Increasing the operation temperature of polymer electrolyte membranes for fuel cells: From nanocomposites to hybrids

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Abstract

Among the possible systems investigated for energy production with low environmental impact, polymeric electrolyte membrane fuel cells (PEMFCs) are very promising as electrochemical power sources for application in portable technology and electric vehicles. For practical applications, operating FCs at temperatures above 100 °C is desired, both for hydrogen and methanol fuelled cells. When hydrogen is used as fuel, an increase of the cell temperature produces enhanced CO tolerance, faster reaction kinetics, easier water management and reduced heat exchanger requirement. The use of methanol instead of hydrogen as a fuel for vehicles has several practical benefits such as easy transport and storage, but the slow oxidation kinetics of methanol needs operating direct methanol fuel cells (DMFCs) at intermediate temperatures. For this reason, new membranes are required. Our strategy to achieve the goal of operating at temperatures above 120 °C is to develop organic/inorganic hybrid membranes. The first approach was the use of nanocomposite class I hybrids where nanocrystalline ceramic oxides were added to Nafion. Nanocomposite membranes showed enhanced characteristics, hence allowing their operation up to 130 °C when the cell was fuelled with hydrogen and up to 145 °C in DMFCs, reaching power densities of $350\,\mathrm{mW\,cm^{-2}}$. The second approach was to prepare Class II hybrids via the formation of covalent bonds between totally aromatic polymers and inorganic clusters. The properties of such covalent hybrids can be modulated by modifying the ratio between organic and inorganic groups and the nature of the chemical components allowing to reach high and stable conductivity values up to $6.4 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ at 120 °C.
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1. Introduction

Among the possible systems investigated for energy production with low environmental impact, fuel cells are very promising as electrochemical power sources both for stationary energy production and application in portable technology and electric vehicles. Polymeric electrolyte membrane fuel cells (PEMFCs) are the most promising candidates for the latter application. The material most widely used for electrolyte membranes is Nafion, a perfluorinated sulfonated polymer. Because of its water assisted conduction mechanism, Nafion can be used only at temperatures below 100 °C [1].

For practical applications, however, operating PEMFCs at higher temperature is desired, both for hydrogen and methanol-fuelled cells. When hydrogen is used as a fuel, an increase in the cell temperature above 100 °C produces enhanced CO tolerance,

faster reaction kinetics, easier water management, and reduced heat exchanger requirement. The use of methanol as a fuel for vehicles has several practical benefits such as easy transport and storage, but the slow oxidation kinetics of methanol and its crossover through the membrane reduce the efficiency of direct methanol fuel cells (DMFCs). Therefore, increasing the operation temperature of proton conducting membranes is a key issue in the development of PEMFC technology [2]. In particular, for automotive applications, operating a FC vehicle at ambient temperature above 20 °C requires either a large radiator, a solution certainly not sought after by most car manufacturers, or an increase in the operation T above 100 °C. For the optimization of water management and thermal balance, reasonable standards have been set at an operating temperature of ca. 120 °C with 25% RH [3].

Significant research efforts are devoted to the achievement of the above mentioned goals, and several reviews on the state of the art have been published [4,5]. Two main topics have been identified: understanding the mechanisms of functioning of Nafion, so that proper modification may be designed,

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and sulfonation and/or modification of different polymers [1,6-9].

The strategy followed in our laboratories to achieve the goal of obtaining PEMs capable to operate at temperatures up to and above 120 °C is to develop organic/inorganic hybrid membranes. Organic/inorganic hybrids are investigated for a variety of applications, ranging from optics to electronics, to sensors and many others, since they offer the possibility to combine the properties of the two components in a unique material [10]. They have been classified into two classes: in Class I hybrids the two components are held together by weak non-covalent interactions, and in Class II hybrids the organic and inorganic moieties are linked through covalent bonds. In this latter case, control at atomic level of the proper dosage and dispersion of the inorganic component can be reached, leading to very interesting and novel properties [11].

We have thus prepared nanocomposite Class I hybrids, where nanocrystalline ceramic oxides of different chemical nature and morphology were added to Nafion, and Class II hybrids via the formation of covalent bonds between totally aromatic polymers and inorganic clusters. The properties of such covalent hybrids can be modulated by modifying the ratio between organic and inorganic groups and the nature of the chemical components. The main results of our work are reviewed in this paper.

