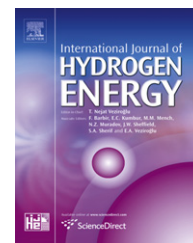


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Sulfonated PEEK-based polymers in PEMFC and DMFC applications: A review

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ABSTRACT

Nowadays, polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) are devices known for using proton conducting membranes. From a conceptual point of view, DMFC and PEMFC systems are very similar, except for being supplied by different fuels such as methanol and hydrogen, respectively. Commonly, PEMFCs are performed at temperature lower than 100 °C owing to the failure of the electrochemical performances of Nafion. Nevertheless, taking into account the poisoning effect of CO on the fuel cell catalyst (conventionally based on Pt), the ideal working temperature of the PEMFCs should be above 100 °C, where CO poisoning could be drastically reduced or avoided. Today, Nafion is recognized as the most used proton exchange membrane in the market, useful for both PEMFC and DMFC applications. It is based on a perfluorinated polymer and shows good thermal stability and high proton conductivity as main benefits. On the contrary, Nafion is an expensive material and suffers high fuel crossover (particularly, methanol crossover in DMFC applications) besides the proton conductivity loss above 100 °C. Therefore, in the last decades many scientists paid special attention on the development of new materials based on non-fluorinated polymers as an alternative to Nafion. One of the most promising class of is represented by the polyetheretherketone (PEEK). According to the specialized literature, interesting performances in terms of proton conductivity and thermo-chemical properties as well as low fuel crossover and costs are noticeable for sulfonated PEEK-based polymers. Indeed, many scientific applications are devoted to modify PEEK polymer for manufacturing membranes alternative to Nafion for both PEMFC and DMFC applications. Among them, important methods are exploited for preparing electrolyte membranes from PEEK such as: a) PEEK electrophilic sulfonation (S-PEEK); b) S-PEEK and non-functional polymers blending; c) S-PEEK, heteropolycompounds and poly-ether-imide doping with inorganic acids, etc.

In this review, the potentialities of PEEK-based polymers are discussed, pointing out the main benefits and drawbacks of these proton exchange membranes for fuel cell applications. As a case study, the use of sulfonated PEEK with cardo-group (PEEK-WC) is particularly stressed, pointing out the main characteristics for its applications in PEMFCs and DMFCs as an alternative to Nafion membrane.

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1. Introduction

In the last years, PEMFCs and DMFCs have attracted growing attention since they represented an alternative technology for power production in the field of both portable and stationary applications owing to their ability to convert the chemical energy of a fuel (hydrogen and methanol, respectively) directly into electrical energy with relatively high efficiency as well as for their adaptable size and relatively low operating temperature [1,2]. As a general consideration, DMFCs perform worse than PEMFCs even if they show some benefits over the latter ones. Among these advantages, DMFCs do not need a previous reforming stage to produce pure hydrogen because methanol may be directly supplied. Furthermore, in a possible future scenario, the existing infrastructure for gasoline could be useful for stocking methanol necessary to DMFCs supplying without significant variations. Nevertheless, the main drawback of DMFCs is the severe fuel crossover, which makes more competitive and attractive PEMFCs for their development and exploitation.

However, the growing environmental pollution due to the massive exploitation of derived of fossil fuels has imposed severe restrictions for the harmful emissions during the conventional processes for power productions (i.e. Kyoto Protocol). Therefore, PEMFCs and DMFCs could constitute a green and viable solution to these problems since they limit CO₂ and other harmful emissions in the atmosphere. Nevertheless, the main drawbacks that afflict their full commercialisation are represented by [3]:

- a) high cost of the proton exchange membrane;
- b) fuel crossover;
- c) anodic catalyst poisoning mainly caused by the CO, etc.

Today, commercial PEMFCs and DMFCs are operated housing such a sulfonated perfluorinated polymer as Nafion, manufactured by DuPont as an electrolyte membrane. Nafion shows excellent performances at low-medium temperature (up to 80–100 °C) and under fully hydrated conditions, while high cost and fuel crossover as well as loss of performances at temperatures higher than 100 °C are the main drawbacks [4]. Therefore, in the last years the scientific community has been involved in the development of several kinds of proton exchange membranes alternative to Nafion such as: sulfonated poly(ether-ether-ketone) [5–9], sulfonated polybenzimidazole [10,11], sulfonated polysulfone [12–16], sulfonated polyphosphazene [17] and many other modified and/or composite novel membranes [18–26].

Among the aforementioned opportunities, several studies pointed out that sulfonated PEEK polymer (S-PEEK) seems to constitute a real alternative to commercial Nafion since, in some cases, it shows comparable (or superior) proton conductivity performances to Nafion as well as a superiority in terms of thermo-chemical properties, lower fuel crossover and, particularly, lower costs [27,28].

Different sulfonation procedures can be utilized for producing electrolyte membranes from PEEK, which could be strictly resumed as reported below:

- a) PEEK electrophilic sulfonation [1,5–7,9,23,24],
- b) S-PEEK and non-functional polymers and/or solids blending [28–33,35],
- c) S-PEEK, heteropolycompounds and polyetherimide doping with inorganic acids, etc. [18,19,26,27,34].

Furthermore, among other studies, the sulfonation of a derivative, modified with cardo-group, PEEK-based polymer, the polyetheretherketone/cardo-group (PEEK-WC), represents another class of sulfonated PEEK-based polymers (S-PEEK-WC) showing interesting electrochemical performances, low fuel crossover and very good thermo-chemical properties with respect to Nafion [36–43].

However, it should be taken into account that the main aim of many scientists involved in PEMFCs and DMFCs development is to synthesize polymer electrolyte membranes showing high proton conductivity (σ) and low electronic conductivity, low fuel crossover, low electroosmotic drag coefficient, high chemical/thermal stability and mechanical resistance and, particularly, low-cost. All these characteristics are categorized into the “iron triangle” of performance, durability and cost. Therefore, the choice of PEEK instead of perfluorinated polymer backbones such as Nafion is mainly due to cost and electrochemical and chemical/physical stability considerations.

Nowadays, Victrex Company is the main producer of PEEK polymer in the market and its sulfonation is generally performed via sulfonic acid groups (SO₃H), which are directly introduced onto the polymer backbones, by modification or by polymerization of sulfonated monomers.

Sulfonated PEK, PEEK, PEEKK and PEEK-WC show interesting behaviours in terms of wettability, water flux, anti-fouling capacity, low fuel crossover and increased solubility in solvents for fuel cell processing. Indeed, the sulfonic acid functional groups aggregate to form a hydrophilic domain and, in case of hydrated conditions, the protonic charge carriers form, within inner space, charge layers caused by the dissociation of the acidic functional groups and the proton conductivity, assisted by water dynamics.

Various studies in the open literature confirmed that S-PEEK membranes may be durable enough under fuel cell operating conditions [1–4] and with a long life-time (sometimes >3000 h). Nevertheless, depending on the variation of the sulfonation degree (DS), the mechanical properties of S-PEEK membranes could deteriorate progressively (at higher DS). Indeed, according to a DS increase, the long term stability of highly sulfonated PEEK membranes is considerably affected owing to the hydroxyl radical initiated degradation. Otherwise, low sulfonated PEEK membranes show high thermal and chemical stability but, unfortunately, relatively low proton conductivity.

To solve this key issue, S-PEEK has been used as a major component in the synthesis of hybrid/blend membranes. In several cases, S-PEEK content ranging from 50% to 80% seems to be the most suitable for exhibiting high proton conductivity and thermo-mechanical performances, even if recently higher contents (>80%) have made possible high temperature tolerance and electrochemical performances comparable (or superior) to Nafion [1,27,33,35].

Nevertheless, many variables influence the performances of pristine S-PEEK and S-PEEK-based membranes and, only by means of a good combination among them, real competitive and alternative membranes to Nafion are possible. The present work reviews the most recent findings in the field of S-PEEK and its derivative polymers, paying special attention on the development of S-PEEK-WC membranes for both PEMFC and DMFC applications.

