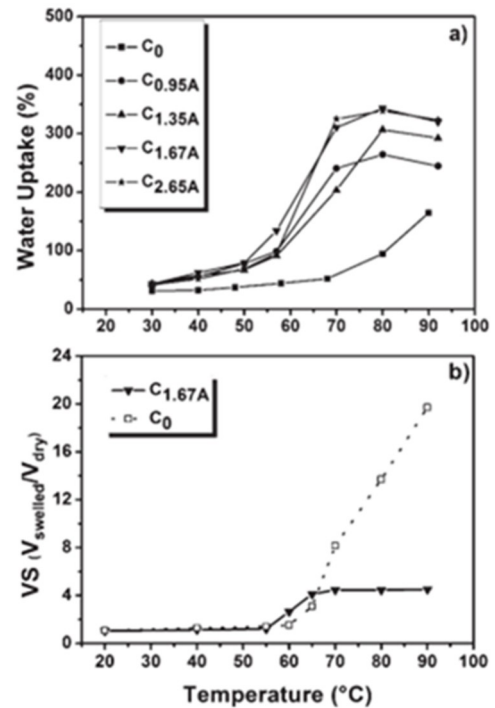


Figure 6. (a) Mass water uptake as a function of temperature for unfilled SPEEK (C_0) and acid treated SPEEK/TNS composite membranes (b) Comparison of volume swelling as a function of temperature for C_0 and composite $C_{1.67A}$ [42]

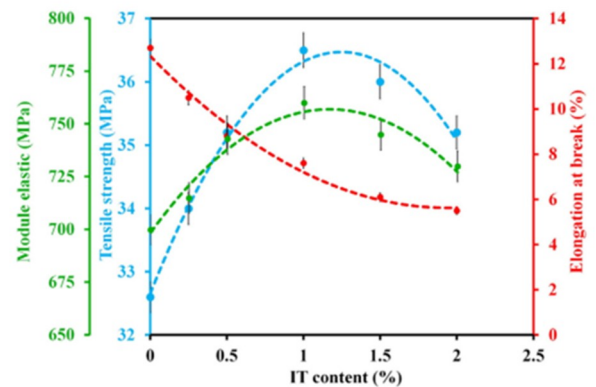


Figure 7. The mechanical properties of SPEEK and SPEEK/IT nanocomposite membranes [43]

Incorporating of IT nanoparticles enhanced the water uptake values from 49% (for SPEEK/IT0.25) to 61% (for SPEEK/IT1) due to its water retention character and hydrophilic nature of IT which demonstrated even a very small amount of IT could effectively enhance the hydrophilicity of SPEEK and facilitated the absorption and retention of water. But, a further increasing the filler content resulted decreasing of the water uptake coefficient, because of blockage effect of agglomerated nanoparticles and also the reduction of available void space in the polymer matrix as water transfer route. Indeed, the proton transfer through vehicle mechanism

was reduced. By increasing IT content up to 2 wt%, the swelling of the membranes decreased from 26% to 16%, due to the interaction between SPEEK and IT nanoparticles through the hydrogen bond which was formed between $-\text{SO}_3\text{H}$ groups of SPEEK and $-\text{OH}$ groups of IT nanoparticles and reduction of polymer chain movement by incorporating of IT. The IT nanoparticles, as a water store, enhanced the water retention properties of the membrane at low humidity due to the hygroscopic properties.

The conductivity of the SPEEK/IT composite membrane increased from 0.048 at 25°C to 0.096 $\text{S}\cdot\text{cm}^{-1}$ at 80°C compared to SPEEK membrane (0.058 $\text{S}\cdot\text{cm}^{-1}$ at

80°C), due to hygroscopic and acidic properties of the IT nanoparticles (Fig. 8a). The activation energy values were calculated from Arrhenius plots (Fig. 8b). Increasing the nanoparticle loadings caused the decreasing of the activation energy from 15.61 $\text{kJ}\cdot\text{mol}^{-1}$ (SPEEK membrane) to the range of 14.40–10.81 $\text{kJ}\cdot\text{mol}^{-1}$ for the SPEEK/IT $_x$ membranes that demonstrated better proton transfer. However, above the threshold content of filler, over 1 wt%, the existing pathways for proton conduction in the membrane was probably clogged by the IT fillers which were not conducive enough to form connected proton transfer channel.

