

Composite sPEEK-TPyP Membranes Development for Portable Applications

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ABSTRACT

Composite membranes based on sulphonated Polyetheretherketone (sPEEK) and 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) were developed for portable applications. A sulphonation degree of 65% and different weight percentages (0-5%) of TPyP porphyrin were used. The membranes were realized with a standardized doctor-blade method, thermally and chemically treated. Physical-chemical characterizations were carried out in terms of spectroscopic studies (UV-Vis and Fluorescence), ionic exchange capacity, water uptake, dimensional variations and swelling, structural and morphological analyses. Moreover, proton conductivity measurements at a temperature useful for portable applications, were performed. SEM analyses of composite membranes highlight a similar morphology to the pristine sPEEK membrane. XRD profiles of composite membranes correspond to the amorphous pattern of sulphonated polymer, while the fundamental peaks of TPyP were completely suppressed. This effect indicates that a good interaction occurs between the filler and the polymer matrix. This interaction, in particular between nitrogenous groups of porphyrin and sulphonic groups of polymer, leads to slight changes in physico-chemical properties and a proton conductivity respect to the sPEEK membrane, used as a reference. In particular, the membrane with the lowest loading (~1 wt%) of TPyP, shows slightly lower water uptake and unaltered λ values than the reference membrane, resulting in quite unaltered proton conductivity. This behavior could be attributed to the interaction of porphyrin groups and polymer matrix able to contribute to the proton conduction mechanism. In addition, the developed membranes were characterized in a PEFC 25cm² single cell to verify their applicability in portable devices. Also in this case the sample with the lowest loading of TPyP is the best compromise for a real application.

Keywords: Sulphonated PEEK; TPyP; PEFC.



Introduction

Fuel cells are clean and highly efficient electrochemical systems for energy conversion, that are fed by hydrogen in advanced systems with the highest performance, or by alternative fuels (e.g. methanol or ethanol) with significant reduction in performance [1]. Among the existing typologies of fuel cells, the system that has attracted most interest is the Proton Exchange Membrane Fuel Cell (PEMFC) due to its wide range of power density (1×10^{-3} -100 kW), simplicity of components and its friendly user operating conditions.

A polymer electrolyte membrane fuel cell (PEMFC) is composed of a membrane able to conduct protons, between the anodic and cathodic compartments, separating two catalytic electrodes where the fuel oxidation and the comburent reduction take place.

Due to the high energy density with respect to the traditional batteries, fuel cells are particularly suitable for the fabrication of portable systems, more efficient and less bulky than currently available systems.

The Portable Fuel Cell systems tend to use either DMFC (direct methanol fuel cells) or PEFC (polymer electrolyte fuel cells fed by hydrogen) technology, even if the DMFC are nowadays the most diffused.

However, several problems to be solved, such as catalyst poisoning during methanol oxidation reaction and methanol crossover through solid-polymer-electrolyte membrane, limit their commercialization [2]. The most used polymer electrolyte membrane is Nafion[®], that has high proton conductivity, chemical and mechanical stability, but suffers a high methanol permeability, that drastically reduces the performance. To solve this problem, associated to a high production cost of this polymer, the research aims at developing low-cost and highly efficient proton conducting membranes to be used as polymer electrolytes for portable fuel cells fed with hydrogen and air under air-breathing conditions.

The development of poly-aromatic based membranes plays a key role as an alternative to Nafion[®] membranes [3-7]. A wide literature exists on this class of polyelectrolyte but some problems should be overcome such as a low proton conductivity at reduced relative humidity, the mechanical stability and lifetime. One of the most used polymer membrane is based on sulphonated polyetheretherketone (s-PEEK) with a sulphonation degree in the range 40-70%. Compared to the membranes reported in the state-of-the-art, the alternative membranes exhibit reduced cost (by a factor of about 40); better mechanical properties; improved stability to radical species; reduced hydrogen crossover; similar unit area resistance.

