

Short communication

Composite S-PEEK membranes for medium temperature polymer electrolyte fuel cells

A. Carbone*, R. Pedicini, A. Saccà, I. Gatto, E. Passalacqua

CNR-ITAE, Advanced Technologies for Energy Institute, "N. Giordano", Via Salita S. Lucia sopra Contesse 5, Messina, Italy

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Abstract

Sulphonated-PEEK polymers with two different sulphonation degrees (DS) were obtained by varying the sulphonation parameters. Ionomeric membranes were prepared as a reference. Composite membranes were obtained by mixing different percentage of 3-aminopropyl functionalised silica to the polymers dissolved in DMAc. The resulting membranes were characterised in terms of water uptake, IEC and proton conductivity in different conditions of temperature and relative humidity.

The introduction of amino-functionalised silica in the lowest DS polymer slightly increases the water uptake, because it retains the water and in this case the hydrophilic property of the material is predominant. In the highest DS polymer the presence of SiO–NH₂ decreases the water uptake and swelling, probably due to a major interaction between the amino groups of silica and the sulphonic groups of polymer. The proton conductivity of the highly sulphonated polymer does not change even if the swelling decreases, while in the poorly sulphonated polymer a slight increases of water retention increases the conductivity. A composite membrane was tested in PEFC at 120 °C reaching a maximum power density of 246 mW cm⁻².

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1. Introduction

One of the main problem of fuel cell for application in automotive systems is the use of perfluorinated polymer membranes that suffer of water management problems, need a fully humidification and the optimal operative temperature is limited below 100 °C [1,2]. For this kind of application the requested target is to operate over 100 °C by reducing the gases pressure and humidification without losing the proton conductivity. Higher temperatures allow processed gases to be operated in order to increase the CO tolerance of the used catalysts and to avoid the use of more expensive Pt-alloys.

The sulphonated-poly(ether ether ketone) has been widely studied among other poly-aromatics materials for application in low and medium temperature fuel cells, due to its low production costs, thermal and chemical stability, easy functionalisation reactions and formation of membranes with a dense structure

[3–6]. Sulphonated polymer electrolyte membranes can be easily obtained by casting the polymer dispersion in a proper solvent, and drying at a suitable temperature. The water uptake is influenced by sulphonation degree of the membrane, in fact the membranes hydration number (λ , $n\text{H}_2\text{O}/n\text{SO}_3\text{H}$) depends on water activity and temperature, moreover it strongly influences the proton conductivity and dimensional stability. At the beginning of the swelling process, a softening effect occurs in the membrane, which becomes mechanically weak. Then, at high λ values [7] the hydrophilic regions of the polymer undergo a profound deformation that produces an irreversible swollen state and a degradation of the membrane. This is one of the main problems associated with the membrane failure during fuel cell operations.

For improving the performance issues of pure polymeric membranes is desirable to form polymer inorganic composites with the aim to enhance proton conductivity, water retention at high temperatures and mechanical resistance.

This is possible in two ways: the insertion of an inorganic compound into the polymeric matrix or in situ formation of an inorganic network in the pre-formed membranes, in order to give

* Corresponding author. Tel.: +39 090 624 240; fax: +39 090 624 247.
E-mail address: carbone@itae.cnr.it (A. Carbone).

to the membrane the ability to operate at temperatures higher than 100 °C [8,9]. This type of composites can be configured in different ways:

- both polymer and inorganic components can be ionically conductive;
- an ionically conductive polymer can be modified with not conductive inorganic filler as mechanical support;
- an ionically conductive polymer can be modified with water-retaining inorganic filler;
- an ionically conductive inorganic additive can be introduced in an insulating supporting polymer.

Polymer inorganic composite membranes are interesting because many of the inorganic additives used are able to operate at much higher temperatures than pure polymers.

Another approach for increasing the operative temperature by limiting the loss of proton conductivity is the development of blended polymer membranes containing both sulphonic and nitrogenous groups [10–12]. These membranes utilise different acidic strength between the two different functionalities of the two polymers. In fact, the sulphonic acid groups interact with the nitrogenous base by forming hydrogen bridges, protonation of the nitrogen sites and polysalts formation.