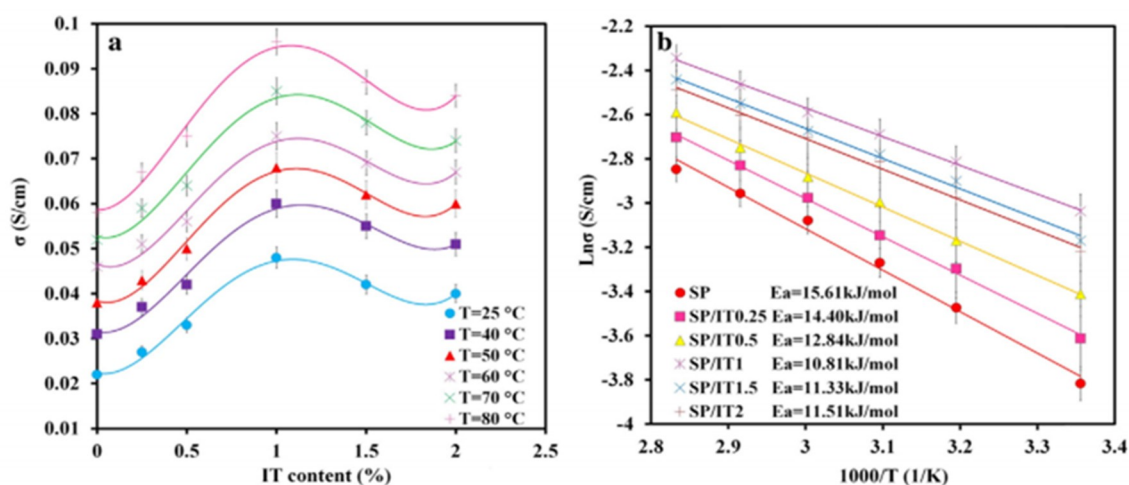


Figure 8. (a) Proton conductivity of SPEEK and SPEEK/IT $_x$ nanocomposite membranes at different temperatures (b) Arrhenius plot of the proton conductivity [43]

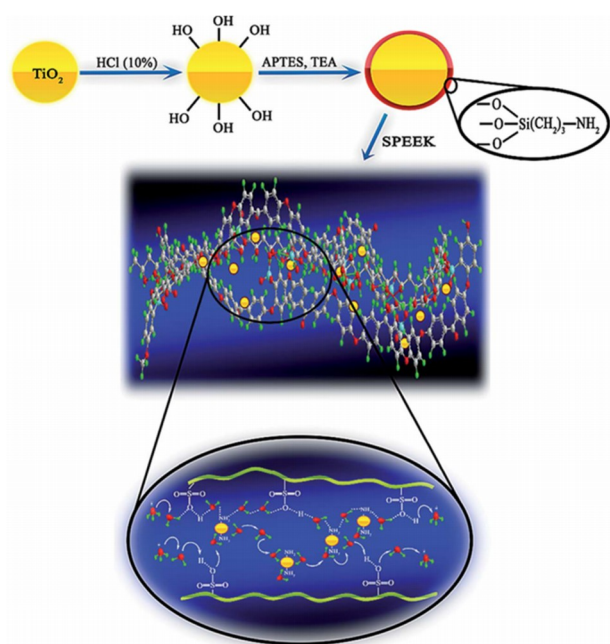


Figure 9. Schematic of amine-functionalization reaction of TiO_2 nanoparticles and the proton transfer mechanism in the nanocomposite membrane [44]

Also, amine functionalized titanium dioxide nanoparticle (AFT) had been investigated as an inorganic filler in SPEEK-based membrane [44]. The results showed that the optimized loading of AFT nanoparticle, 7.5 wt%, would increase proton conductivity up to 0.135 $\text{S}\cdot\text{cm}^{-1}$ which was 1.5 fold greater than composite membrane with 7.5% TiO_2 due to well distribution of AFT and new pathways created for proton transfer. A schematic illustration of the amine-functionalization reaction of TiO_2 nanoparticles and the proton transfer mechanism in the nanocomposite membrane are presented in Fig. 9.

2.4. Zirconia

There are several studies on the incorporating of ZrO_2 or its combination in SPEEK to improve physicochemical properties of the membrane for using in PEMFC and DMFC [45-47]. For example, Gashoul et al. developed a new SPEEK/ ZrO_2 nanocomposite membrane for using in medium temperature PEMFCs [18]. Improvement of thermo-mechanical behavior and enhancing hydrolytic and oxidative stability were the results. The results of hydrolytic stability test are shown in Fig. 10. As presented, the main weight loss happens

at first 40h for plain SPEEK and the weight loss after that is negligible, while only 35% weight loss is happened for the composites at the first 40 h. By increasing nanoparticle percentage, membranes become more stable and as a result the percentage of weight loss is decreased. So, ZrO_2 content enhances water uptake and hydrolytic stability. Moreover, results of oxidative stability show an improvement of composites stability up to 77% compared to plain SPEEK due to destruction effects of zirconia nanoparticles on radicals, which are responsible for membrane decomposition.

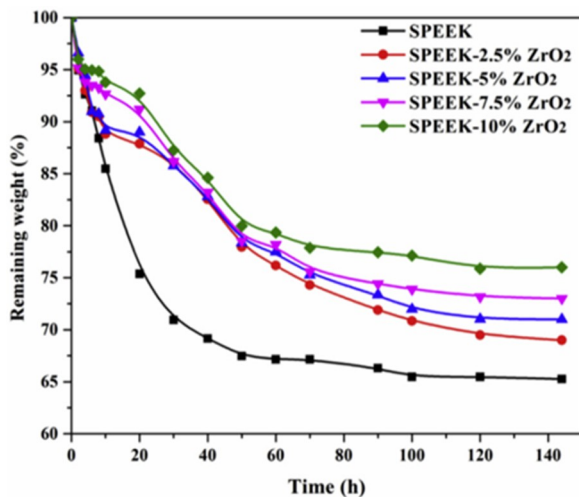


Figure 10. Hydrolytic stability of membranes during time for different contents of ZrO_2 [18]

The sulfated form of zirconia is one of the strongest solid acids, with Hammett acid strength H_0 of -16.0323, which had been studied by many researchers as an additive to fabricate composite membrane for higher temperature/lower humidity fuel cell application. Zhang et al. [48] prepared a self-humidifying SPEEK-based membrane blend with sulfated zirconia (SO_4^{2-}/ZrO_2 , SZr)-supported platinum catalyst (Pt-SZ catalyst). To determine the cross-sectional morphology of the SPEEK/Pt-SZ membrane and the distribution of the Pt-SZr catalyst in the membrane, the SEM-EDX measurement was conducted and the results were shown in Fig.11.