2. Synthesis of pristine S-PEEK membranes

The distinct differences in the microstructures and in the acidity of the sulfonic acid functional groups may qualitatively explain the difference within S-PEEK and Nafion [1,3,44]. Indeed, Nafion membrane is based on a perfluorosulfonic polymer that naturally combines an extremely high hydrophobicity related to the perfluorinated backbone with an extremely high hydrophilicity induced by the sulfonic acid functional groups in one macromolecule. When Nafion is humidified, the presence of water emphasizes these two distinct behaviours, making possible the coexistence of two hydrophobic/hydrophilic regions completely separated. In particular, a well-connected hydrophilic domain is formed due to the sulfonic acid functional groups aggregation, which is responsible for the protons and water transport. In the meanwhile, the hydrophobic domain prevents the polymer dissolving in water also providing it with the morphological stability. Otherwise, owing to a smaller polymer backbone flexibility, the separation into a hydrophilic and a hydrophobic domain is less pronounced for the S-PEEKs with respect to Nafion [3]. Therefore, concerning the transport properties and the morphological stability of S-PEEKs, by taking into account its smaller difference within hydrophilic/hydrophobic regions caused by a lower hydrophobicity of the backbones as well as a lower acidity and polarity of the sulfonic acid functional groups, a different behaviour takes place with respect to Nafion. In detail, as schematically shown in Fig. 1, the water filled channels of the S-PEEKs are narrower compared to those of Nafion. Indeed, they are less separated and more branched with more dead-end “pockets”. These features correspond to the larger hydrophilic/hydrophobic interface and, therefore, also to a larger average separation of neighbouring sulfonic acid functional groups [3].

2.1. Sulfonation of PEEK polymers

Regarding S-PEEK polymers, it should be taken into account that their mechanical properties are affected by different variables such as molecular weight, etc., whereas the membrane characteristics depend on the polymeric structure, casting solvents, membrane thickness uniformity, etc. However, the most significative parameter affecting S-PEEK behaviours is the polymer sulfonation procedure, which can be performed following various approaches, each one showing a series of benefits and drawbacks. In particular, S-PEEK polymers may be synthesized via direct electrophilic sulfonation by using concentrated sulphuric acid or chlorosulphuric acid. If concentrated sulphuric acid at 95–98% is used during the sulfonation procedure, PEEK polymer degradation and the

cross-linking reactions may be avoided. Otherwise, they occur when 100% of sulphuric acid or chlorosulphuric acid are used. Presumably, the cross-linking involves the sulphone groups formation and, therefore, by using a mixture containing H_2SO_4 and a low water content, the decomposition of the aryl pyro-sulfate intermediate is achievable. For instance, it is required for sulfone groups formation owing to the role played by water. Furthermore, PEEK sulfonation may be performed introducing directly the sulfonic acid group onto the polymer backbone [45–47] as well as by modification or via polymerization of the sulfonated monomers [15,18]. However, the direct synthesis of S-PEEK from sulfonated monomers seems to be more advantageous than the post-sulfonation since the cross-linking formation and other side reactions are avoided, allowing to reach better thermal stability and mechanical properties. Furthermore, the concentration as well as the sulfonate groups positions (e.g., *meta*-, *para*- and *ortho*-) within the directly-synthesized S-PEEKs may be easily controlled [9]. On the contrary, by following a post-sulfonation procedure, not only both mechanical and thermal degradation of S-PEEK polymers are possible but also loss of control on the sulfonating process [5]. However, whatever sulfonation procedure affects the chemical character of PEEK polymer, reducing the crystallinity and, as a consequence, modifying the polymer solubility, Table 1. As shown in this table, the polymer solubility strictly depends on the DS, which briefly represents the sulfonic groups concentration in the matrix of PEEK polymer.

In the case of $\text{DS} < 30\%$, S-PEEK polymers are soluble in dimethylformamide (DMF), dimethylsulfoxide (DMSO) or in *N*-methylpyrrolidone (NMP). For $\text{DS} > 50\%$, S-PEEK is soluble in DMAc also at room temperature [27], while for DS above 60%, S-PEEKs are highly swollen in methanol/water solution at 80–90 °C and, for these reasons, they are not suitable for the DMFC applications [6]. At $\text{DS} > 70\%$, S-PEEKs are soluble in methanol and, at $\text{DS} = 100\%$, in hot water [45,46]. When PEEK sulfonation is carried out via concentrated sulphuric acid procedure, it is limited and takes place only on the four chemically equivalent positions of the hydroquinone segment and the DS does not overcome the value of 100% owing to the electron-withdrawing deactivating effect of $-\text{SO}_3\text{H}$ group once it is exactly introduced in the correct ring [48,49]. The restant two phenyl rings connected through the ether linkages are, then, deactivated by electron-withdrawing effect of the carbonyl group for electrophilic sulfonation [50]. If this sulfonation procedure takes place, DS can be determined quantitatively by ^1H NMR analysis [19]. According to the nomenclature of the aromatic protons for S-PEEK repeating unit, Fig. 2 shows the presence of a sulfonic acid group in the ^1H NMR spectra, which determines a significant down-field shift of the hydrogen H_E pick compared with H_C , H_D picks in the hydroquinone ring, Fig. 3. Thus, the H_E content is estimated by means of the intensity of the H_E signal, being equivalent to the SO_3H group. The ratio between the peak area of the distinct H_E signal (A_{H_E}) and the integrated peak area of the signals, corresponding to all the other aromatic hydrogen atoms ($A_{\text{H}_{\text{A,B,C,D}}}$), represents the DS, which may range from 0 to 100%.

Nevertheless, not-sulfonated PEEK is insoluble in most of the common solvents all solvents and, as a consequence, its ^1H NMR spectrum could be not recordable. Therefore, considering what reported in Fig. 3, low sulfonation level of

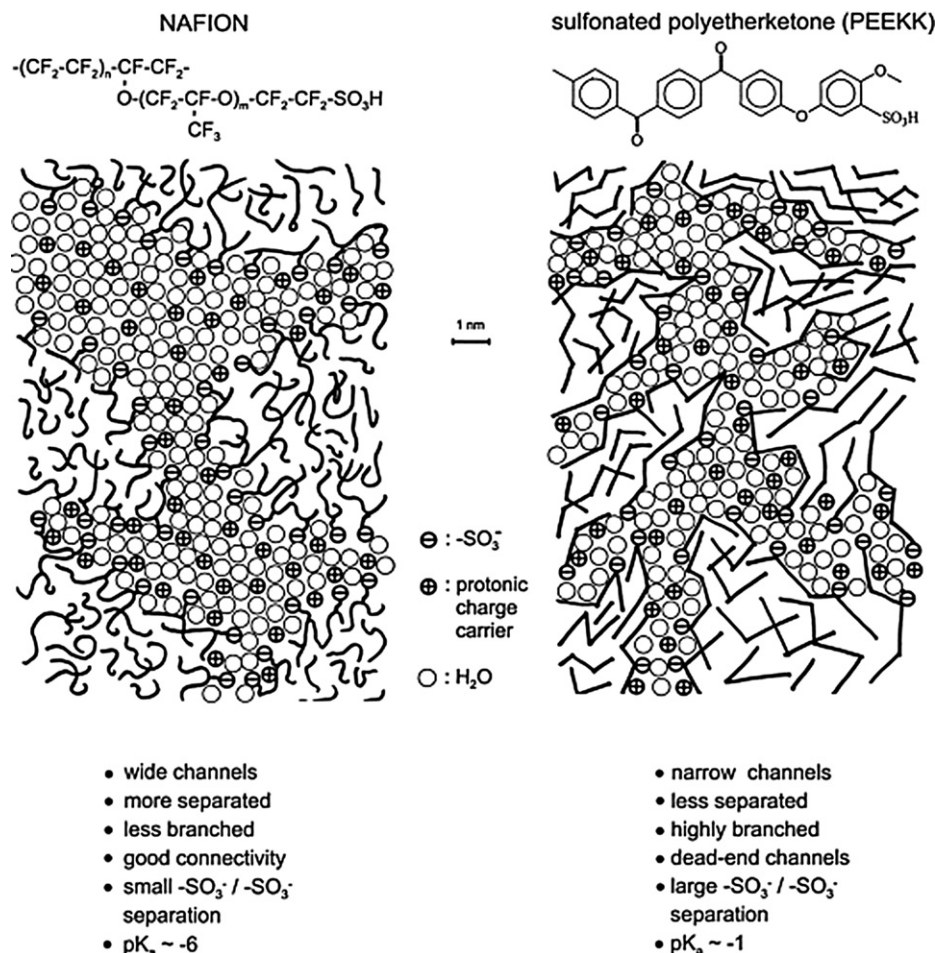


Fig. 1 – Scheme for the comparison between hydrophobic/hydrophilic separation regions in the microstructures of NAFION and S-PEEK [2].

S-PEEK corresponds to low DS, which means that a significant proportion of repeating units are non-sulfonated as well as that H_C and H_D of the unsubstituted hydroquinone ring appear as a characteristic singlet.