2. Class I hybrid proton conducting membranes

2.1. Nafion-based nanocomposite with nanocrystalline oxides

Composite materials have been shown to develop new multifunctional properties deriving from the synergic merge of the characteristics of each individual component [12]. In the case of polymeric electrolytes, the addition of nanocrystalline oxides is effective in improving ionic conductivity, mechanical strength, and thermal stability [6]. Since performance is strongly influenced by the filler particle size, we developed a simple and versatile route for the preparation of ceramic oxides with nanometric grain size [13]. M_xO_y (M = Ti, Nb, In and Zr) were synthesized by rapid hydrolysis of an alcoholic solution of metal alkoxides. The preparative conditions were optimized to enhance the reaction kinetics leading to fast nucleation and favoring the formation of nanoparticles.

Fig. 1 shows the TEM micrograph of TiO_2 (chosen as a representative example) obtained by thermal treatment of the sol–gel precursor at 500 °C. The particle size was in agreement with the XRD measurements (12 nm), although the presence of aggregates was determined.

The in-house prepared nanocrystalline titania was used as a filler in the preparation of Nafion based composite membranes to be used as electrolytes in PEMFCs, with the aim of increasing the operation temperature. The electrochemical performance of such membranes was investigated both in methanol and hydrogen fuelled fuel cells.

To understand the influence of the inorganic filler content on the performance of a DMFC, membranes containing various amounts of TiO_2 (3, 5 and 10 wt.%) were prepared and an investigation of the influence of particle size and crystallographic
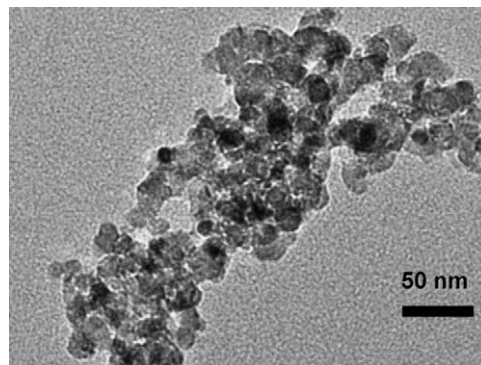

Fig. 1. TEM micrograph of sol–gel derived titania calcined at 500 °C.

phase transition (from anatase to rutile) on the electrochemical behavior was also carried out [14].

Fig. 2 shows the diffraction patterns of TiO_2 powders heated at different temperatures. The powders heated at 500 and 650 °C showed the anatase structure, while heating to 800 °C caused transformation into the rutile crystallographic structure. Heating caused the increase of particle size from 12 to 22 nm, to 39 for the powders treated at 500, 650, and 800 °C, respectively.

At first, the electrochemical behavior of the membranes prepared with different TiO_2 loadings was investigated. The powder heated to 500 °C was selected for such a comparison because of the oxide smaller particle size. All the membrane electrode assemblies (MEAs) prepared with the membranes of different composition were capable to operate in a DMFC up to 145 °C, a temperature much higher than that reached by a bare Nafion recast membrane.

Fig. 3 shows the polarization (a) and power density (b) curves obtained for the DMFC prepared with such MEAs with a 2 M methanol solution feed at the anode, and using oxygen as oxidant. A maximum power density of 350 mW cm^{-2} was reached at a current density of about 1.1 A cm^{-2} with the membrane containing 5 wt.% TiO_2.

Moreover, the cell was subjected to a 1 month cycled operation (6 h per day including start up and shut down procedures) without significant performance decrease.
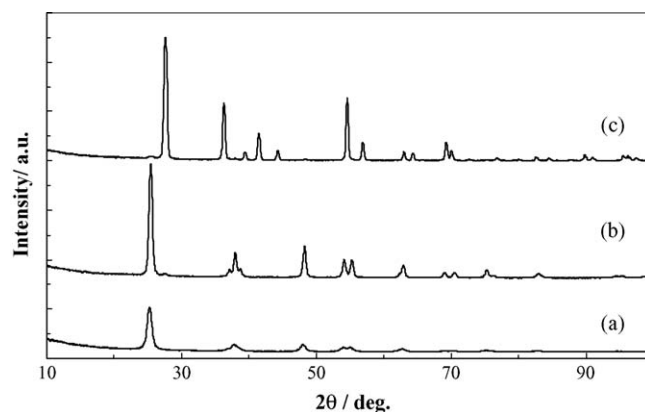