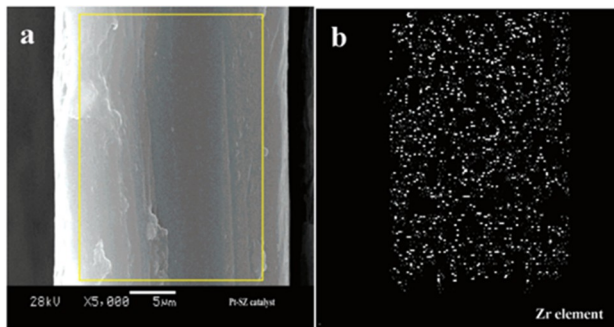


Figure 11. SEM-EDX image of the SPEEK/Pt-SZ composite membrane [48]

As shown in this figure the cross-section of the SPEEK/Pt-SZr membrane was very dense and smooth, with no defect. Fig. 11b showed the zirconium element had a very uniform distribution along the cross-section of the SPEEK/Pt-SZ membrane, which indicated a good distribution of Pt-SZ particles in the membrane. The high-uniformly dispersion of the Pt-SZ catalyst could increase the interface between the Pt-SZ catalyst and the SPEEK matrix and the possibility of their synergism.

The homogeneous and good distribution of nanoparticles in the polymer matrix reserves water effectively, as a result increasing the proton conductivity even at low humidity. Fig. 12 shows the proton conductivity results of samples measured at 10% RH, 50% RH, 75% RH, and 100% RH at temperature of 60°C. It was observed that two self-humidifying membranes showed higher proton conductivity values compared to the plain membrane at unsaturated RH conditions. The SPEEK/Pt-SZ self-humidifying membrane had the highest proton conductivity values among these three membranes.

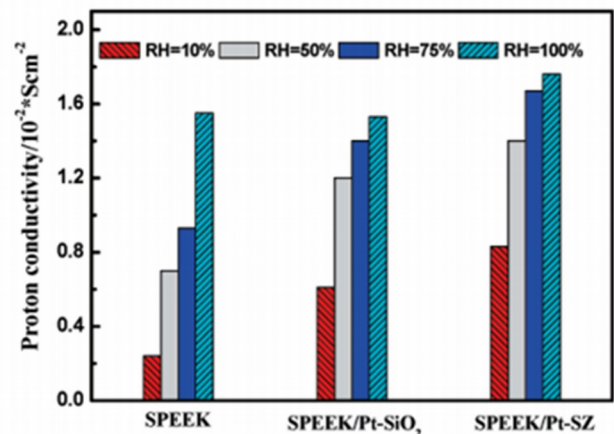


Figure 12. Proton conductivity of the plain SPEEK, SPEEK/Pt-SiO₂ and SPEEK/Pt-SZ membranes at 10% RH, 50% RH, 75% RH, and 100% RH at 60°C [48]

According to the cluster network model, operating of a single cell under low-humidified or non-humidified reactant gases reduced the existing clusters and thus the elongation of the interconnecting channels. For the plain SPEEK membrane this situation was worse due to its natural microstructural deficiency (narrower channel and more branched with more dead-end “pockets” [13]). Despite, the nanoparticles could easily interact with the sulfonic acid groups of SPEEK in the nanocomposite membranes, increasing the number of available proton exchange sites of polymer and magnified the diameter of the clusters for their hygroscopic property, thus the membrane proton conductivity through the vehicle mechanism would be increased. Besides the similar effect of Pt-SiO₂ catalyst, the Pt-SZ particle in the SPEEK/Pt-SZ membrane could provide an additional

strong acid group for transporting of proton and bridging neighboring shrunken clusters to effectively shorten the distance of proton transport; in this case, the membrane proton conductivity through the Grotthus mechanism would be enhanced [48].

Luu and Kim [17] had proposed a composite SPEEK-based membrane, which contains zirconium oxide and phosphomolybdic acid (ZPMA). Although the proton conductivity of composite membranes was more than plain SPEEK, due to the high conducting nature of phosphomolybdic acid, very low fuel crossover compared to the plain one. Moreover, the composite membrane was dimensionally stable in hot water, due to its much lower water uptake nature than the plain SPEEK membrane.

Further, our group developed polymer electrolyte membranes based on SPEEK polymer and sulfated zirconia as inorganic part [45]. Interactive effects of SPEEK sulfonation time and the amounts of fillers were studied on the proton conductivity and the oxidative stability of the nanocomposite membranes. The importance of this issue, as mentioned before, is the extreme loadings of metal oxide nanoparticles could block the proton transfer routes of the membrane [49]. Both proton conductivity and oxidative stability as responses were optimized and SPEEK with the degree of sulfonation $\sim 60\%$ and sulfated zirconia loading of ~ 6 wt% was obtained. The results showed that the adding of the optimized amount of sulfated zirconia nanoparticles into SPEEK polymer matrix improved oxidative stability and proton conductivity, simultaneously and increased the thermo-mechanical properties of the composite membranes; where the existence of the nano crystalline materials in SPEEK matrix could limit the segmental motion of the polymer chains and as a result increased the values of glass transition temperature.