In this work, amino-functionalised silica (SiO-NH_2) was used to prepare composite membranes with the aim to improve both the mechanical resistance and the proton conduction of the membrane. This inorganic compound overworks both the hydrophilic characteristics of the silica and the amino functionality, to limit the reduction of proton conductivity of the membrane by utilising the interactions between the sulphonic groups of the polymers and the aminic groups of the silica. The influence of the SiO-NH_2 content in S-PEEK poorly and highly sulphonated was investigated and the hydrophilic characteristics of the membranes were correlated to the proton conductivity.

2. Experimental

2.1. Preparation of sulphonated-PEEK powders

S-PEEK polymers (Victrex 450PF) with two different sulphonation degrees (35 and 52%) were prepared by varying the sulphonation temperature as already reported [13]. Elemental analysis on the sulphonated polymers was carried out to calculate the sulphonation degree (DS).

2.2. Membranes preparation

The obtained polymers were used to prepare the correspondent membranes, by a cast procedure, used as a reference. The polymers were dissolved in 6–10% (wt/wt) Dimethylacetamide (DMAc) dispersion and then they were cast on a glass sheet by a doctor-blade technique [13]. Composite membranes were obtained by mixing different weight percentage of a commercial 3-aminopropyl functionalised silica gel (Aldrich, $\sim 1 \text{ mmol g}^{-1} \text{ NH}_2$ loading) to the polymers dispersion before the casting step. Different SiO-NH_2 percentages (10, 20 and 50%, wt/wt) were

used for the 35% DS polymer and (10 and 20%, wt/wt) for the 52% DS polymer. The membranes were dried at 80 °C for about 3 h and at room temperature for about 16 h to eliminate the solvent residual, washed in water and acid treated to purify the obtained films.

2.3. MEAs preparation

Home-made electrodes were prepared by a spray technique described elsewhere [14]. The same Pt loading (0.5 mg cm^{-2}) in the catalytic layer was used for both anodes and cathodes and a 30% Pt/Vulcan (E-Tek Inc.) was used as an electro catalyst. MEAs were prepared by cold pressing the membranes on the prepared electrodes.

2.4. Polymers and membranes characterisations

2.4.1. Powder polymer characterisation

An elemental analysis (CHNS-O Carlo Erba CHNS-O Analyzer mod. EA 1108) was carried out on the sulphonated polymers powder to calculate the sulphonation degree (DS). The exact value of DS was determined as the ratio between S/C obtained from the elemental analysis (S/C_{exp}) and the theoretical S/C (S/C_{theo}) calculated assuming the complete sulphonation of the polymer.

2.4.2. Functionalised silica thermal characterisations (TGA)

Thermo gravimetric analyses (TGA) were performed using a thermo balance Netzsch (mod. STA 409) by monitoring the percentage mass loss change in air in the temperature range 20–700 °C with a temperature rate of 5 °C min^{-1} .

2.4.3. Polymers and membranes X-ray analyses (XRD)

The X-ray powder diffraction (XRD) analyses were performed by using a Philips X-ray automated diffractometre (model PW3710) with Cu $K\alpha$ radiation source. The 2θ Bragg angles were scanned between 5° and 100°.

2.4.4. IEC, water uptake and swelling measurements

The ionic exchange capacity was calculated by determining the equivalent point of an acid–base titration, by using an automatic titrator (Metrohm Mod.751GPD Titrino) and NaOH 0.01M (Carlo Erba, normex) as a titrant [15].

The water uptake data were calculated from the difference in weight of the dried and the wetted samples. The dry mass was obtained after a desiccation of the sample in an oven under vacuum (1000 mbar) for 2 h, while the wet mass was obtained after the immersion in water at 100 °C for 2 h of the dried samples.

The swelling of the membranes was calculated as the ratio between the volume of the wet sample (V_{wet}) and the volume of the dry sample (V_{dry}) measured in the same conditions of the water uptake measurements.