In addition to the above mentioned characteristics, nowadays, the research is moving on the development of membranes containing nitrogenous groups that promotes specific acid-base interactions between functional amino-sulphonic groups, by improving the proton conductivity [8-10]. In fact, the sulphonic acid groups interact with the nitrogenous base by forming hydrogen bridges, protonation of the nitrogen sites and polysalts formation. Particular attention is addressed to a class of modified membranes containing porphyrins as nitrogenous sources, in which porphyrin protons are bonded to the ion channel of the SPEEK membrane to form a hydrogen ion sieve structure, resulting in a higher proton transmissibility.[11-15]. This class of porphyrin is able to aggregate in different form and creates a network as a function of the used solvent, the aim of the work is to exploit this ability in a polymeric matrix containing polar functional groups to create specific interactions that stabilize the polymer maintaining a proton path for the conduction mechanism. In this work composite membranes based on sulphonated Polyetheretherketone (sPEEK) and 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) were developed and tested for their use in portable applications.

Experimental



2.1 Polymer sulphonation

A Polyetheretherketone (Vitrex PF450) was functionalized in concentrated sulphuric acid according to a standardized procedure, reported elsewhere [16], in order to obtain a a sulphonation degrees (SD) of 65%.

2.2 Membrane Preparation

Membranes were prepared with a doctor-blade standardized procedure [16] Composite membranes were further prepared using the sulphonated polymer. The 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine (TPyP) was purchased from Aldrich Chemical Co. and used without further purification. The porphyrin was added to the polymer in different weight percentages 0.77, 1.5 and 5wt% in DMAc solution. This latter, used for membrane recasting procedure, ensures the presence in solution of the porphyrin in monomeric form and avoid the formation of aggregates. In order to better solubilize the porphyrin, the resulting mixture was stirred for 1 hr before to be added to the polymeric solution. All the membranes were dried at 80°C for 3 hours then detached from the glass by impregnation with H₂O. A thermal treatment was carried out at 120°C for 16 hrs, followed by an acid treatment (1M H₂SO₄) at 60°C to purify them of any residual solvent and activate groups for proton ion exchange for the coordination of water molecules. Membranes with a thickness ranging from 50 to 70 μ m were obtained.

2.3 Polymers and membranes X-ray analyses (XRD)

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

2.4 UV-Vis and Fluorescence

UV/Vis spectra were obtained on a Hewlett-Packard mod. 8453 diode array spectrophotometer directly on the membranes. Fluorescence measurements were carried out on a Jasco mod.FP-750 spectrofluorimeter.

2.5 SEM–EDX analyses

A field emission Scanning Electron Microscope (Philips mod. XL30 S FEG) was used to investigate the cross-section morphology of the membranes. A gold coating was used to avoid sample charging and to permit electronic conduction. Samples for cross-section were prepared dipping the membrane in liquid Nitrogen and breaking the samples to have a perfect fracture.

2.6 Ion Exchange Capacity (IEC)

An acid-base titration was carried out to determine the membrane IEC_m (meqSO₃H/mg) and is based on the neutralization of H⁺ ions, belonging to the acid group -SO₃H. The experimental procedure is described elsewhere [6] The IEC is calculated using the following formula:

$$IEC_m = \frac{V_{tit} \cdot [M]}{m_{dry}} \quad (1)$$

where:

V_{tit} = titrant volume (ml);



[M] = titrant molarity;

m_{dry} = dry mass of the sample (g);

To determine the interaction between SPEEK and TPyP, IEC of SPEEK polymer (IEC_p) within the composite membrane was determined considering the Polymer Fraction (PF) calculated from Eq. (2):

$$IEC_p = \frac{IEC_m}{PF} \quad (2)$$

where IEC_m is the experimental IEC of the membrane

2.7 Water uptake and lambda

The ability to retain the water of the membrane ($W_{up}, \%$) is usually calculated from the difference in weight between the dried and the wet sample. The wet weight (m_{wet}) is determined after immersion of the sample in distilled water at room temperature for 24 hours, while for the dry weight (m_{dry}), the sample is dried in a vacuum oven at 80°C for 2 hrs. The percentage of water absorbed is given by the following expression:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \cdot 100 \quad (3)$$

The λ value (expressed as moles H_2O /moles- SO_3H) was calculated through the water uptake and IEC values ratio, both expressed in moles:

$$\lambda = \frac{mol\ H_2O}{mol\ SO_3H} \quad (4)$$

Through this parameter is possible to evaluate the capability of the SO_3H groups in the composite membranes to coordinate water molecules.