In the case of S-PEEK procedure realized through such two stages as monomer synthesis and polymer preparation, the DS indicates the ratio between the sulfonate monomer group number and the repeating unit in the PEEK polymer chain, which may overcome 100% [9]. Therefore, when the synthesis

of S-PEEKs is carried out via nucleophilic aromatic substitution reaction, the first stage is represented by the synthesis of sulfonated monomer, realized through fuming sulphuric acid. Then, the S-PEEKs formation is achieved by co-condensation reaction and the DS is controlled by the ratio between the sulfonated monomer and the unsulfonated monomer. By increasing this ratio, the DS of S-PEEKs may, then, overcome 100%, Fig. 4.

However, the DS may affect several important parameters not depending strictly of PEEK sulfonation procedure utilized. In the following, the main parameters useful for describing the behaviours of S-PEEK polymers and potentially affected by DS variation are summarized:

- a ion exchange capacity (IEC),
- b glass transition temperature (T_g),
- c water uptake (W.U.),
- d weight loss,
- e proton conductivity (σ).

2.1.1. IEC and DS influence for S-PEEK membranes

The IEC of the S-PEEKs depends on DS as well as on the reaction time of the sulfonation reaction. As shown in Table 2, IEC may be higher than 2.0 meq./g when the DS is higher than

Table 1 – S-PEEK polymer solubility at various DS (sulfonation degree) and different solvents.

S-PEEK polymer solubility	
DS	Type of solvent
<30%	DMF DMSO NMP
>50%	DMAc
>60%	MeOH/Water solution
>70%	MeOH
100%	Hot water

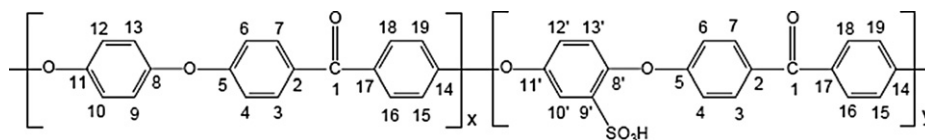


Fig. 2 – Structure and atom numbering of S-PEEK, $x + y = n$, $y/(x + y) = \text{DS}$.

90%, while lower values between 1.3 and 1.9 are achievable at $\text{DS} < 70\%$. However, as sulfonated cation-exchange membranes, S-PEEKs should have IEC, at least, ranging between 1.4 and 1.7 meq/g in order to allow low ionic resistances and making them suitable for the application in electromembrane processes. For instance, IEC indicates the density of ionisable hydrophilic groups in the membrane matrix, which are responsible for the membrane ionic conductivity. Furthermore, the uncrosslinked sulfonated membranes show quite high swelling, which leads to poor mechanical properties and low ion permselectivity, making them not suitable for PEMFC applications, particularly at $T > 80^\circ\text{C}$. Therefore, a key issue is the depletion of S-PEEK swelling in order to improve both mechanical and conductive properties. In particular, different strategies are available for depleting the swelling of cation-exchange membranes such as the a) cross-linking of sulfonated polymers, b) blending of cation-exchange polymers, showing a specific interaction with the cation-exchange group, c) blending with polymers capable of hydrogen bonds formation, d) compatibilization of blend polymers by hydrogen bonds formation.

2.1.2. T_g and DS influence for S-PEEK membranes

The T_g represents an indicator of thermo-resistance of the polymers. PEMFC and DMFC normally work at temperature ranging between 80 and 120°C and, therefore, a T_g higher than these values indicates if the electrolyte polymer is temperature resistant and if any thermo-degradation may take place during the fuel cell operations. Commonly, T_g increases with DS, depending on the gradual introduction of $-\text{SO}_3\text{H}$ groups into the PEEK polymer. This depends on the increase of the intermolecular interaction due to the hydrogen bonding of SO_3H groups (ionomer effect) and to the increased molecular bulkiness.

2.1.3. W.U. and DS influence for S-PEEK membranes

The sulfonation of PEEK polymer enhances its hydrophilicity and, as a consequence, the water absorption becomes a function of DS. In the highly sulfonated S-PEEKs, the density of the

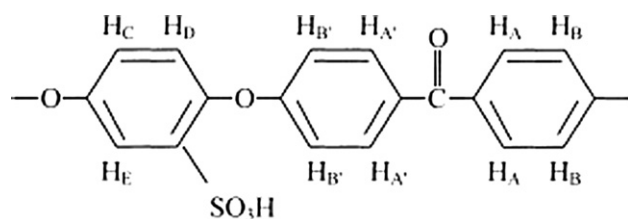


Fig. 3 – Aromatic protons nomenclature for a generic S-PEEK repeat unit.

sulphuric groups is high and may involve clustering or agglomeration. Clustered ionomers absorb more water and, therefore, a large W.U. may suggest the presence of ion-rich regions where proton transfer is particularly fast [6,19].

2.1.4. Weight loss and S-PEEK membranes

Concerning the weight loss, it should be considered that PEEK polymer is temperature resistant and, therefore, the weight loss starts at temperature not lower than around 520°C [19]. In particular, the pyrolytic degradation of PEEK results in the formation of benzene and phenols. The latter is the main product of PEEK's pyrolysis, which is produced in the early chain scission reaction involving ether instead of carbonyl linkages. For example, Zaidi et al. [19] found two weight loss steps for their S-PEEK polymer, which are reflected by two broad peaks in the DTG curve in two separate temperature ranges. The authors stated that the first weight loss peak in S-PEEK is probably due to the splitting-off of sulfonic acid groups. The second weight loss is, then, accounted for the sulfonic acid decomposition. Therefore, Zaidi et al. affirmed that, generally speaking, S-PEEK membranes may be considered thermally stable up to around 300°C and that this temperature is only marginally affected by a DS increase up to 80%.

2.1.5. Proton conductivity and S-PEEK membranes

One of the most important indicator of the S-PEEKs electrochemical performances is the proton conductivity, which strictly depends on DS and humidity status (relative humidity–R.H.) as well as on other important parameters such as temperature, W.U. and so on.

In most of cases, DS plays the principal role concerning the proton migration through an electrolyte polymer such as

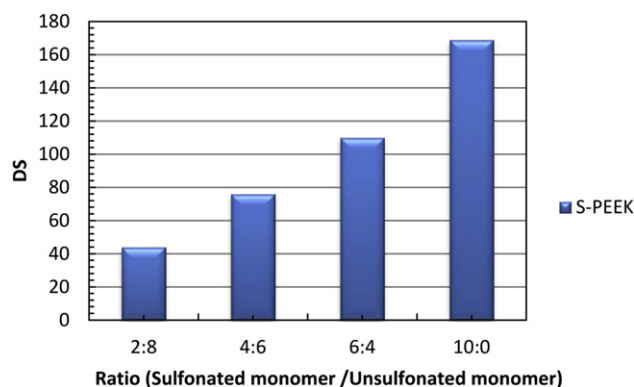


Fig. 4 – Sulfonation degree (DS) of S-PEEK polymer (obtained by titration) vs sulfonated monomer over unsulfonated monomer ratio.

Table 2 – Ion exchange capacity (IEC) and sulfonation degree (DS) of pristine S-PEEK polymers: literature data.

Pristine S-PEEKs			
Polymer	DS (%)	IEC (meq./g)	Reference
S-PEEK	80	1.31	[9]
S-PEEK	70	1.43	[2]
S-PEEK	60	1.79	[35]
S-PEEK	64	1.88	[27]
S-PEEK	–	2.07	[33]
S-PEEK	93	2.37	[21]
S-PEEK	–	2.48	[51]
S-PEEK	90	2.50	[35]
S-PEEK	98	2.68	[29]

S-PEEKs. As DS increases, S-PEEKs show an increase of solubility in organic solvents (e.g. DMAc), caused by a crystallinity decrease [45]. As a consequence, the polymer becomes more hydrophilic and absorbs more water, which facilitates the proton transport. Therefore, the sulfonation status of S-PEEKs raises their conductivity not only by increasing the number of protonated sites (SO_3H), but also through the formation of water mediated pathways for protons. Furthermore, the DS makes an influence superior to the temperature affection on S-PEEK conductivity. Indeed, a S-PEEK membranes having a DS around 40% do not show any conductivity improvement by increasing the operating temperature, but, on the contrary, it decreases. From the open literature [19], some example indicates that the conductivity of a S-PEEK with a DS = 48% may increase up to 85 °C and, then, drop sharply to very low values. In the meanwhile, for a DS ranging between 70 and 74%, S-PEEK membrane shows an increase of conductivity and, only at $T > 100$ °C, it gradually decreases. S-PEEKs with a DS around 80% show a different conductivity behaviour with respect to samples having lower DS: the conductivity increases slowly in the range of 20–50 °C, more rapidly between 50 and 100 °C and, then, gradually up to 145 °C [19]. The aforementioned conductivity dependence/variation on DS may be better explained pointing out that two different competing behaviours take place and depend on temperature. At low temperature, the effect of dehydration on proton conductivity may be negligible, but at high temperature the effect of dehydration on proton conductivity cannot be neglected and may be assumed as a dominant effect. The dehydration apparently starts at room temperature for S-PEEKs having a DS = 40% and, then, it shifts towards higher temperatures with an increase of DS. For instance, S-PEEK samples with DS = 40% or less lose water so fast that the dehydration suppresses any conductivity rise, whereas for S-PEEKs with DS around 60%, the water loss rate induces a conductivity depletion at temperature of around 50 °C. S-PEEK membranes with higher DS start to lose conductivity at higher temperature owing to their stronger ability of retaining water. Indeed, for S-PEEKs with DS = 80%, the water retention is quite high and the dehydration only lowers the rate of conductivity increasing trend up to 145 °C. Therefore, to improve the proton conductivity of S-PEEKs, not only the W.U. plays an important role but also the capacity of retaining water [21].