2.5. Heteropolyacids (HPAs)

Heteropolyacids (HPAs) have drawn a considerable interest as a high proton conducting material due to their loose structure which absorbs high water, and thermally stable in crystalline form with the ambient conductivity of 0.19 S.cm^{-1} . Their typical structure is the Keggin anion cluster $(\text{PM}_{12}\text{O}_{40})^{3-}$ where M is W, Mo, or Si and its acidic forms include phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, PWA), phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, PMA) and phosphosilicate acid ($\text{H}_3\text{PSi}_{12}\text{O}_{40}$, PSiA). Despite, $\text{H}_3\text{Mo}_{13}\text{PO}_{40}$ has a high conductivity; long-term use of this filler is impossible in the moist environment of a fuel cell, since HPA are soluble in water and alcohols. So leaching out of the membrane would happen. For solving this important issue, entrapment of HPA in some stable materials like metal oxides or mesoporous materials are done. For instance, entrapment of HPA in silica oxide causes negligible leaching out of solid acids even after

prolonged exposure with an aqueous environment [17, 50].

Zaidi et al. [51] investigated a series of heteropolycompounds (tungstophosphoric acid, its disodium salt or molybdophosphoric acid) which were embedded in SPEEK polymer matrix. Improving proton conductivity, up to $10^{-1} \text{ S.cm}^{-1}$ above 100°C , and glass transition temperature, up to 250°C , resulted from this incorporation.

Oh et al. [52] claimed the water retention, surface structure and electrochemical performance of composite membrane would be improved by incorporation of Cs^+ into HPAs, because of incorporating of Cs-HPAs into the polymer matrix would be increased the number of protonate sites. Also, the maximum power density of 247 mW.cm^{-2} were obtained in a single cell tests at 80°C and 80 RH%.

Moreover, our team has prepared self-humidifying nanocomposite membranes based on SPEEK and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ supported Pt catalyst (Pt- $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalyst or Pt- $\text{Cs}_{2.5}$) and studied their performance in non-humidified proton exchange membrane fuel cell [20, 21]. It was concluded that the SPEEK/Pt- $\text{Cs}_{2.5}$ self-humidifying nanocomposite membranes have higher acidic properties, more water uptake, and proton-conductivity, up to $3.26 \times 10^{-2} \text{ S.cm}^{-1}$, compared to the plain SPEEK membrane and Nafion-117 membrane due to their self-humidifying nature and acidic effects of Pt- $\text{Cs}_{2.5}$ catalyst. Fig. 13 presents the OCV test result which supports the oxidative stability test. Indeed, the heteropolyacids decompose hydrogen peroxide and convert to the water. Also, reduction of fuel crossover due to the presence of Pt happens which catalyzes the reaction between permeated H_2 and O_2 , and improves the membrane stability as a result.

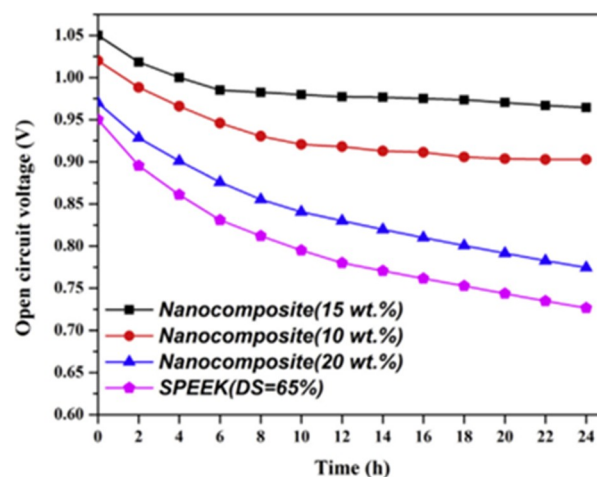


Figure 13. Durability test results of OCV measurements on SPEEK and their nanocomposite membranes with 10, 15 and 20 wt% [20]

Also, in Fig. 14, the polarization curves show that the single cells employing the SPEEK/Pt- $\text{Cs}_{2.5}$ self-

humidifying nanocomposite membranes exhibited higher cell performances than plain SPEEK membrane and Nafion-117 membrane under dry or wet conditions. Also, the SPEEK/Pt-C_{s2.5} nanocomposite membranes have acceptable water stability in an aqueous medium.

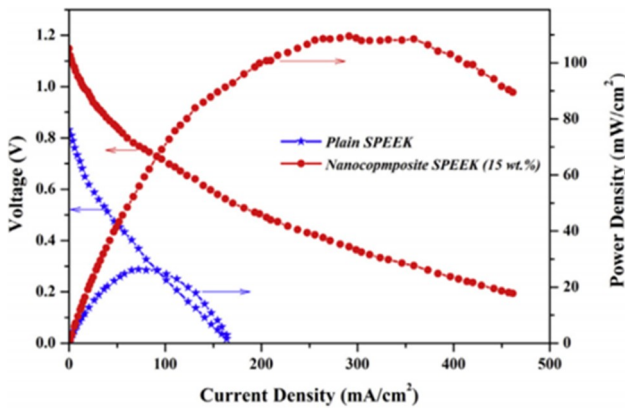


Figure 14. Polarization and power density curves of PEM fuel cell including plain SPEEK and SPEEK/Pt-C_{s2.5} self-humidifying nanocomposite membranes at 60°C under dry operation condition [20]