2.8 Proton conductivity

The conductivity was measured at 30°C and full humidification (100% RH) using a commercial cell (Bekktech). The measure is carried out in the longitudinal direction of the sample with a four-probe technique and calculated using the formula:

$$\sigma = \frac{L}{RWT} \quad (5)$$

Where:

L = 0.425 cm, constant distance between the two Pt electrodes;

R = resistance in Ω ;

W = sample width in cm;

T = sample thickness in cm.

2.9 Fuel cell tests

Home-made electrodes were prepared by a spray technique described in the referenced paper [17] and coupled to the membranes to obtain MEAs. The same Pt loading ($0.5\text{mg}/\text{cm}^2$) in the catalytic layer was used for both anodes and



cathodes and a 50% Pt/C (Alfa Aesar) was used as an electrocatalyst. A Sigracet-24BC (SGL group) was used as a gas diffusion layer. Membranes and electrodes were assembled by cold-pressing.

Fuel cell tests, in terms of polarisation curves, were carried out in a commercial 25cm² single cell at 30°C, with fully humidified H₂/air and dry H₂/humidified air at 1 absolute Bar. The gas fluxes were fixed at 1.5 and 2 times the stoichiometry at the current work for hydrogen and air, respectively.

Electrochemical impedance spectroscopy (EIS) was performed by using a potentiostat/galvanostat (AUTOLAB PGSTAT30) equipped with a frequencies response analyzer (FRA module) and a 20A BOOSTER. All impedance measurements were performed in the potentiostatic mode of fuel cell operation at a constant potential of 850mV. The impedance spectra were obtained varying the frequency of the voltage perturbation signal from 0.1 Hz to 100 kHz, by using amplitude of 10mV for the perturbing signal.

Results and discussion

The membranes were first characterized in terms of XRD profile, to understand the good dispersion of porphyrin in the polymeric matrix. In Fig.1 is reported the comparison among the XRD patterns of pristine SPEEK membrane, composite membranes with different amount of tetra(4-pyridyl)porphine (TPyP, hereafter) and TPyP powder. It is visible the typical amorphous profile of the sulphonated polymer centred at about 18° 2θ, that remains quite unaltered after the TPyP introduction. Moreover, no peak of the TPyP is visible in composite membranes, due to their preparation procedure. In fact the TPyP is solubilized within the confined membranes environment and it is present or in monomeric form or in small oligomers/aggregates without a crystalline structure.



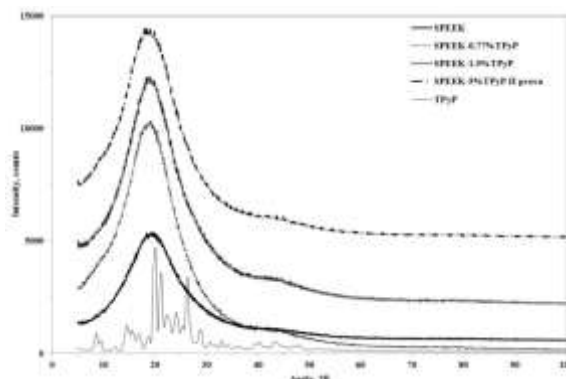


Fig.1 XRD patterns of developed membranes compared to TPyP

Due to their structural features, i.e. the extended planarity, the porphyrins favour the formation of van der Waals, π - stacking and hydrophobic interactions, that allow, in appropriate experimental conditions, the formation of dimers, trimers small oligomers or larger aggregates. The aggregation phenomena for this class of molecules are accompanied by characteristic changes in their spectroscopic properties, i.e. bathochromic or ipsochromic shifts of the absorption and emission bands, Beer law's deviation, quenching of the luminescence. In this framework, in order to exclude the presence in the membranes of porphyrin aggregates or small oligomers spectroscopic investigation on the composites were performed.

The photophysical properties of this porphyrin in its monomeric form have been reported in organic solvents. [18,19] while a report on its aggregation behaviour in mixed organic-aqueous media pointed out the elusive nature of the aggregates [20]. The TPyP is insoluble in aqueous solution where it is readily soluble under acidic conditions. The X-ray structure of its fully protonated form has been reported.[21]. The TPyP porphyrin solubilized in organic solvent show in the UV/Vis spectra a B-band centred at 417 nm and 4 Q bands in the absorption region 500-700 nm. The fluorescence emission spectra evidence two typical emission bands centred at 653 and 713 nm [18]. In Figs. 2 and 3 the UV-Vis and fluorescence emission spectra of SPEEK-5% TPyP are shown. This profile remains unchanged for all the investigated samples.