As previously introduced, another important variable affecting S-PEEK proton conductivity is the relative humidity, which indicates the hydration status of the sulfonated polymer. Firstly, the acid strength has an appreciable influence on proton conductivity only at low R.H. Otherwise, at higher R.H., the increased hydration of the material allows to level the acid strength of the sulfonic group, determining its full dissociation. Accordingly, the differences in the S-PEEKs' protonic conductivity become progressively smaller at high R.H. values. However, the acid strength of the SO_3H groups in perfluorinated polymers is considerably higher than that in non-perfluorinated polymers. Nowadays, Nafion is the best protonic conductor at low R.H. but, in comparison with other less superacids polymers such as S-PEEKs, the differences in conductivity become small or vanish for R.H. close to 100%.

As stated above, S-PEEK conductivity increases appreciably with increasing DS and, contrary to Nafion, the temperature plays a strong effect on proton conductivity. Furthermore, at medium temperature and high R.H., the conductivity essentially depends on the concentration of the sulfonic groups, while the effect of the acid strength is evident only at low R.H. A reasonable explanation could be given by considering that, according to a temperature increase, a gradual decrease of the interaction forces between the polymeric chains favours a greater hydration of the polymer for a given constant value of R.H. [51].

In Table 3, for pristine S-PEEKs, various literature data such as proton conductivity, casting solvent, temperature and so on are resumed. Regarding proton conductivity, as shown in Table 3, several discrepancies are evident within the reported literature data. However, as a general comment, the higher the DS the higher the proton conductivity. Indeed, in Table 3, at 25 °C the highest proton conductivity corresponds to high DS values of S-PEEK sample. For example, Jones et al. [53] found $\sigma = 8.0 \times 10^{-2}$ S/cm for their S-PEEK samples, similarly to Kreuer [2] with $\sigma = 7.5 \times 10^{-2}$ S/cm (DS = 70%) and Li et al. [33] with $\sigma = 5.7 \times 10^{-2}$ S/cm (DS = 80%). On the contrary, other authors found lower proton conductivities at the same temperature: Gil et al. [9] and Robertson et al. [49] obtained $\sigma = 2.8 \times 10^{-3}$ S/cm (DS = 80%) and $\sigma = 5.5 \times 10^{-3}$ S/cm (DS = 82%), respectively, while Xing et al. [8] reached $\sigma = 1.0 \times 10^{-5}$ S/cm (DS = 65%). At higher temperature ($T = 80$ °C), these discrepancies still exist, even if some authors obtained very high proton conductivity, sometimes higher than Nafion. For example, Intaraprasit et al. [27] and Li et al. [33] reached $\sigma = 2.3 \times 10^{-1}$ S/cm (DS = 64%) and $\sigma = 1.9 \times 10^{-1}$ S/cm (DS = 80%), respectively. Otherwise, low proton conductivity values were found by Alberti et al. [51] and Xing et al. [8]: $\sigma = 4.0 \times 10^{-3}$ S/cm and $\sigma = 7.5 \times 10^{-4}$ S/cm (DS = 65%), respectively. However, similar discrepancies were observed in many other cases. A possible reason may be accounted for the preparation and treatment conditions of S-PEEKs. In fact, the SO_3H groups of S-PEEK, responsible for charge transfer in PEMFCs, are able to form strong hydrogen bonding with such solvents as DMF or DMAc, affecting significantly the conductivity of the membranes and reducing the charge carrier number and/or mobility. Therefore, depending on the casting solvent, different conductivity values are possible owing to the different interactions between the casting solvent and the S-PEEK samples.

Table 3 – PEMFC and DMFC performances of pristine S-PEEK from open literature.

Polymer	DS (%)	W.U. _{25 °C} (%)	MeOH permeability [cm ² /s]		Conductivity [S/cm]		β [S·s/cm ³]	Casting solvent	PEEK sulfonation procedure	Reference
			T = 25 °C	T = 80 °C	T = 25 °C	T = 80 °C				
S-PEEK	64	32	—	—	—	2.3×10^{-1}	—	DMAc	Concentrated H ₂ SO ₄	[27]
S-PEEK	80	71	—	9.8×10^{-7}	5.7×10^{-2}	1.9×10^{-1}	5.3	NMP	Aromatic nucleophilic substitution	[33]
S-PEEK	—	92	—	—	8.0×10^{-2}	1.6×10^{-1}	—	DMAc	Aromatic nucleophilic polycondensation	[53]
S-PEEK	70	—	—	—	7.5×10^{-2}	1.5×10^{-1}	—	—	Concentrated H ₂ SO ₄	[2]
S-PEEK	98	40	—	—	—	1.1×10^{-1} ^a	—	NMP	Concentrated H ₂ SO ₄	[29]
S-PEEK	68	—	—	—	—	8.0×10^{-2} ^b	—	DMSO	Concentrated H ₂ SO ₄	[28]
S-PEEK	93	67	1.54×10^{-6}	—	9.3×10^{-3}	5.5×10^{-2}	3.8	DMAc	Concentrated H ₂ SO ₄	[21]
S-PEEK	47	100	—	1.5×10^{-7}	5.0×10^{-3}	1.7×10^{-2}	5.1	DMF	Concentrated H ₂ SO ₄	[6]
S-PEEK	80	37	5.00×10^{-8}	3.0×10^{-7}	2.8×10^{-3}	6.7×10^{-3}	4.3	DMF	Direct synthesis by sulfonated monomer	[9]
S-PEEK	—	75	—	—	—	4.0×10^{-3}	—	NMP	Concentrated H ₂ SO ₄	[51]
S-PEEK	90	—	—	—	—	3.0×10^{-2} ^b	—	DMSO	Concentrated H ₂ SO ₄	[35]
S-PEEK	82	—	—	—	5.5×10^{-3}	2.4×10^{-2}	—	DMAc	Concentrated H ₂ SO ₄	[49]
S-PEEK	69	23	—	—	3.8×10^{-2}	—	—	DMF	Concentrated H ₂ SO ₄	[52]
S-PEEK	65	—	—	—	1.0×10^{-5}	7.5×10^{-4}	—	DMF	Concentrated H ₂ SO ₄	[8]
S-PEEK	79	32	—	—	1.6×10^{-2}	—	—	DMAc	Concentrated H ₂ SO ₄	[50]

a calculated.

b 100 °C.

In particular, it is possible that S-PEEK samples at high DS contain some amount of residual sulphuric acid, difficult to be washed out. In the presence of DMF or DMAc, it can react making possible the decomposition of the solvents into DMAc sulphate and formic or acetic acid. As a consequence, this interaction causes a conductivity decrease due to a lower sulphuric acid concentration. In the presence of water, SO₃H groups inevitably form hydrogen bonds with oxygen. The intensities of the H-bonding absorption is exactly two and six times the intensity of the aromatic hydrogen in *ortho*-position with respect to the sulfonic acid group. Afterwards, one molecule with exactly two types of hydrogen atoms in the ratio of 1:6 is present for each SO₃H group after interaction with DMF. Indeed, DMF shows exactly these hydrogen atom numbers: six in the two methyl groups and one on the aldehyde carbon. By using another solvent such as DMAc or NMP for preparing S-PEEK membranes, no evidence of hydrogen bonded is recognized. This suggests that DMF molecule is particularly prone to hydrogen bonding with SO₃H groups, while the contrary takes place with DMAc. Therefore, the discrepancies among many values of proton conductivity for S-PEEKs present in literature may depend on the differences existing between the membranes prepared through different casting solvents. This is obviously explicable on the basis of strong bonding, which blocks the protons of the SO₃H groups excluding them from charge transfer and causing a proton conductivity depletion [49,54].