2.4.5. Proton conductivity measurements

The ionic conductivity of membranes was measured in the longitudinal direction with a four-electrodes method and dc cur-

Table 1
Elemental analyses results

Elements	%AW PEEK exp.	%AW S-PEEK (35%)	%AW S-PEEK (52%)
Oxygen	16.114	19.829	26.467
Hydrogen	4.473	4.033	3.910
Sulphur	0.000	3.346	4.656
Carbon	79.342	73.292	64.967
Nitrogen (air)	0.071	0.049	0
	100	100	100

Table 2
Chemical–physical data for bare S-PEEK membranes

Membrane	Thickness (μm)	IEC SO_3H (g^{-1})	Wup, 100 °C (%)	$V_{\text{wet}}/V_{\text{dry}}$, 100 °C
S-PEEK (35%)	70	1.11	49	1.3
S-PEEK (52%)	100	1.55	417	3.9

rent, by using a commercial conductivity cell (Bekktch) and a potentiostat–galvanostat (AMEL mod. 551). A 2 cm \times 3 cm sample was assembled into the cell, in contact with two platinum electrodes placed at a fixed position.

The membranes conductivity was determined as a function of temperature (from 80 to 120 °C) and relative humidity (from 78 to 100% RH).

2.4.6. Electrochemical characterisation

Electrochemical characterisations were carried out in terms of I – V curves. Fuel cell tests were effected in a commercial 5 cm² single cell (Globe-Tech) in a temperature range 80–120 °C, with humidified H₂ and air at three absolute bar. The gas fluxes were fixed at 1.5 and 2 times the stoichiometry at a current density of 1 A cm⁻² for hydrogen and air respectively.

3. Results and discussion

In Table 1 the results of polymers characterisation derived from elemental analysis were shown.

The calculated sulphonation degrees correspond to 35 and 52%.

The characteristics of S-PEEK polymers are strongly influenced from the sulphonation degree (DS). The experimental results obtained on the membranes with low and high DS are reported in Table 2. The parameters related to water absorption (Wup) and swelling ($V_{\text{wet}}/V_{\text{dry}}$) at 100 °C were compared.

The Wup and the swelling of the membranes at 100 °C increase about one hundred times passing from 35 to 52% of sulphonation. This is detrimental for a medium temperature working fuel cell because the swelling influences the mechani-

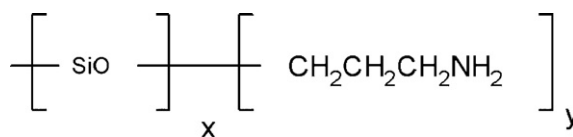


Fig. 1. Aminopropyl functionalised silica structure.

cal resistance of the film and, on the other side, the use of less sulphonated polymer decreases the fuel cell performance due to its lowest proton conductivity. Table 3 shows the conductivity data measured at 100 and 120 °C as a function of RH%.

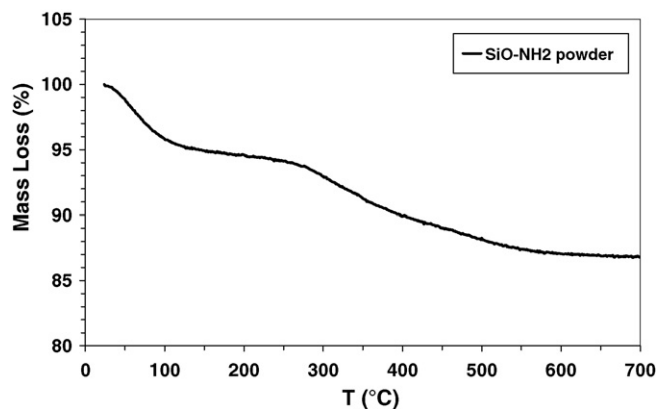
The conductivity increases by increasing the temperature and the relative humidity for both membranes but the increase for the highly sulphonated membrane is small respect the temperature and with full humidification even lower at 120 than 100 °C. This is probably due to the swelling of the membrane that produces a deformation of the conduction channels.

To reinforce the mechanical structure of the membranes supplying a better stability at temperature over 100 °C, the functionalised-silica SiO–NH₂ containing nitrogenous groups has been introduced. The inorganic material improves the water retention and mechanical properties at higher temperatures, due to its hydrophilic characteristics. The amino groups of the silica could interact with the sulphonic groups of the sulphonated polymer through hydrogen bonds by improving the proton conduction. The functionalised silica, as schematised in Fig. 1, has an amorphous structure from XRD analysis.