Due to high porphyrin concentrations it was not possible to detect the B-band typical for this porphyrin. The extinction spectra of the membranes, obtained by using DMAc as a casting solvent, show the presence of 4 Q-bands centred at 523-564-597 and 648 nm. The fluorescence emission spectrum show two typical emission bands for this porphyrin centred at 662 and 718 nm, respectively.

This spectroscopic behaviour, especially the presence of 4 Q bands, points out the presence of an unprotonated porphyrin core, typical of the free base porphyrin (D2h, symmetry). [22] The red shift of Q-bands in extinction spectrum as well as fluorescence emission bands with respect porphyrin in solution may be ascribed to the different polarity of the environment or to the confined micro-enviroments in which the TPyP is located [23].

Independently, from the membrane thickness and from the porphyrin loads, this chromophore embedded in the membranes exhibits good stability and chemical resistance to thermal annealing and acidic treatment. In fact, the spectroscopic features before and after the treatments remain unchanged for all investigated samples. The reported spectra are related to treated membrane having the highest amount of TPyP (5wt%) and are perfectly overlapped to the other samples.



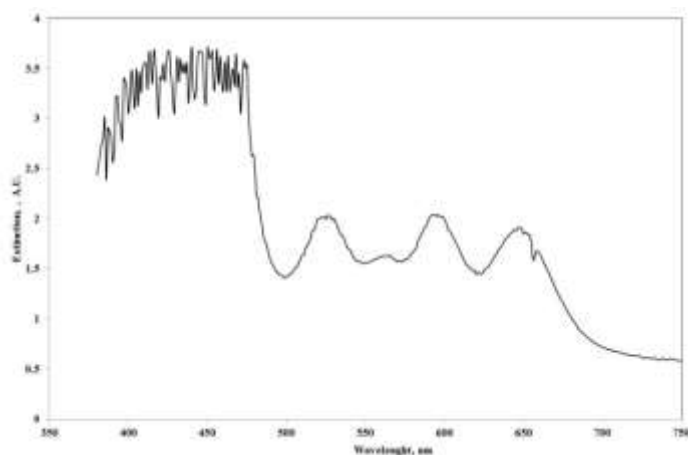


Fig.2 UV-VIS spectrum of SPEEK-5% TPyP

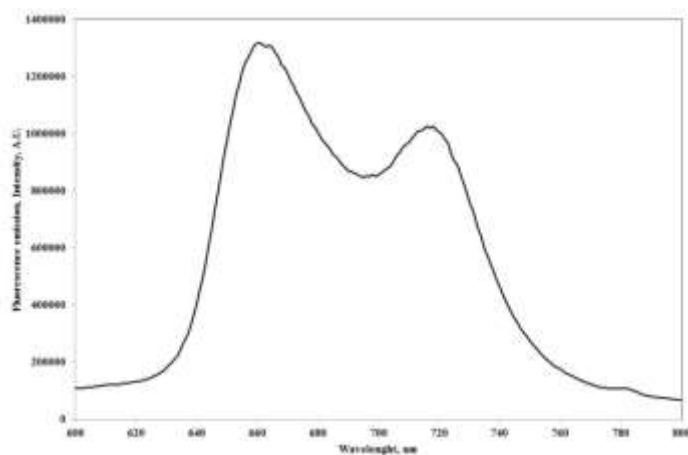


Fig.3 Fluorescence emission spectrum of SPEEK-5% TPyP

SEM analyses were performed to check the morphology of composite membrane compared to pristine SPEEK one (Fig.4). In both cases a dense and homogeneous structure was highlighted, meaning that no agglomeration of TPyP occurred, even for membrane with the highest TPyP content (reported in Fig.4b).