2.1.6. Fuel crossover and S-PEEK membranes

It is well known that the proton conductivity describes the membrane capacity to process the fuel supplied both to PEMFCs and DMFCs with the intent of producing electricity and forming water as a secondary product owing to the

reaction with oxygen at the anode electrode. Nevertheless, part of the feed may also permeate through the polymeric membrane without being processed, with a consequent fuel efficiency loss, well known as a *fuel crossover*. In particular, fuel crossover represents the main drawback of Nafion, specially when used in DMFCs.

Therefore, alternative membranes to Nafion such as the S-PEEKs should be able to guarantee the depletion of the fuel crossover, particularly in DMFC applications. Thus, the main parameter for S-PEEK membranes to be taken into account is the DS, which, if higher than 70%, leads the membranes to become methanol soluble and, consequently, not applicable for this kind of fuel cells.

However, the different methanol permeance through S-PEEKs and Nafion may be accounted for the difference in their microstructures. In Nafion membrane, depending on its high hydrophobicity of the perfluorinated backbone and its high hydrophilicity of the SO₃H groups, it would give rise to form hydrophobic/hydrophilic domains, especially in the presence of water. As previously stated, the sulfonic acid groups aggregate to form hydrophilic domains. These hydrophilic domains are interconnected in Nafion membrane and, not only proton and water but also a smaller polar molecules such as methanol can go through them, leading to the methanol crossover. With respect to Nafion, the microstructure of S-PEEKs is distinctly different owing to the smaller hydrophobic/hydrophilic domains and the lower flexibility of the polymer backbone. Therefore, for S-PEEKs the separation into hydrophilic and hydrophobic domains is less pronounced and, for this reason, their methanol permeances are lower than the Nafion ones [6,21,22].

High proton conductivity and low methanol permeability ($P_{\text{CH}_3\text{OH}}$) are two of the essential characteristics that

a polymer electrolyte membrane should possess to constitute a viable alternative to Nafion in DMFC applications. These parameters may be combined to constitute the β selectivity (or, shortly, selectivity: $\beta = \log[\sigma/P]$), which is useful for clearly comparing various S-PEEK membranes. Indeed, β selectivity is a common metric for evaluating membrane performances and, as reported in Table 3, the few data about β selectivity show how, by increasing DS, the selectivity decreases. Indeed, as previously stated, by overcoming DS = 70%, S-PEEK becomes more soluble in methanol and, as a consequence, methanol permeability increases determining a depletion of β selectivity.

3. Derivative S-PEEK membranes for PEMFC and DMFC applications

According to what discussed in the previous paragraphs, it is well known that, for S-PEEK polymers, the absence of a clear separation within hydrophilic/hydrophobic regions makes possible the presence of narrow and poorly connected water channels and a large separation between the sulfonic acid groups. Therefore, in this case the effect of dehydration may cause the depletion of proton conductivity

and it may affect the morphological stability. With the intent of attaining an equilibrated balance between the hydrophilic and hydrophobic components as well as to avoid the aforementioned effects, various strategy can be proposed such as the use of inorganic fillers for the development of composite membranes, polymer blending and acid/basic doping.

A fruitful approach to enhance the S-PEEK performances in PEMFC and DMFC applications is, for example, the preparation of crosslinked membranes through the ionomeric polymers blending. This technique takes advantage from the combination of the positive characteristics of each component of the blend. In particular, enhanced electrochemical performances are expected, taking into account that one of the components may lower the average separation within acidic groups. Indeed, the proximity of acidic functions could also lead to significant conductivity in anhydrous conditions, in which a non-vehicular mechanism can be considered as a responsible of proton transfer from a donor to an acceptor site, without the role of water as a carrier. The performances of different modified S-PEEK membranes have been reported in this review, particularly those used in fuel cells operating at low/medium temperature (80–200 °C), Table 4. Therefore, for each kind of modified S-PEEK based membranes, the main parameters affecting the proton

Table 4 – Properties of derivative, composite/hybrid S-PEEK based membranes.

Membrane type	S-PEEK DS (%)	W.U.25 °C (%)	IEC (meq./g)	MeOH permeability [cm ² /s]		Conductivity [S/cm]		β [Ss/cm ³]	Casting solvent	Reference
				T = 25 °C	T = 80 °C	T = 25 °C	T = 80 °C			
Si-SPSU/S-PEEK	90	50 ^a	—	—	—	—	6.4×10^{-2} ^a	—	DMA	[23]
Si-SPSU/S-PEEK	90	45 ^b	2.48	—	—	—	3.0×10^{-2} ^b	—	DMA	[35]
SiS-PEEK	90	240	—	—	—	2.0×10^{-2}	—	—	DMSO	[24]
HPA/S-PEEK	80	600	—	—	—	—	9.5×10^{-2} ^b	—	DMAc	[18]
S-PEEK/BPO ₄	50–80	>80	—	—	—	7.5×10^{-2}	—	—	DMAc	[25]
S-PEEK/PANI	44.5	42.2 ^c	1.21	2.1×10^{-7}	—	—	1.8×10^{-3} ^b	3.9	DMF	[26]
S-PEK/ZP-ZrO ₂	60	35.7	—	—	—	1.0×10^{-2}	—	—	DMF	[59]
S-PEEK/Analcime 10%wt	64	32	1.49	—	—	—	4.0×10^{-1} ^e	—	DMAc	[27]
S-PEEK/Beta10%wt	73	—	—	—	—	1.1×10^{-1}	—	—	DMAc	[28]
S-PEEK/MBS15%wt	65	26	—	3.8×10^{-7}	—	—	6.4×10^{-2} ^e	5.2	DMA	[60]
S-PEEK/PBI5%	~82	~35	1.54	5.0×10^{-7}	—	4.6×10^{-2}	8.0×10^{-2}	5.1	DMAc	[32]
S-PEEK/PBI20%	~36	~13	0.67	0.3×10^{-7}	—	1.0×10^{-2}	2.2×10^{-2}	5.5	DMAc	[32]
S-PEEK/PBI15%	—	~50	1.61	3.1×10^{-7}	—	2.8×10^{-2}	1.0×10^{-1}	~5.0	NMP	[33]
S-PEEK/PBI2.5%	—	60	1.98	7.9×10^{-7}	—	5.6×10^{-2}	1.8×10^{-1}	~5.0	NMP	[33]
S-PEEK-WC	82	—	1.47	1.9×10^{-6}	—	—	2.5×10^{-2} ^d	4.1	DMF	[61]
S-PEEK-WC-3h	40	14	0.76	—	—	—	1.7×10^{-2} ^a	—	DMA	[39]
S-PEEK-WC	99	17	—	—	—	—	5.4×10^{-2}	—	DMF	[43]
S-PEEK-WC	90	21	—	—	—	—	2.5×10^{-2} ^b	—	DMF	[62]
S-PEEK-WC	110	44	1.87	1.6×10^{-7}	—	2.9×10^{-2}	5.5×10^{-2}	~5.3	NMP	[41]
S-PEEK-WC-Zr/SPP	57	20	—	2.2×10^{-7}	—	—	2.0×10^{-2}	4.1	DMF	[42]
S-PEEK-WC-HPA	88	20	1.05	—	—	—	$\sim 4.0 \times 10^{-2}$	—	DMA	[64]
PS-PEEK-WC48%	—	9.4	0.22	—	—	—	7.3×10^{-3} ^b	—	DMA	[63]
NAFION117	—	38	0.91	—	—	1.0×10^{-1}	$1.5\text{--}1.9 \times 10^{-1}$	4.4	—	[42]

a 120 °C.

b 100 °C.

c 80 °C.

d 115 °C.

e 90 °C.

conductivity and other important variables are discussed in the following sub-sections.