The thermogravimetric analysis, in the range of temperature between 20 and 700 °C, has shown two main mass losses, as reported in Fig. 2. A first mass loss below 200 °C of about 5.3% can be associated to coordinated water and a second mass loss

Table 3
Proton conductivity data at 100 and 120 °C and different RH% for bare membranes

Membrane	Proton conductivity at 100 °C (S cm^{-1})			Proton conductivity at 120 °C (S cm^{-1})		
	RH 78%	RH 90%	RH 100%	RH 78%	RH 90%	RH 100%
S-PEEK (35%)	5.7×10^{-4}	1.7×10^{-2}	6.7×10^{-2}	9.3×10^{-4}	3.8×10^{-2}	9.3×10^{-2}
S-PEEK (52%)	4.0×10^{-3}	3.9×10^{-2}	1.3×10^{-1}	3.4×10^{-3}	5.7×10^{-2}	1.0×10^{-1}

Fig. 2. TGA profile of SiO-NH₂.

between 300 and 600 °C of about 7.5% is due to the decomposition of functional groups.

The thermal stability of this compound renders it a good candidate for operating in PEFC at 120 °C.

Several membranes were prepared by adding different amount of silica at two differently sulphonated polymers. The membranes have a thickness ranging between 100 and 150 μm, Ion Exchange Capacity of the membranes (meqSO₃H/g membrane) decreases by increasing the amount of silica, as shown in Fig. 3, meaning the effective introduction of material. By considering the theoretical amount of silica introduced in the membranes the IEC related to the S-PEEK polymer was calculated as reported in the following equation:

$$IEC_p \left(\frac{\text{meqSO}_3\text{H}}{m_{\text{polymer}}} \right) = IEC_m \frac{(\text{meqSO}_3\text{H}/m_{\text{membrane}})}{\text{PF}} \quad (1)$$

where PF = fraction of polymer in the membrane.

The IEC_p data plotted in Fig. 3 shows that the ionic exchange capacity of the polymer in the composite membrane is always lower than bare membrane for both DS. This behaviour could be explained considering that probably there is an interaction between the amino groups of silica and the sulphonic groups of the polymer that restrains the involved proton.

The water uptake and the membranes swelling were measured at 100 °C, the comparison between the polymers is shown in Figs. 4a and b respectively.

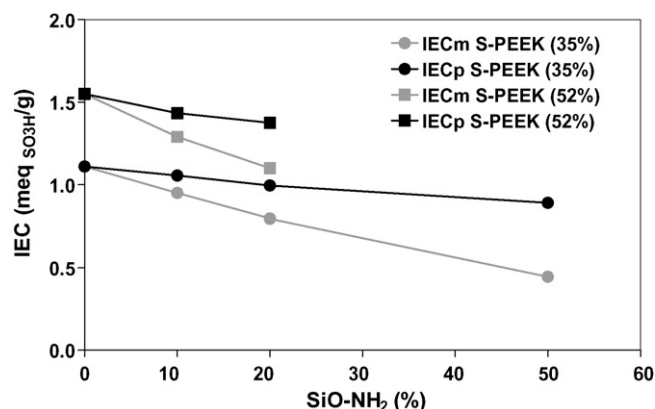


Fig. 3. Ionic exchange capacity as a function of silica content.