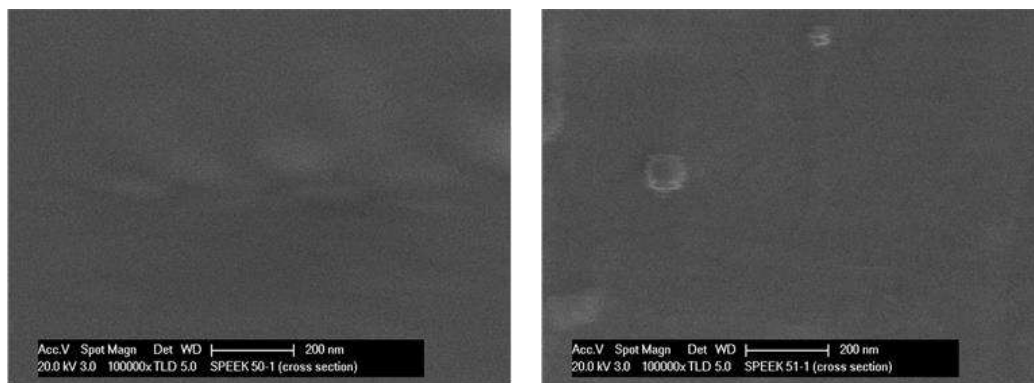


Fig.4 SEM analysis of a) SPEEK membrane

b) SPEEK-5%TPyP membrane

To verify the influence of TPyP on the proton exchange properties of SPEEK, the experimental (IEC_m) and the calculated IEC_p were compared and reported in Fig.5.

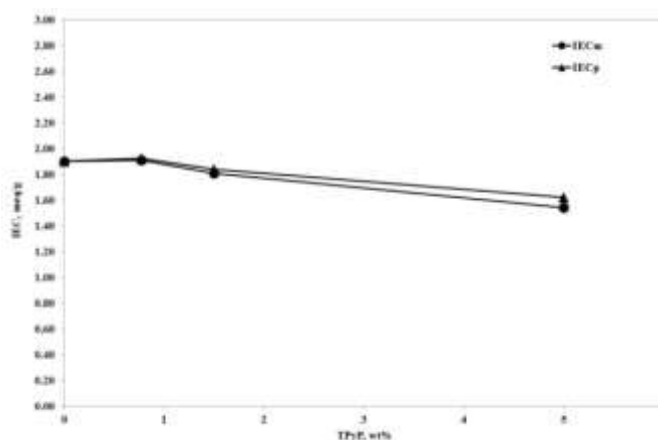


Fig.5 IEC behaviour as a function of TPyP loading

The IEC_m decreases with the increase of porphyrin amount, because the TPyP has not own exchangeable protons. In addition, the ability of SPEEK polymer to form interactions with nitrogenous groups is known and elsewhere reported [16]. Also with the TPyP introduction, specific interactions between sulphonic and nitrogenous groups are present, as highlighted from IEC_p data. This values were calculated by considering the theoretical amount of TPyP introduced in the membranes and the obtained values are related to the SPEEK polymer in the composite membranes. As reported in Fig. 5, the IEC_p is still lower than pristine SPEEK membrane, indicating that interactions occurred that limit the proton exchange capacity.

The behaviour of water uptake (w.u.) and dimensional variation (area %) is shown in Fig.6, as a function of the TPyP content.