3.1. SiS-PPSU/S-PEEK and SiS-PEEK hybrid membranes

An example of the physical blending useful for improving the mechanical properties of the composite membrane is represented by the combination of a fully aromatic polymer such as polyphenylsulfone (PPSU), having high thermal stability and resistance to oxidation, and S-PEEK at elevated DS. The PPSU is similar to S-PEEK in the structure, its solubility in organic solvents makes possible to perform the functionalization reactions in homogeneous conditions, giving also the possibility to introduce sulfonic acid groups. Similarly to S-PEEK, the proton conductivity of the sulfonated PPSU (S-PPSU) depends on DS: proton conductivity values of about 10^{-3} S/cm have been reported for S-PPSU with DS = 0.7, while higher DS may cause the water soluble behaviours of the membranes, preventing possible application in fuel cells. A silylated telechelic hybrid polymer may allow the preparation of a composite S-PEEK based membranes with proper mechanical and proton conductivity properties by introducing an inorganic network, covalently linked to the organic backbone of highly sulfonated PPSU, (SiSPPSU), to constitute a blend with a highly sulfonated PEEK (DS = 90%) [23,35]. In detail, the SiSPPSU shows quite low solubility and poor plastic properties in common casting solvents such as DMSO, DMF, DMA, NMP, etc. Di Vona et al. [23] and Sgreccia et al. [35] demonstrated that, in anhydrous conditions, proton transfer takes place through H^+ hopping within sulfonic group; thus, all $-SO_3H$ substituents appear to contribute to proton conductivity. Up to 5 wt.% content of SiSPPSU in blends with S-PEEKs, the huge number of SO_3H groups enhances the conductivity making available at close distance extra sites for proton hopping. Above this SiSPPSU concentration in the S-PEEK blend (7% of SiSPPSU), Sgreccia et al. [35] found a proton conductivity at 100 °C around $3.0 \cdot 10^{-2}$ S/cm similar to that of pristine S-PEEK membrane used during the experimental campaign, demonstrating that a hybrid SiPPSU/SPEEK membrane may be useful for PEMFC application above 80 °C, guaranteeing good proton conductivity and thermal stability.

Regarding other hybrid S-PEEK based membranes, by adding a sufficient amount of inorganic component such as $SiCl_4$ to a highly sulfonated PEEK (DS up to 90%), improvements of S-PEEK mechanical properties are noticeable without altering significantly the proton conductivity performances. The preparation of this hybrid membranes involves as a first stage the reaction within S-PEEK and butyllithium. Afterwards, a successive reaction with $SiCl_4$, followed by alcoholysis, drives to the formation of a the SiS-PEEK composite membrane. One of the benefits of this hybrid membrane is that, contrary to pristine S-PEEK at elevated DS, SiS-PEEK is not soluble and does not form gel if immersed in water [50]. Furthermore, SiS-PEEK membranes show elevated water uptake, remaining flexible and easy to handle. This is due to the formation of covalently bound inorganic clusters, which increase the level of water uptakewithout excessive swelling or solubility in water. SiS-PEEK membranes show also good proton conductivity values, around 2.0×10^{-2} S/cm at 25 °C (Table 4), combined to their enhanced solubility properties [24].

3.2. S-PEEK/HPAs hybrid membranes

The incorporation of solid heteropolyacids (HPA) into partially sulfonated PEEK polymeric matrix constitutes a fruitful approach to enhance the S-PEEKs proton conductivity. Tungstophosphoric acid (TPA), its sodium salt (Na-TPA) and molybdophosphoric acid (MPA) are an example of HPAs and are recognized as the most conductive solids electrolytes at room temperature among the inorganic solids [19,55,56]. HPAs show high solubility in polar solvents and their strong acidity is accounted for the large size of the polyanion that yields low delocalized charge density. In the case of hydrated HPAs adequately embedded in a hydrophilic polymer matrix, they transfer to the composite membrane their high proton conductivity, maintaining the mechanical properties of the polymeric membrane. In detail, the binder matrix is constituted of partially sulfonated PEEK, which provides the polymer matrix with some hydrophilicity. Thus, composite S-PEEK/HPA membranes are synthesized by means of the incorporation of HPA (TPA, MPA and Na-TPA) into the S-PEEK polymeric matrix, showing higher T_g than the pristine S-PEEK membranes with a thermal stability up to around 250 °C. Increased T_g are probably caused by a reduction of the chain mobility, which is due to the interaction of the solid acid with polar groups of the S-PEEK polymeric chain.

S-PEEKs with a DS ranging between 70% and 80% may take advantage by the incorporation of 60 wt.% of HPAs, which involves an enhancement of proton conductivity and its stability, compared to pristine S-PEEK at temperatures higher than 80 °C. TPA incorporation in S-PEEK based membranes allows higher proton conductivity values to be achieved with respect to membranes incorporating Na-TPA and MPA. Indeed, TPA is a stronger acid and yields a higher proton conductivity enhancement as well as a better water retention at relatively high temperature. As a consequence, increased W.U. are expected for hybrid membranes based on HPAs incorporation into the S-PEEK polymeric matrix because they absorb more water than pristine S-PEEK membranes. The enhancement of W.U. due to the HPAs incorporation into S-PEEK polymeric matrix represents only one of the factors affecting the proton conductivity. Other factors such as the polymeric intrinsic conductivity, the particle size and spatial distribution, the aqueous phase dispersion, the solid phase loading, the strength, density and softness of the solid acid sites affect the dependence of conductivity on the water content. In the case of Nafion membranes, defined as nanoporous inert ‘sponges’ of hydration, water shows a little interaction with the polymer chain and forms a hydration shell around the SO_3H acid groups [57]. In HPA/S-PEEK hybrid membranes, the aqueous phase is more continuous and, therefore, it leads to higher W.U. and contributes to a greater extent to proton conductivity, achieving values of around 10^{-1} S/cm, as reported in Table 4.

3.3. BPO₄/S-PEEK hybrid membranes

Other hybrid membranes may be manufactured by using, for example, fine powder of boron orthophosphate (BPO₄) incorporated into partially sulfonated PEEK polymer. Sometimes, BPO₄/S-PEEK composite membranes may show higher

conductivities than HPAs/S-PEEK, even if the intrinsic conductivity of HPAs is about twice that of BPO_4 under the same operating conditions (room temperature, fully hydration). Both DS and BPO_4 content play a role towards the swelling increase of the composite membranes. In the meanwhile, W.U. due to the BPO_4 substantially exceeds the sorption capacity of the unsupported solid electrolyte. The reason of this effect may be only explained by considering the BPO_4 /S-PEEK membrane porosity similarly to the HPAs/S-PEEK, while the pristine S-PEEK is essentially nonporous. The affection of solid electrolyte incorporation into the S-PEEK polymeric matrix produces two effects: the porosity rise, which does not improve the electrochemical performances of the hybrid membranes, and the conductivity increase due to the higher intrinsic conductivity of the BPO_4 solid electrolyte, which allows to reach BPO_4 /S-PEEK conductivity of around 7.5×10^{-2} S/cm, Table 4.

3.4. S-PEEK/PANIs hybrid membranes

Another example of composite S-PEEK based membranes is represented by the synthesis via chemical polymerization of a thin layer of polyaniline (PANI) in the presence of a high oxidant concentration on a single face modification to constitute a sulfonated PEEK/polyaniline (S-PEEK/PANI). This hybrid membrane prevents the methanol crossover, maintaining medium proton conductivities. Indeed, in some case, methanol permeability of these membranes is four times lower than Nafion117, whereas the medium proton conductivity of S-PEEK/PANI may be due to the sulfonic acid and amine groups present in the membrane matrix, which give rise to hydrophilic regions in the polymer owing to their strong affinity towards water. These hydrophilic regions present around the cluster of chains lead to absorption of water, enabling an easy proton transfer [58]. Protons as hydronium ions pass through these hydrophilic regions of S-PEEK/PANI and this could be the possible reason why the proton conductivity increases with respect to pristine S-PEEK membrane. As shown in Table 4, for S-PEEK/PANI membranes with high PANI coating density Nagarale et al. [26] found slightly lower conductivity, 1.8×10^{-3} S/cm, with respect to Nafion, while the increasing and decreasing trends of the methanol permeability, as a function of polymerization time, arise depending on the presence of hydrophilic groups (SO_3H) with amine groups. Therefore, methanol permeability may be influenced either by cross-linking between these charged moieties or by significant phase segregation of PANI. For instance, a cluster formation on polymeric matrix induced by PANI deposition is responsible for a lower methanol crossover with respect to both pristine S-PEEK and Nafion, as a consequence of its chemical interaction with methanol [26].

3.5. Inorganic materials incorporated into S-PEEK based hybrid membranes

In the open literature, several functionalized inorganic materials (organo-silica precursors and porous materials) such as zeolite and mesoporous silica materials have been studied as additive materials and applied to synthesize derivative S-PEEK hybrid membranes in order to guarantee

economic and safe operation in PEMFCs, also in conditions of low humidity. For example, Ruffmann et al. [59] studied the in situ generation of inorganic oxides such as zirconia by means of hydrolysis of the alkoxides in a S-PEK/ZP polymer solution, achieving a depletion of the permeating flux through the hybrid membrane of both water and methanol vapours. Furthermore, the incorporation of well-dispersed zirconium phosphate (ZP) into the polymer solution to constitute S-PEK/ZP- ZRO_2 increases the proton conductivity (Table 4). Both the effects may be due to the swelling behaviour of the composite membranes. Concerning the fuel crossover, it should be taken into account that water/methanol permeating flux increases linearly with the degree of swelling. The inorganic modification with zirconia reduces the S-PEK swelling, but some region of lower resistance to water/methanol transport may be present, especially at the interface between polymer and zirconium phosphate [59].