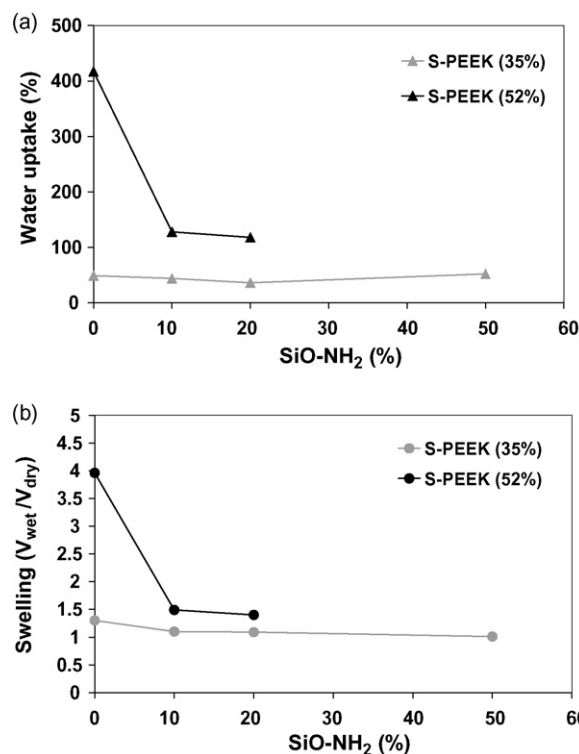


Fig. 4. Water uptake (a) and swelling (b) measurements as a function of silica content.

The less sulphonated polymer is slightly influenced from the presence of silica maintaining a low water uptake and swelling, probably in this case the hindering of the sulphonic groups is balanced from the hydrophilic property of the silica that is predominant respect the polymer. For the highly sulphonated polymer the introduction of silica substantially reduces the water uptake and the swelling by meaning an appropriate water content. This effect could be attributable both to the hydrophilic property of silica and to the interaction between sulphonic–aminic groups, in this case the interaction between sulphonic–aminic groups is predominant.

The proton conductivity was measured at 100 and 120 °C at different % RH from 78 to 100% and plotted as a function of the functionalised silica percentage. The behaviour for the 35% sulphonated polymers is shown in Fig. 5a and b. The conductivity decreases by increasing the silica content but it is positively influenced from the increase of humidification and the cell temperature.

Regard to the 52% sulphonated polymer (Fig. 6a and b), the benefit of inorganic introduction is more evident, in fact the conductivity at 100 °C is less influenced from the inorganic content at RH < 100% and by increasing the cell temperature the influence of SiO-NH₂ content is already evident at lower RH than 100%.

S-PEEK 52–20%SiO-NH₂ membrane was assembled between two home made electrodes, tested in a single cell at 120 °C with fully humidified H₂ and air at three absolute bar and compared to bare membrane used as a reference.

As scheduled in Table 4, the OCV value of composite membrane is higher than bare membrane, indicating a more compact

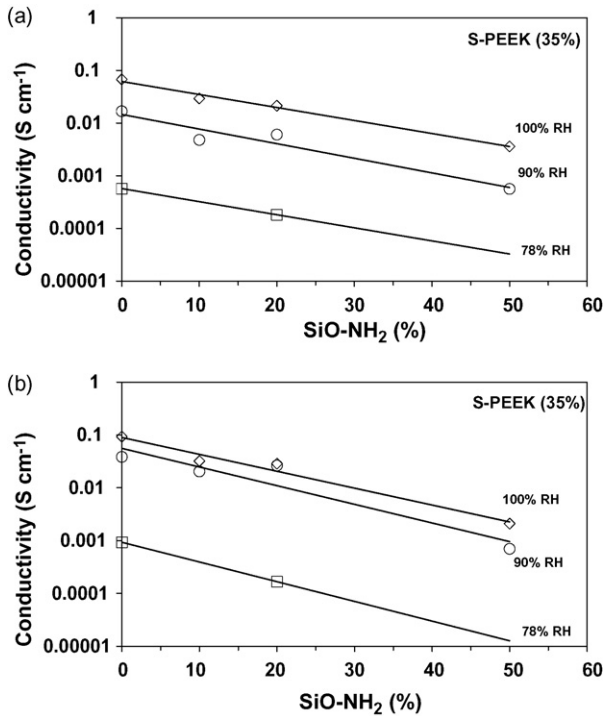


Fig. 5. Conductivity at (a) 100 °C and (b) 120 °C for S-PEEK (35%) with different percentage of SiO-NH₂.