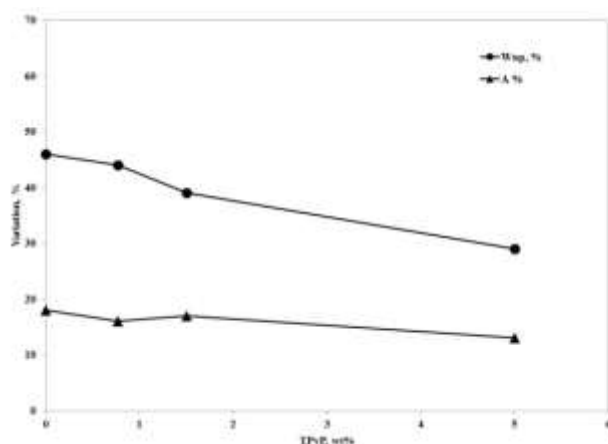


Fig.6 Water uptake and area variation as a function of TPyP amount

In accordance to IEC behaviour, both w.u. and A% decrease by increasing filler loading, meaning that the TPyP interaction with the sulphonic groups of the PEEK reduces the swelling of the polymeric matrix. An interesting trend is highlighted in Fig.7, where is reported the proton conductivity as a function of the lambda values. Because of the lambda values is generally related to the hydration of sulphonic groups of the polymer, the capability to maintain unaltered the properties to coordinate water in composite membranes is an important feature to be considered. As expected, the proton conductivity increases with the increase of water content but sample SPEEK-0.77% TPyP maintains its proton conductivity quite similar to pristine recast SPEEK (values at $\lambda=13$), even if a slight reduction of w.u. and A% is found. Moreover, if compared to the other investigated samples, it has the ability to retain water in drastic conditions (dry gas) and consequently to maintain a proton conduction, as reported in Tab.1.

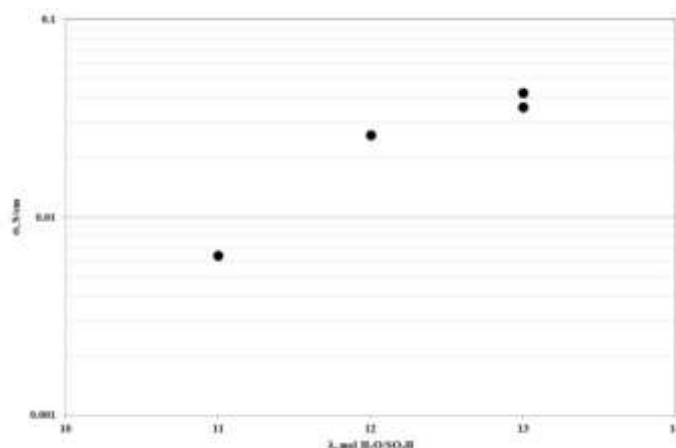


Fig.7 Proton conductivity as a function of lambda values

In fact, in Tab.1 the proton conductivity data measured at 30°C, 100%RH and dry hydrogen are compared. Because the setup of the measurement is different from fuel cell, in which the membrane is constrained in the MEA, in this kind of measurement the sample is more available to hydration changes and can prompt respond to these changes. The SPEEK-0.77 TPyP sample is the only that maintains a suitable hydration to reach a proton conduction,



due to its intrinsic properties. The other samples showed a drop in the proton conduction with a reported value <0.01 mS/cm, under the instrument sensitivity limit, due to a rapid de-hydration.

Tab.1 Proton conductivity values at different operative conditions			
Membrane	λ , mol H ₂ O/SO ₃ H	Proton Conductivity at 30°C, mS/cm	
		100%RH	Dry
SPEEK	13	42	<0.01
SPEEK-0.77% TPyP	13	36	10
SPEEK-1.5% TPyP	12	26	<0.01
SPEEK-5% TPyP	11	7	<0.01

To verify the single cell performance useful for portable applications, the composite membranes, were tested in the operative conditions of low temperature and pressure and compared to recast SPEEK. In Fig.8, the polarisation curves at 30°C, 1 abs. bar and full hydrated gases are shown. Since the useful voltage range, for a real application, is between 0.6-0.7 V, the I-V curves are cut off at 200mA/cm². The performance of composite membranes are in accordance to the previous chemical-physical and ex-situ electrochemical data, in fact the performance decreases with the increase of TPyP amount. The SPEEK-0.77% TPyP shows slight higher performance than SPEEK recast membrane.

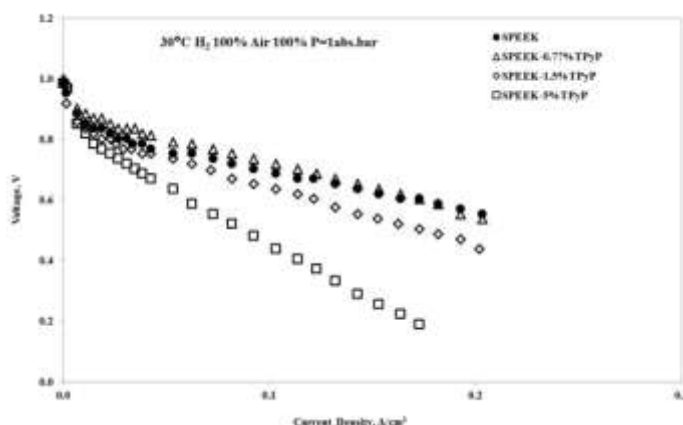


Fig.8 I-V curves comparison at low T, P and 100%RH H₂/air

All the investigated samples present good OCV values (Tab.2), confirming the dense structure of the membranes. The R_s values, obtained from EIS spectra, are in general high and they increase with the amount of TPyP. The power density at 0.7 V is reported in tab.2, it is still evident the benefit of the small amount of TPyP (0.77%) in the polymer matrix, in fact a power density of 80mW was reached against 65mW of SPEEK.