2.6. Carbonaceous materials

2.6.1. Carbon Nanotubes

Currently, carbon nanotubes (CNTs) are known as a novel advanced inorganic fillers used in fuel cell applications due to their unique properties, including a high tensile modulus and strength, a large surface-to-volume ratio, low density, excellent plasticity, and great electrochemical characteristics [23]. The short-circuiting in PEMs caused through high electrical conductivity of CNTs may be eliminated by controlling the CNT concentration below the percolation threshold. However, it is difficult to disperse pristine CNTs in a polymer matrix, because of the Van der Waals interactions of the bare tubes. This problem can be solved by modification of CNTs by carboxylation and sulfonation before distribution in the polymer matrix. Moreover, grafting of polystyrene sulfonic acid (PSSA) on the surface of the CNTs could be another solution; this way has the privilege of increasing ionic conductivity due to the presence of sulfonic acid groups. So, efficient and easy coating methods are essential to acceptable modification of CNTs in fuel cell applications [22, 53]. For example, silica-coated CNTs eliminated the problem of short-circuiting and enhanced the interfacial interaction between the CNTs and matrix; so, promoted the homogeneous dispersion of the CNTs in the polymer matrix. Despite, they have improved the mechanical properties and high thermal and oxidative stability; the composite membranes exhibited decreased proton conductivities in both cases because of the inert proton conduction activity of silica. For solving this problem, Gong et al. [22] functionalized CNTs with an

inorganic proton conductor, boron phosphate (BPO₄) which belonged to the class of orthophosphates in which P^V and B^{III} were tetrahedrally coordinated by oxygen. Boron phosphate could also show interesting humidity sensing properties due to its peculiar structure. The connection of the PO₄ and BO₄ tetrahedron (corrugated structure) would simplify proton transportation phenomena, especially at the high temperature [54]. Another modification method could be done by polydopamine coating layer, which could function as an excellent paste to homogeneously adhere BPO₄ nanoparticles on CNTs, hence, diminish the problem of short-circuiting and prepare alternative proton-conducting routes in the composite membranes (Fig. 15). The measurements showed that the thermo-mechanical properties of electrolyte polymer were fulfilled outstandingly. Further, the proton conductivity of SPEEK/BPO₄@CNTs-2 was improved remarkably compared to the plain SPEEK. Also, the fuel cell performance of SPEEK/BPO₄@CNTs-2 membrane showed a higher peak power density (340.7 mW.cm⁻² at 70°C) than plain SPEEK (254.2 mW.cm⁻²).

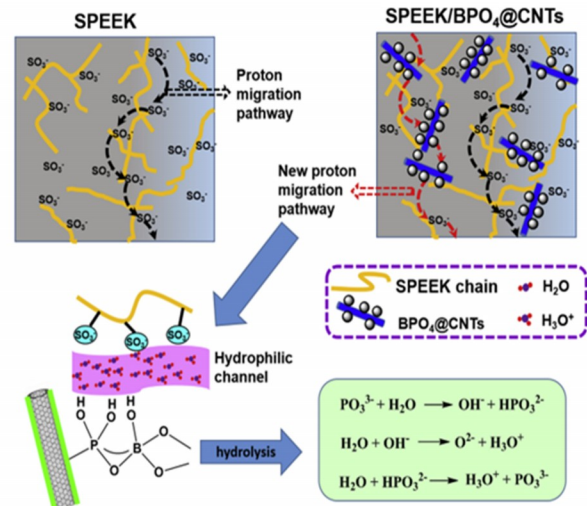


Figure 15. Schematic illustration of proton conduction in the SPEEK and SPEEK/BPO₄@CNT composite membranes [22]

Further, Rambabu et al. [53] modified CNTs with PSSA and dispersed it in the SPEEK matrix for using as a membrane electrolyte in direct methanol fuel cells (DMFCs). The composite membranes were prepared by various loadings of PSSA-CNTs. Homogeneous distribution of PSSA-CNTs in SPEEK matrix improved the thermo-mechanical properties and ionic conductivity and reduced fuel crossover compared to plain SPEEK membrane. Composite membranes of SPEEK-PSSA-CNTs exhibited more DMFC performance compared to plain SPEEK and Nafion membranes. Fig. 16 shows the cell polarization data for Nafion-117; recast Nafion, SPEEK and SPEEK-PSSA-CNTs composites. Peak power density of 93 mW.cm⁻² at a load current density

of $300 \text{ mA}\cdot\text{cm}^{-2}$ was observed for SPEEK–PSSA–CNTs (0.5 wt%) which is higher than the other tested samples. Limitation of fuel crossover and more proton conductivity were the major symptoms of improving DMFC performance. In the case of Nafion 117, the main drawback was the higher methanol crossover from the anode to the cathode through its ionic clusters. Whereas in the case of SPEEK composite, the pore size was relatively low, that led to lower methanol permeability improving the overall DMFC performance.

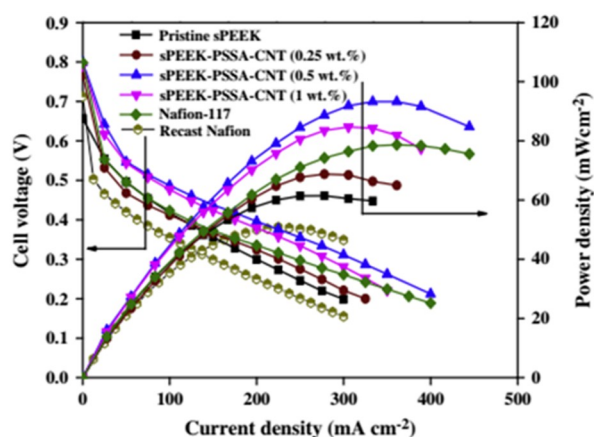


Figure 16. DMFC cell polarization for Nafion, pristine SPEEK and composite membranes of SPEEK–PSSA–CNTs [53]

The stability test was done with the optimized membrane of SPEEK–PSSA–CNTs, 0.5 wt%, compared to the recast Nafion as shown in Fig. 17. It was found that SPEEK–PSSA–CNTs composite membrane showed relatively higher stability due to the presence of CNTs.