Another example of inorganic phase incorporation with S-PEEK polymeric matrix is constituted by the use of zeolite. Intaraprasit et al. [27] studied the incorporation of Analcime natural zeolite (10%wt) in S-PEEK reaching a great proton conductivity equal to $\sim 4.0 \times 10^{-1}$ S/cm at 90 °C and R.H. = 100%, Table 4. This result may be accounted for the protons inside the connected 3D channels of Analcime, obtained after H-form transformation. Therefore, these protons play a role of bridges for the proton transport, making possible the enhancement of the proton conductivity. Furthermore, the incorporation of solid particles in the hybrid membrane increases the resistance to hydrogen diffusion through the membrane, lowering its fuel crossover in PEMFC applications. Nevertheless, at $T > 90$ °C, S-PEEK/Analcime membrane loses water fast with a consequent depletion of proton conductivity [27].

Another application of zeolite incorporation in S-PEEK has been studied by Sengul et al. [28]. In this case, the zeolite Beta at 10%wt of content in the hybrid membrane (S-PEEK/Beta) has been used with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 50% and the correspondent proton conductivity reached at 25 °C was equal to around 1.1×10^{-1} S/cm, Table 4. Nevertheless, at temperature higher than 60 °C, S-PEEK/Beta hybrid membrane exhibits a larger water adsorption and swelling problem was observed at $T > 60$ °C [28].

Xie et al. [34] synthesized a composite membrane based on S-PEEK functionalized with mesoporous benzene-silica (MBS), which shows attractive behaviours such as the homogeneous incorporation of large amounts of organic groups with high surface and a narrow pore size distribution. In particular, the authors found that, at 90 °C, the hybrid S-PEEK/MBS membrane with MBS content of 15% reached a proton conductivity of around 6.4×10^{-2} S/cm.

3.6. S-PEEK/PBI hybrid membranes

In literature, various studies are present concerning composite membranes based on S-PEEK and small molecules containing benzimidazole groups, which show as a main benefit the low methanol crossover [10,32,33]. Nevertheless, some drawbacks are present in this kind of blended membranes such as reduced water up-take and, particularly, inhomogeneity of the blend owing to the poor solubility of polybenzimidazole (PBI)

[33]. PBI shows good mechanical strength and high chemical and thermal stability at relatively high temperature. Furthermore, it is able to deplete methanol crossover because PBI is impermeable to methanol. However, hybrid membranes based on S-PEEK and PBI (S-PEEK/PBI) may present a proton conductivity decrease and, therefore, S-PEEKs at high sulfonation degree are necessary to prepare hybrid membranes.

Recently, Zhang et al. [32] found that, by increasing PBI content in the blend from 5 to 20%wt, proton conductivity decreases from 8.0×10^{-2} to 2.2×10^{-2} S/cm (Table 4). This trend was confirmed also by Li et al. [33], who reported that, at 80 °C, by increasing PBI content in the blend, proton conductivity decreases from 1.8×10^{-1} to 1.0×10^{-1} S/cm, even if methanol crossover (evaluated as a methanol permeability) decreases from 7.92×10^{-7} cm²/s to 3.10×10^{-7} cm²/s (Table 4). However, S-PEEK/PBI membranes appear good candidates for substituting Nafion membranes for both PEMFC and DMFC applications.

3.7. S-PEEK-WC and its derivative sulfonated polymers for PEMFC and DMFC applications

As well known, PEEK, PEEKK and PEK are polymers having high degree of crystallinity, insoluble in water and in most of the common organic solvents. The insolubility properties of PEEK polymer may be overcome by a new type of polymer, the PEEK-WC, which is not classified as a blend, composite or a hybrid membrane but only as a new kind of polymer. In particular, this polymer is characterized by the presence of the cumbersome lattonic group, which is responsible of the reduction of the crystallinity degree and, as a consequence, it appears as an amorphous polymer. Furthermore, PEEK-WC polymer presents high thermal, chemical and mechanical stability [60] and it may be used as a sulfonated polymer for both DMFC and PEMFC applications. Various studies are present in literature concerning the possible applications of S-PEEK based polymers. In particular, S-PEEK-WC polymers may be synthesized following two procedures: via chlorosulfuric acid [38,41–43,62–64] and by using concentrated sulphuric acid [39,40,61,63]. By means of chlorosulfuric acid sulfonation procedure, at temperature around 70 °C it is possible to sulfonate PEEK-WC reaching high DS, with the further behaviour to be water soluble and useful as a proton exchange membrane. In the meanwhile, the main drawback related to this sulfonation procedure is represented by the not easy control of the substitution degree. For instance, at low temperature, around 0 °C, this issue may be avoided, even if the S-PEEK-WC shows lower sulfonation degree, around 30%, with a decrease of the electrochemical performances. However, also at higher DS (DS = 82%), proton conductivity of S-PEEK-WC (Table 4) at 115 °C and R.H. = 100% is equal to 2.5×10^{-2} S/cm, still lower than Nafion117 [61]. Otherwise, concerning the sulfonation of PEEK-WC via concentrated sulphuric acid, as reported by Basile and coworkers [39,40], a DS = 40% is achieved after 3 h of sulfonation reaction, with a proton conductivity at 120 °C of 1.7×10^{-2} S/cm [39] (Table 4). This proton conductivity is comparable to S-PEEK-WC prepared by chlorosulfuric acid sulfonation (at DS = 82% and 120 °C) [61] and higher than chlorosulfonated S-PEEK-WC (5.4×10^{-3} S/cm) at 80 °C and with a DS = 99% [43]. However, in

the latter study, the low value of proton conductivity was accounted for the high DS, the inhomogeneity of the membrane samples as well as for the thin thickness. Indeed, Iulianelli et al. [62] improved the quality of chlorosulfonated PEEK-WC membranes, founding a proton conductivity of 2.5×10^{-2} S/cm at 100 °C and for a sample at DS = 90%, Table 4. However, at lower sulfonation degree, DS ~60%, the same authors found a proton conductivity around 6.7×10^{-2} S/cm at 120 °C, making this kind of chlorosulfonated PEEK-WC membranes interesting candidate as an alternative to Nafion for high temperature PEMFC applications.

Also Luo et al. [41] studied the chlorosulfonation of PEEK-WC polymer particularly for DMFC applications. As shown in Table 4, a highly chlorosulfonated membrane was synthesized by these authors with a DS exceeding 100% and with an IEC equal to 1.87 meq/g. At 80 °C, Luo et al. found a proton conductivity around 5.5×10^{-2} S/cm with a low methanol crossover at 20 °C equal to 1.6×10^{-7} S/cm, confirming that S-PEEK-WC represents a viable alternative to Nafion also for DMFC applications.

Other studies have been carried out for the preparation of modified S-PEEK-WC membranes, for example by incorporating a 20%wt of an amorphous zirconium sulphophenylphosphonate (Zr/SPP) as a proton conductivity carrier in order to enhance the transport behaviours of the composite membranes (S-PEEK-WC-Zr/SPP). Furthermore, Zr(SPP)/S-PEEK-WC membrane absorbs less water and methanol than pristine S-PEEK-WC and methanol absorption does not increase significantly with temperature, contrary to pristine S-PEEK-WC, particularly at high DS. Another benefit of the Zr/SPP incorporation is related to methanol permeability, which is lower than Nafion owing to its microstructure with narrow and highly branched channels, which are responsible for the lower methanol crossover. Concerning proton conductivity, nevertheless, as demonstrated by Regina et al. [42], only at lower DS proton conductivity of these composite membranes is improved by Zr/SPP incorporation, reaching as a best value $\sim 2.0 \times 10^{-2}$ S/cm at 80 °C and with a DS = 57% (Table 4).

In another study, the embedding of HPAs in chlorosulfonated PEEK-WC (S-PEEK-WC/HPA) was also followed without reaching substantial improvements on proton conductivity of the composite membranes, although better than Nafion at $T \geq 100$ °C. Indeed, at around 100 °C and R.H. = 85%, S-PEEK-WC/HPA shows a proton conductivity of 4.0×10^{-2} S/cm, even if, compared to the other results reported in Table 4, it appears similar to other S-PEEK-WC based membranes [64].