Fig. 2. X-ray diffraction patterns of TiO_2 powders calcined at different powders. (a) 500 °C; (b) 650 °C; (c) 800 °C.
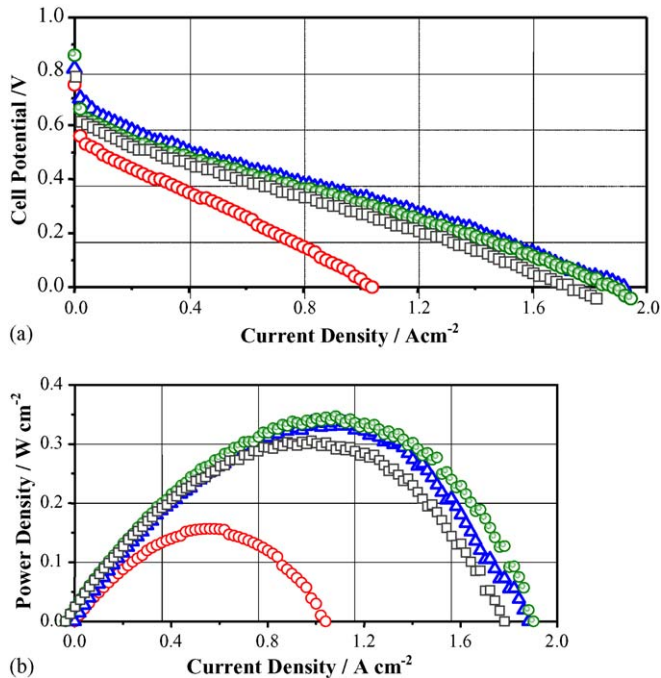
(a)

(b)

Fig. 3. DMFC polarization (a) and power density curves (b) at 145 °C for various MEAs equipped with composite membranes containing different amounts of titania calcined at 500 °C compared with a bare Nafion recast membrane. 2 M methanol feed, 2.5 atm rel.; oxygen feed, 2.5 atm. rel. (△) 3 wt.%; (◎) 5 wt.%; (□) 10 wt.%; (○) Nafion.

The composition 5 wt.% was thus chosen to compare membranes containing titania powders of different particle size, morphology and crystallographic phase. The best electrochemical performance was obtained with the powder having the anatase structure and the smaller particle size, i.e. with the oxide calcined at 500 °C.

To further clarify the influence of the physico-chemical properties of the filler on the electrochemical performance of composite membranes, a study of the filler characteristics in terms of specific surface area (SSA) and oxygen functional groups by means of X-ray photoelectron spectroscopy and pH measurements on titania powders heated to different temperatures was carried out [15].

Fig. 4. Variation of cell resistance as a function of the operating temperature for MEAs prepared with TiO$_2$ calcined at 500 °C (♦), 650 °C (■) and 800 °C (▲).

The powders calcined at lower temperatures showed a larger content of oxygen species associated with the presence of surface OH groups. The concentration of surface Ti–OH groups can be correlated with the oxide acidic character, as demonstrated also by the pH of slurry determined for the various powders. Table 1 summarizes some of the physico-chemical properties of the TiO$_2$ powders calcined at different temperatures.

The surface oxygen species might be responsible of interactions of water and of the Nafion polymeric backbone with the fillers during membrane operation at temperatures above 100 °C. The presence of the fillers may further contribute to inhibiting the direct permeation of reaction gases by modifying the transport pathways [16].

The filler physico-chemical characteristics affected the DMFC operation at 145 °C of the MEAs containing 5 wt.% of titania calcined at the various temperatures.

Fig. 4 shows the variation of the cell resistance as a function of the operating temperature and Fig. 5 shows the polarization and power density curves measured for the various MEAs prepared with the titania powders calcined at different temperatures. The membranes containing powders treated at 650 and 800 °C having different crystallographic structure showed similar electrochemical performance. The best performance was obtained with the powder calcined at 500 °C having smaller particle size, higher specific surface area and higher surface acidity.

Table 1
Physico-chemical properties of TiO$_2$ powders

Calcination temperature (°C)	XPS O 1s B.E. (eV)	Relative XPS O 1s peak area (%)[a]	Crystallographic structure	Mean particle size (nm)[b]	pH of slurry	Specific Surface Area (m^2 g^{-1})[c]
500	529.5	72.91	Anatase	12	5.3	130
	530.8	21.08				
	532.0	5.01				
650	529.6	75.52	Anatase	22	6.2	70
	530.7	12.61				
	532.3	11.87				
800	529.5	84.23	Rutile	39	9.0	35
	530.9	11.20				
	532.2	4.57				