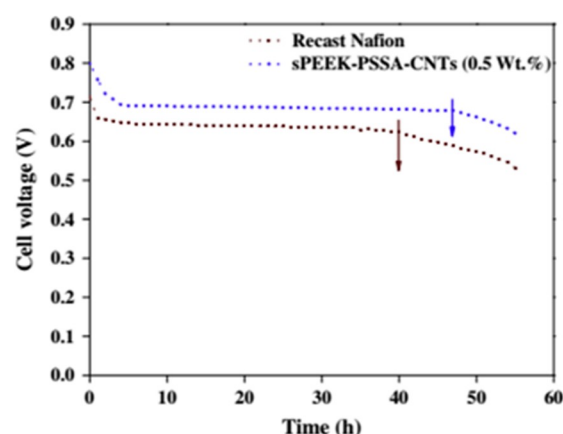


Figure 16. Open circuit voltage (V) in relation to time for Nafion and SPEEK–PSSA–CNTs (0.5 wt%) [53]

2.6.2. Carbon nanofibers

The other groups of carbonaceous material are carbon nanofibers (CNFs). This continuous fiber is distributed in the polymer matrix easily. In addition, incorporating of this fiber mats into the polymer matrix will be improved physical properties of membrane. For instance, Zhang et al. [55] incorporated CNF and activated carbon nanofiber (ACNF) into the SPEEK polymer to use as PEM in the fuel cell. Fig. 18 presents the properties of samples at the different temperatures. As shown the mechanical properties of composite samples were higher than the plain SPEEK and acceptable for PEMFC using. The composite samples which were contained ACNF, had the most water uptake due to its cellular structure, which could retain the water more effectively. As a result, proton conductivity improved. Furthermore, Fig.18c shows the positive effects of CNFs on proton conductivity between of 20–80°C.

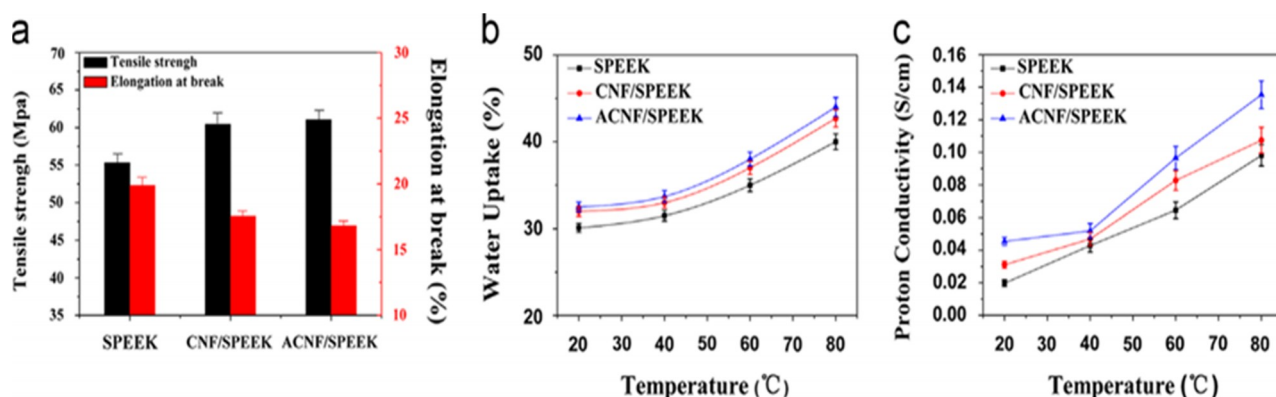


Figure 17. Properties of different membranes at different temperatures [55]

2.6.3. Graphene

The other carbon based material which has gained more attention than CNTs, is graphene, due to its great conductivity, extremely high aspect ratio ($2630 \text{ m}^2\cdot\text{g}^{-1}$

compared to $1315 \text{ m}^2\cdot\text{g}^{-1}$ for CNTs), and good interaction with the polymer matrix which can improve mechanical and thermal properties of membrane effectively [56]. However, graphene or graphene oxide

(GO) is not a proton conductor and would inhibit the proton transportation. Therefore, functionalization of GO has an important role in the good performance of PEMFCs [57, 58]. Heo et al. [57] prepared a composite SPEEK-based membrane and used sulfonated graphene oxide (SGO) as an inorganic filler to improve mechanical characteristics and reduce methanol crossover while retaining the proton conductivity. As presented in Fig. 19, SGOs were dispersed homogeneously through polymer matrix because of the hydrogen bonding between polar groups in SPEEK and sulfonic groups ($-\text{SO}_3\text{H}$) in SGOs.