An alternative way to prepare S-PEEK-WC membranes was followed by Gosalawit et al. [63], who prepared a S-PEEK-WC membrane via post-sulphonation procedure (PS-PEEK-WC). In order to prevent the attack of concentrated sulphuric acid, a PEEK-WC membrane was synthesized and, successively, it was post-sulphonated by using low/medium concentrated sulphuric acid (24 and 48%). Unfortunately, this solution does not guarantee great proton conductivity performances, 7.3×10^{-3} S/cm at 100 °C for the sample synthesized with 48% concentrated sulphuric acid (PS-PEEK-WC48%) and 5.5×10^{-3} S/cm for the sample synthesized with 24% concentrated sulphuric acid (PS-PEEK-WC24%), because the post-sulphonation procedure affects only the surface of the membrane instead of the polymeric matrix.

However, as previously discussing about the performances of pristine S-PEEK, also for the derivative, composite/hybrid S-PEEK membranes, many discrepancies about experimental results in terms of proton conductivity, water up-take, and so on are noticeable. Each of the methods utilized for improving the performances of derivative and/or hybrid S-PEEK based membranes presents benefits and drawbacks. Most recently, Brunetti et al. [65] introduced the concept of the “hydro-thermal history” of the membranes, which describes how their behaviours and durability are affected by the combination of operating temperature and R.H. Furthermore, to clearly individuate the useful derivative or hybrid S-PEEK based membranes with the ideal/desired characteristics for PEMFC and/or DMFC applications, β selectivity and transport performance index (the ratio between hydrogen permeability and proton conductivity) should be always taken into account to compare correctly the performances of various S-PEEK based membranes.

4. Ohmic resistance of pristine S-PEEK and its derivative, composite/hybrid membranes in PEMFC and DMFC applications

Commonly, the polarization curve is the most significative characteristic of both PEMFC and DMFC and it is used for diagnostic purpose as well as for sizing and control. From a theoretical point of view, the volt–ampere behaviours of a PEMFC or DMFC may be explained taking into account thermodynamic and electrochemistry. By considering such proton exchange fuel cell as a fully reversible process, the maximum voltage generated (defined as “E”) should correspond to the electromotive force (EMF) generated at the output. The process is fully reversible if, during fuel cell operation by combining hydrogen (or any suitable fuel) and oxygen into water, unrecoverable losses do not take place (for example it does not produce heat). If the reversibility of the process is confirmed, it may be assumed that the energy change in the system (Gibbs free energy of formation) is converted into electrical energy (1),

$$E = \Delta G(T, P, f_n) / nNe \quad (1)$$

where “ ΔG ” is the variation of Gibbs free formation energy in the system, “ n ” the number of electrons transferred during the reaction (2 for hydrogen), “ N ” Avogadro’s number and “ e ” the charge of an electron. The Gibbs free formation energy depends on temperature (T), pressure (P) and the phase state of the reactants and product (liquid or gas, “ f_n ”). For all feeds supplying in gaseous state to PEMFCs and/or DMFCs, at atmospheric pressure and temperature around 80 °C, the calculated value of E is equal to 1.17 V. This derived voltage may represent the maximum value obtainable under no-loss conditions. Ideally, this voltage should be independent of the electrical current drawn but, in real applications, some loss is always noticeable and, furthermore, other limitations may also occur. As a consequence, the process is irreversible and involves lower output voltage. Indeed, four different processes are, at least, responsible of the depletion of the output voltage. The ohmic resistance to both currents (electrons and protons) generates heat and results in slowly linear voltage drop,

correspondent to a current increase. This voltage drop can be presented as reported in the following equation (2):

$$\Delta V_r = i(R_e + R_p) \quad (2)$$

with $R_e = R_{cont} + R_{backpl}$

where, “ i ” is the current, R_e the resistance to electron current, R_p the resistance to proton current through the PEM, R_{cont} the contact resistance between catalyst and backplate, R_{backpl} the resistance of backplates. In Table 5, a few literature data about ohmic resistance of both pristine S-PEEK and derivative S-PEEK based membranes are reported in comparison with Nafion. As summarize in Table 5, R values may cause mainly the linear variation of the cell potential with current density and, also in this case, the reported literature data are quite different. Furthermore, compared to the other data in Table 5, Nafion shows the lowest ohmic resistance as well as the highest value of open circuit voltage (OCV). As a general consideration, the voltage and current relationship during the electrochemical reaction itself are linked by a simple dependence such as Tafel equation (3), which is used as an electrochemistry law for irreversible reactions.

$$\Delta V_{OV} = \frac{2.3RT}{\alpha nF} \ln \left(\frac{i}{i_0(M, T, S)} \right) \quad (3)$$

where R is the gas constant, T temperature, “ α ” a symmetry coefficient (usually around 0.5), “ n ” the number of exchanged electrons, “ i_0 ” a exchange current depending on the materials utilized (M), temperature and active area of the material (S).

Two different electrodes in a fuel cell with two different reactions lead to two different current/voltage dependences. Commonly, under PEMFC operation, molecular hydrogen passes through the proton exchange membrane and ends at the cathode area. The cathodic catalyst effectively splits this hydrogen to protons, which react with oxygen making a small electrical load on the cathode side, even in absence of external current. Since the activity of the cathode is not particularly high, this leads to a noticeable over-voltage. For this reason, a real OCV is lower than the ideal EMF [67–69] and this is confirmed by the literature data reported in Table 5. Indeed, all OCVs from literature are lower than 1.17 V, with Nafion showing the highest value with respect to pristine S-PEEK and its derivative polymer, S-PEEK-WC.

Table 5 – Open circuit voltage and ohmic resistance for a few literature data about pristine S-PEEK and its derivative polymers, compared to Nafion.

Reference	Polymer	OCV [V]	R [Ωcm^2]
Li et al. [6]	S-PEEK	0.64	20.60 ^a
Zhang et al. [29]	S-PEEK	0.77–0.79	0.18–0.23
Ren et al. [22]	S-PEEK	–	1.34 ^b
Iulianelli et al. [62]	S-PEEK-WC	0.80 ^d	0.55 ^d
Basile et al. [40]	S-PEEK-WC	0.87	0.24 ^c
Wakizoe et al. [66]	Nafion	0.96	0.17

a [5].

b 60 °C.

c 120 °C.

d 100 °C.

5. Conclusion

Perfluorosulfonic polymers such as Nafion and low-cost sulfonated polyaryls such as S-PEEK and its derivative, composite/hybrid polymers present different mechanical and transport properties owing to the differences in the acidity of the sulfonic groups and microstructures. The less pronounced hydrophobic/hydrophilic separation regions of pristine S-PEEKs compared to Nafion corresponds to narrower, less connected hydrophilic channels and to larger separations between the less acidic sulfonic acid functional groups. This leads to a disadvantageous swelling behaviour and a stronger decrease of water and proton transport with decreasing water content. On the other hand, the hydrodynamic flow of water is reduced compared to Nafion, which is an essential benefit, especially for DMFC applications.

Composite and/or hybrid membranes based on S-PEEK and its derivative polymers have been investigated in this review paying particular attention to the new findings both on pristine S-PEEKs and on the incorporation of other polymers such as PPSU in sulfonated form or inorganic component such as SiCl_4 , inorganic oxides like zirconia as well as solid heteropolyacids such as HPA, TPA and Na-TPA or with BPO_4 . In particular, for the latter case, the membrane swelling behaviours, mechanical properties and proton conductivity may be significantly improved. Furthermore, this review has focused the recent studies on the experimental results of different PEEK modification procedure such as the chemical polymerization with polyaniline or PEEK chemical modification such as PEEK-WC polymer, useful for both PEMFC/DMFC applications in sulfonated form and/or blended with zirconia oxides. In detail, various S-PEEK based composite membranes show also to reduce the hydrophilic/hydrophobic region separation and the hydrodynamic solvent transport (water and methanol permeation). Therefore, pristine S-PEEK and its derivative, composite/hybrid membranes constitute not only an interesting cost effective alternative to Nafion in PEMFC but also in DMFC applications owing to their reduced methanol crossover. Particular attention has been devoted to the proton conductivity performances of the various S-PEEKs and S-PEEKs based membranes and in different cases, the new and recent researches showed how proton conductivity of Nafion membranes may be overcome, also at temperature higher than 100 °C, where as well known it fails mainly owing to its poor hydration conditions in the fuel cell.

However, concerning both pristine S-PEEK and hybrid membranes, various discrepancies on the experimental results from literature have been noticed and this may be probably accounted for the different experimental history of the membranes as well as by the absence of a wide accepted protocol for the experimental testing during PEMFC/DMFC operations used in the several studies cited in this review.

Concerning the literature data on voltage and power density characterisation of both pristine S-PEEKs and its derivative, composite/hybrid S-PEEK based membranes, unfortunately, only a few studies may be noticed and they do not allow to make a deep and exhaustive discussion on their benefits and drawbacks over Nafion when applied in PEMFC and DMFC applications.

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