[a] Derived from curve fitting of the XPS spectra.
[b] From XRD; (1 0 1) reflection for anatase and (1 1 1) reflection for rutile.
[c] Evaluated from particle size assuming an approximately spherical shape for primary particles.
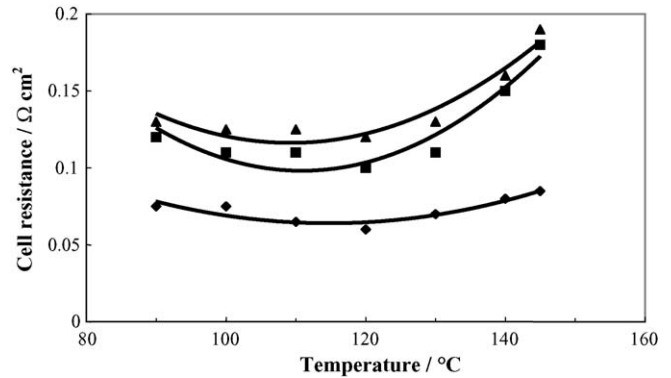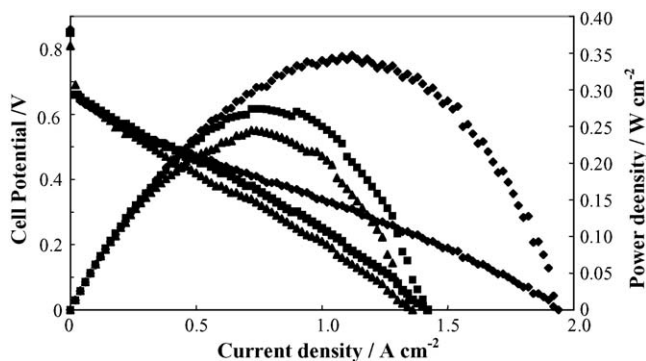
Fig. 5. DMFC polarization and power density curves at 145 °C for various MEAs equipped with composite membranes containing 5 wt.% titania calcined at 500 °C (◆), 650 °C (■) and 800 °C (▲) (2 M methanol feed, 2.5 bar; oxygen feed, 2.5 bar).

Table 2
Water uptake and ion exchange capacity data for different Nafion-based membranes

Membrane	Water uptake (%)	IEC (mequiv. g^{-1})
Nafion 115	27	0.91
Nafion recast	20	0.89
Nafion–TiO_2	29	0.93

Operation at temperatures above 100 °C is needed also for hydrogen-fuelled polymer electrolyte fuel cells, both for direct hydrogen (DH-PEFC) and processed hydrogen (PH-PEFC) cells, to enhance reaction kinetics, reduce heat-exchange requirements and, in PH-PEFC, increase CO tolerance. We have thus studied the electrochemical performance of a Nafion based composite membrane, containing 3 wt.% nanometric TiO_2 calcined at 400 °C [17].

Table 2 summarizes the water uptake and ion exchange capacity (IEC) of the nanocomposite membrane compared with the values relative to a pure Nafion recast membrane prepared in the same experimental conditions and a commercial Nafion 115 membrane. The water uptake and ion exchange capacity of the composite membrane were significantly higher than those determined for the reference pure Nafion recast membrane, while commercial Nafion 115 gave intermediate values.

The proton conductivity of the membranes was examined in the temperature range from 80 to 130 °C. The conductivity was always higher for the composite membrane, reaching a value of 0.18 S cm^{-1} at 130 °C.

The commercial Nafion 115 and the composite membrane were tested in DH-PEFC, in a single cell, in humidified H_2/air, between 80 and 130 °C. In the whole temperature range tested, the best performance was obtained with the composite membrane. Fig. 6 shows the polarization and power density curves obtained for the two membranes at 110 °C and those relative to the nanocomposite membrane at 130 °C. A power density of 0.514 mW cm^{-2} was recorded for the composite membrane versus 0.354 mW cm^{-2} obtained with Nafion 115 at 0.56 V and 110 °C. Most important is to notice that while the pure Nafion membrane was damaged at temperatures above 100 °C, the composite membrane continued to operate up to 130 °C reaching a power density of 0.254 mW cm^{-2} at 0.5 V.