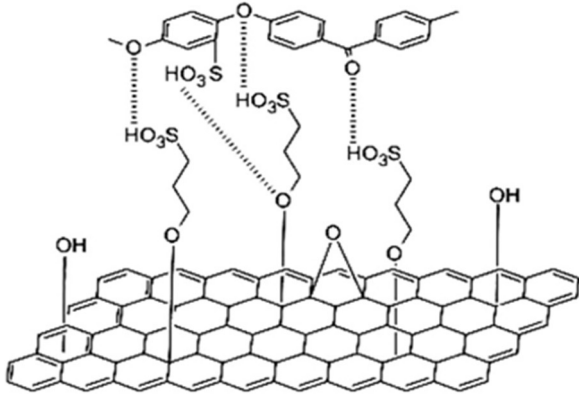


Figure 18. Scheme diagram of interaction between SPEEK and SGO [57]

The proton conductivity of SPEEK/SGO membranes would be increased by SGO content (up to $8.41 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$). This trend was descending at SGO loading above 7 wt%, since the “blocking effect” would be happened above the threshold amounts of filler, so formed ionic channels for proton transportation will be clogged. The same trend was observed for mechanical behavior. Mechanical characteristic would be improved by increasing SGO up to 5 wt% due to the brilliant elastic modulus ($\sim 1100 \text{ GPa}$) and intrinsic strength (125 GPa) of graphene-based material. Moreover, the hydrogen bonds between SGO and polymer matrix increased the interfacial adhesion, so mechanical behavior of composite membranes improved. However, modulus would be increased slightly by increasing the filler from 5 wt% to 10 wt% due to the phenomenon of graphene-based material restacking [57].

Indeed, the presence of SGOs groups in the polymer matrix enhanced the proton conductivity of the composite, improved the mechanical characteristics and reduced methanol crossover. Hence, incorporating of SGO into SPEEK membrane would significantly increase the selectivity of the membrane. So, SPEEK/SGO composite membrane is an acceptable candidate to use in direct methanol fuel cells.

2.7. Ionic liquid

Ionic liquids (ILs) are one of the most interesting fillers for using in PEMs which have been considered in the

last decade. These materials have excellent physical and chemical properties, such as high ionic conductivity, low vapor pressure, good thermal characteristic and being in liquid state at temperatures below 100°C [59, 60]. Trindade et al. [59] suggested SPEEK-based membranes, which were impregnated with IL 1-butyl-3-methylimidazolium tetrafluoroborate ($\text{BMI}\cdot\text{BF}_4$). Due to the interaction between SO_3^- groups and BMI^+ cations, higher dimensional and thermal stability than the plain SPEEK membrane and higher decomposition temperatures were observed for the composite membranes. As shown in Fig. 20 the overall performance of fuel cell had improved by using the composite membrane. However, plain SPEEK (DS=65%) was not suitable for fuel cell conditions and the puncture would be happened above 90°C .

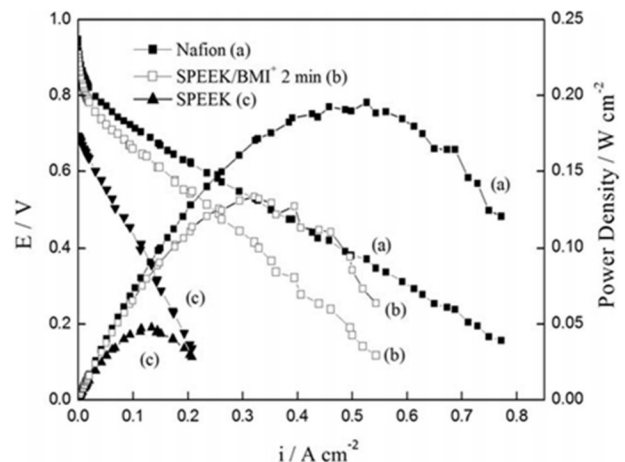


Figure 19. Polarization curves of the SPEEK membrane (a) SPEEK/BMI1, 2-min contact time (b) Nafion membrane (c) $P_{\text{H}_2} = 2 \text{ bar}$, $P_{\text{O}_2} = 2 \text{ bar}$, $T_{\text{PEMFC}} = 80^\circ\text{C}$ [59]

Leaking is the problem of such composites, which could be solved by doping. For instance, Arias et al. had prepared hybrid membrane by composition of IL, diethylmethylammonium trifluoromethane sulfonate, SPEEK (DS=73%), and MMT modified with dema+ cation [61]. The results showed that the synergic effect between Grotthuss and Vehicular mechanism due to the nature of modified MMT. As a consequence, composite membranes presented excellent conductivity and ionic liquid leaching. Furthermore, Chen et al. [62] had investigated the conductivity and some physical properties of SPEEK-based membrane which was doped with ILs, such as 1-ethyl-3-methylimidazole tetrafluoroborate (EB) or 1-butyl-3-methylimidazole methanesulfonate (BS), and Y_2O_3 . The water uptake of samples was enhanced by increasing the temperature. However, plain SPEEK showed more water uptake since the combination of ILs and Y_2O_3 caused reducing the sulfonic acid groups. However, as shown in Fig. 20, proton conductivities of composite samples at 100% and 50% RH were higher than the plain one due to ILs had

an effective role in preparing the proper route for proton transportation. Moreover, the proton conductivity of plain SPEEK was reduced by the increasing the

temperature from 70 to 90°C due to dehydration. Also, the thermal and mechanical behavior of composite samples improved slightly.