Tab.2 Electrochemical data at 100%RH H ₂ /air			
Membrane	OCV V	Rs (EIS)	PD @ 0.7V
		Ωcm^2 850mV	mW/cm ²
SPEEK	0.985	0.612	65



SPEEK-0.77%TPyP	1.000	0.672	80
SPEEK-1.5%TPyP	0.999	0.855	50
SPEEK-5%TPyP	1.000	1.852	24

To simulate the real application in portable devices where gases are not humidified, operative conditions were changed in dry H_2 /100%RH air, supposing a hydrated cathode for the atmospheric humidity (air-breathing) and the water reaction formation. The polarisation curves are reported in Fig.9.

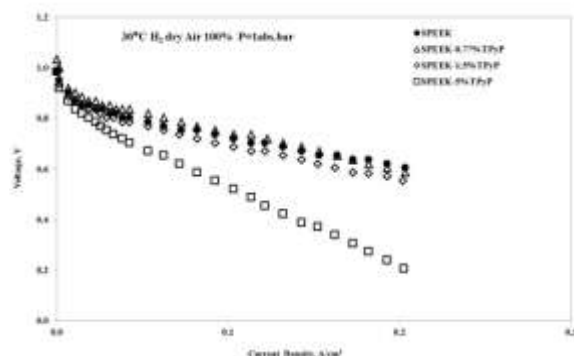


Fig.9 I-V curves comparison at low T, P and dry H_2 /100%RH air

Also in this case the trend is similar to the full humidification. The performance slightly increased despite the dry condition of the anode. This behaviour could be probably caused by a not good water management in full humidification operative conditions, that affects the performance.

Tab.3 Electrochemical data at dry H_2 /100%RH air

Membrane	OCV	Rs (EIS)	PD @ 0.7V
	V	Ωcm^2 850mV	mW/cm ²
SPEEK	0.985	0.590	85
SPEEK-0.77%TPyP	1.018	0.780	93
SPEEK-1.5%TPyP	0.985	0.720	65
SPEEK-5%TPyP	1.000	2.367	29

Also in these operative conditions the OCV data remains good and the power density is increased, with the highest value of 93 mW/cm² at 0.7V for membrane containing 0.77wt% TPyP (Tab.3).

Anyhow, the SPEEK-0.77% TPyP membrane represents the best compromise between chemical-physical properties and electrochemical performance. Taking into account that for a portable device, such as smartphone or tablet or handheld radio, could be sufficient a power of about 20W, the SPEEK-0.77 TPyP could be considered a good candidate to be used in a small stack for a real application.



Summary and perspectives

Composite membranes based on sulphonated Polyetheretherketone (sPEEK) and 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) were developed for portable applications. A sulphonation degree of 65% and different weight percentages (0-5%) of TPyP porphyrin were used for membranes realization. A complete chemical-physical and electrochemical characterization was carried out. The TPyP introduction does not modify the structural and morphology properties of the polymer while some changes occurs in the IEC, water uptake, dimensional variation and lambda values. This behavior is attributed to the formation of interactions between the sulphonic groups of the polymer and the nitrogenous group of the TPyP. This interaction with a hydrogen sieve material such as TPyP, produces a not aggregated form of the TPyP but a good interaction with the polymeric matrix with a network formation. The proton conductivity of the membrane with the lowest loading (0.77wt% TPyP) does not change respect the pristine SPEEK reference, despite a reduction of water uptake and area % and is maintained in the same order of magnitude in dry conditions. In addition, during fuel cell operation at low temperature, pressure and dry hydrogen, this sample supplies the best power density. The properties of this membrane configuration renders it a good candidate for a real application in portable devices.

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