Tests were also carried out in a PH-PEFC. The cell was fed with steam reforming synthetic fuel (SR: 10 ppm CO; 20% CO_2; 75% H_2; 1% CH_4). Fig. 7 shows a comparison between polarization curves at 110 °C in pure hydrogen and SR for the nanocomposite membrane. For both fuels, the measured OCV values were good, almost reaching 1 V. A power density value of about 182 mW cm^{-2} at 0.6 V in synthetic fuel, versus the 366 mW cm^{-2} value measured in pure hydrogen, was obtained. Although the performance for tested MEA fed with SR is lower by about 50% if compared to the performance in pure hydrogen, it is reasonable to assume that the use of suitable electrodes containing Pt–Ru as an electro-catalyst would minimize such loss.
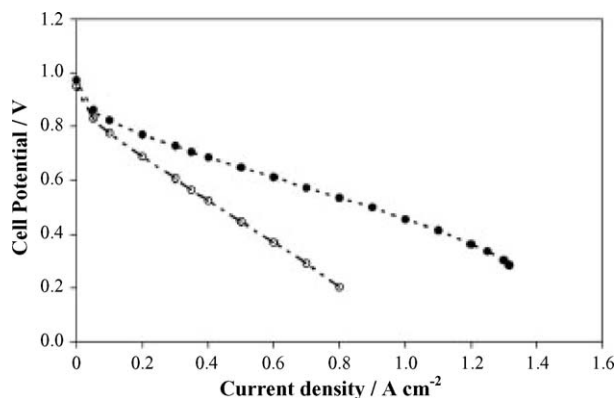

Fig. 7. Polarization curves measured with MEAs equipped with the nanocomposite Nafion-based membrane containing 3 wt.% TiO_2 at T = 110 °C in pure H_2 (●) and steam reforming synthetic fuel (○).
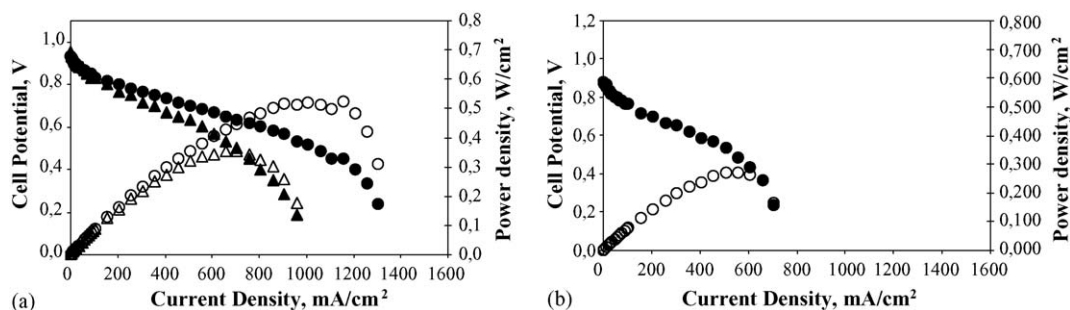

Fig. 6. DH-PEFC polarization and power density curves at 100 °C for (a): composite Nafion–TiO_2 membrane (●, ○) compared to Nafion 115 (▲, △) and (b): composite membrane at 130 °C.
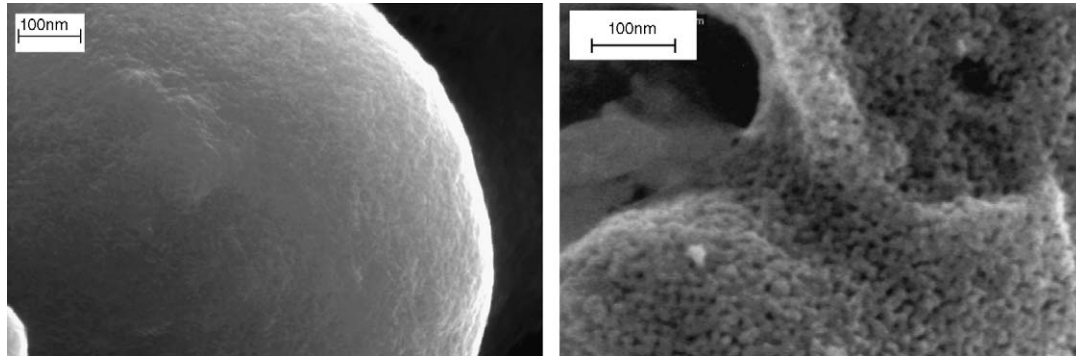
Fig. 8. FE-SEM image of titanium oxide powder as-synthesized (a) and after calcination at 450 °C for 6 h (b).

Nevertheless, it appeared evident that the filler exerts a beneficial effect in allowing operation at $T > 100$ °C even in SR fuel.

2.2. Nafion-based nanocomposites with mesoporous titania

As an extension of our studies on the electrochemical performance of Nafion-based membranes containing nanocrystalline oxides, we investigated the influence of increasing the filler specific surface area by preparing composite membranes containing mesoporous titania.