TABLE 1. Summary of the inorganic filler in SPEEK-based membranes, their advantages and disadvantages

Inorganic component	Advantages compared to plain SPEEK	Disadvantages compared to plain SPEEK	Applications	Reference
SiO ₂	Better water retention, resistance to swelling, Higher proton conductivity, Cell performance at high temperature and low humidity, Very low methanol crossover	Less ductile	PEMFC, MFC and DMFC	[1, 12, 16, 31, 63-65]
Montmorillonite Clay	Improvement of thermal resistance, Improvement of proton conductivity, More water uptake, Increasing hydrolytic stability	Low oxidative stability	DMFC	[33, 34, 61]
TiO ₂	Superior proton conductivity, Superior strength, More connected proton pathways, Increment of maximum power density, decreasing of water swelling, Lower methanol permeability, Improved electrochemical properties	Less ductile	PEMFC, DMFC	[35, 42, 44, 66]
ZrO ₂	Improved thermal and mechanical stability, Higher hydrolytic stability, Enhanced oxidative stability, Lower methanol crossover, Improved cell performance under dry operation	Less ductile	PEMFC, DMFC	[17, 18, 48, 67]
HPA	Flexible, Hot water stable, Higher water uptake, Higher proton conductivity, Lower methanol permeability, Increasing T _g , Electrochemical performance improvement	Leakage	PEMFC, DMFC	[50-52]
Carbonaceous nanomaterials	More proton conductivity particularly at low hydration, Improved mechanical properties, Increasing selectivity of membrane, Superior performance of cell	Inert ionic conduction, short-circuiting	PEMFC, DMFC	[22, 55, 57, 58]
ILs	Improved conductivity at low hydration, improved dimensional and thermal stability, Higher decomposition temperatures, Excellent conductivity, Ionic liquid lixiviation	Leakage		[59, 61, 62]

3. SUMMERY

Nafion is the most common proton electrolyte membrane used for both PEMFC and DMFC. However, there have been a lot of researches to find new alternative martial due to its high price, fuel crossover (especially in DMFC) and losing performance at the temperature above 80°C. Modified hydrocarbon-based materials, especially in the form of organic/inorganic hybrid membranes are exhibited comparable or even superior electrochemical performance than Nafion, particularly at high temperature. Among these materials, SPEEK-based polymers are considerable due to their high thermochemical properties, low fuel crossover, and mainly low costs. However, highly sulfonation (>80%) of PEEK membranes essential to have good proton conductivity, cause extreme swelling under the humidified fuel cell conditions and deteriorate the mechanical stability.

Also, dehydration in fuel cell conditions, which mainly happens at high temperature, is another major problem which causes mechanical damage, high fuel crossover and lowering fuel cell performance, as the results. This structural drawback makes SPEEK membranes with high sulfonation as a poor choice for electrolytes in fuel cells. Hence, various scientific studies are concerned to improve PEEK polymer as an alternative to Nafion for fuel cell applications. In this field the most important methods are classified to: a) sulfonation of PEEK; b) SPEEK and non-functional polymers blending; c) SPEEK/ heteropolycompounds; d) SPEEK/ inorganic, etc.

Organic/inorganic composite membranes are a promising class of membranes for high temperature fuel cells. Incorporating of nanosized functionalized materials in SPEEK membranes has various privileges like reduction of fuel crossover, improvement of membrane dimensional stability and thermo-mechanical

properties and improved proton conductivity beside oxidative stability. Indeed, the addition of some inorganic materials into SPEEK matrix could improve the physicochemical properties of the resulted composite membrane for application in fuel cells. In this paper, we focused on the hybrid SPEEK-based membranes with hygroscopic specific additives potentialities. The advantages and disadvantages of the discussed fillers are summarized in Table 1.

When inorganic additives are used, the preparations of the additive and the composite membrane materials are crucial to performing the materials. So, combination of a novel method and materials should be used to achieve a high performance composite membrane for application in high temperature and/or low humidity fuel cells.

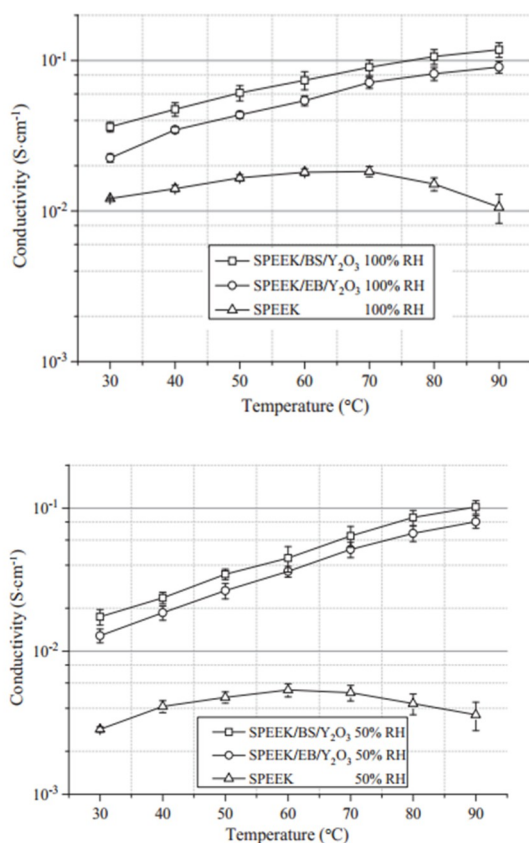


Figure 20. Conductivity of specimens at (a) 100% RH and (b) 50% RH, vs. temperature loading [62]

4. ACKNOWLEDGEMENT

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