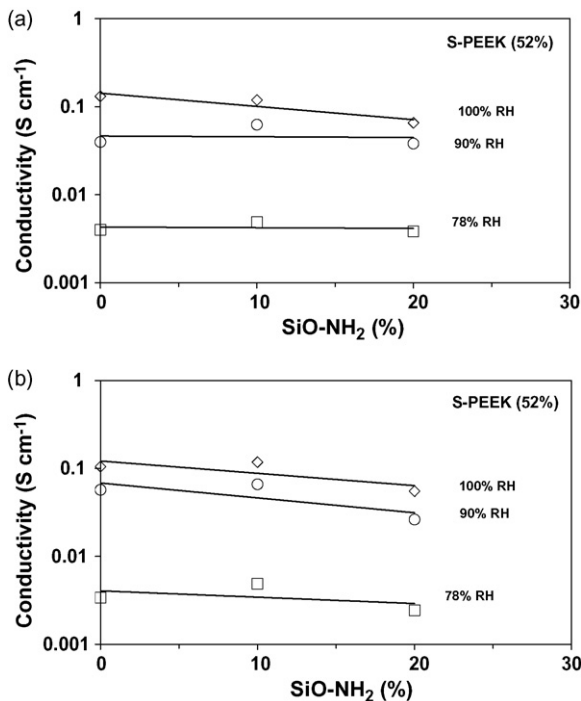


Fig. 6. Conductivity at (a) 100 °C and (b) 120 °C for S-PEEK (52%) with different percentage of SiO-NH₂.

Table 4
Electrochemical data for bare and composite membranes

Membrane	OCV (V)	R cell ($\Omega \text{ cm}^{-2}$)
S-PEEK (52%)	0.855	1.25
S-PEEK (52%) + 20%SiO-NH ₂	0.933	1.10

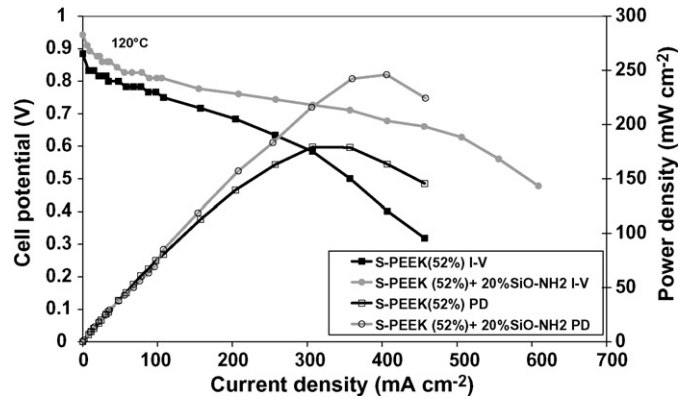


Fig. 7. Polarisation and power density curves at 120 °C for S-PEEK (52%) and S-PEEK (52%) + 20%SiO-NH₂.

and mechanically stable structure. The hydrophilic properties of silica contribute to the water management during fuel cell operation, in particular the cell resistance value for S-PEEK (52%) + 20%SiO-NH₂ is slightly lower than S-PEEK (52%).

In Fig. 7 the obtained performance in terms of *I*-*V* and power density (PD) curves is reported and compared to the bare polymer. The composite membrane reaches a maximum power density of 246 mW cm⁻² respect to 179 mW cm⁻² for bare membrane.

A right compromise between sulphonation degree of polyetheretherketone, amino groups and sulphonic groups ratio could give to the PEEK-based membranes those proper characteristics of stability and conductivity at medium temperature.

4. Conclusions

Functionalised silica was chosen to develop composite S-PEEK membranes. The influence of the silica content relatively to the sulphonation degree was studied in terms of chemical-physical characterisations and electrochemical properties. The IEC, water uptake and swelling measurements highlighted that the silica contribution is to reduce the swelling through interactions between sulphonic and aminic groups. This effect is highlighted in membranes with 52% DS, where the reduction of water uptake and swelling does not interfere with the proton conduction.

In fact, proton conductivity of the 35% DS composite membranes is lower than bare membrane and the values decreased with the increase of silica content. On the contrary, in 52% DS composite membranes the silica content does not influence so much the proton conductivity in particular at RH < 100%.

A membrane with 52% DS and a 20% of silica content was chosen for the electrochemical test in single cell showing that the introduction of inorganic compound produces a beneficial effect on the robustness of the membrane. In fact, the OCV value is higher than bare membrane, indicating a more compact and mechanically stable structure, while the cell resistance value is slightly lower.

The composite membrane reaches a maximum power density of 246 respect to 179 mW cm⁻² for bare membrane.

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