Mesoporous TiO_2 was synthesized using dimethylaminotitanatrane as a precursor to avoid the problems connected with the high reactivity of titanium alkoxides [18]. Cetyltrimethylammonium bromide (CTAB) was used as templating agent to obtain an ordered structure. The powder was characterized with numerous techniques, including nitrogen adsorption–desorption isotherms, simultaneous thermogravimetric–differential thermal analysis, Fourier transform infrared spectroscopy, field emission scanning electron microscopy, and X-ray diffraction [18]. Thermal treatments resulted critical to obtain a mesoporous powder; the best conditions were identified in a stepped thermal treatment: the precursor was heated under N_2 flow at 120 °C for 2 h, then at 350 °C for 5 h, to avoid uncontrolled combustion of the organic phase, and finally calcined in air at 450 °C for 6 h.

Treatments at higher temperatures caused the collapse of the mesoporous structure.

Fig. 8 shows the FE-SEM images of the as-synthesized and thermally treated powders. Mesopores deriving from surfactant removal were clearly observed within the particles of the powder heated to 450 °C. FTIR proved the complete removal of the organic phase after such thermal treatment and absorption–desorption isotherm measurements indicated a narrow pore size distribution with a maximum centered at 3.5 nm. The measured value of BET specific surface area was $115 \, m^2 \, g^{-1}$ for the powder heated to 450 °C for 6 h.

MEAs were prepared with the composite membranes containing mesoporous titania for DMFC measurements and tested in the temperature range between 90 and 145 °C [19]. Fig. 9 shows the polarization and power density curves for the membrane containing 5 wt.% of mesoporous titania calcined at 450 °C. In this case, the maximum power output steadily increased with the temperature up to 145 °C. Rising the temperature from 130 to 145 °C, a significant improvement of both power density and short circuit current density was observed, reaching values of $335 \, mW \, cm^{-2}$ as maximum power density and $1.65 \, A \, cm^{-2}$ as short circuit current density, at 145 °C.

Fig. 10 shows the comparison between the polarization and power density curves determined for a cell operating at 145 °C
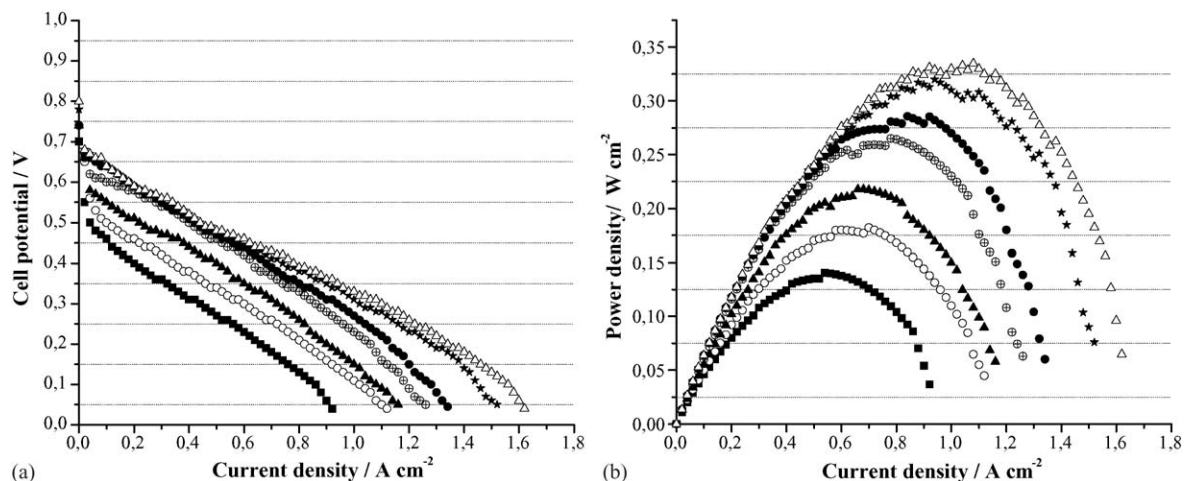

Fig. 9. Polarization (a) and power density (b) curves of a DMFC operated with the composite Nafion-based membrane containing 5 wt.% of mesoporous TiO_2 prepared at 450 °C, in the presence of oxygen feed and 2 M methanol. 90 °C (■), 100 °C (○), 110 °C (▲), 120 °C (⊕), 130 °C (●), 140 °C (★), 145 °C (△).
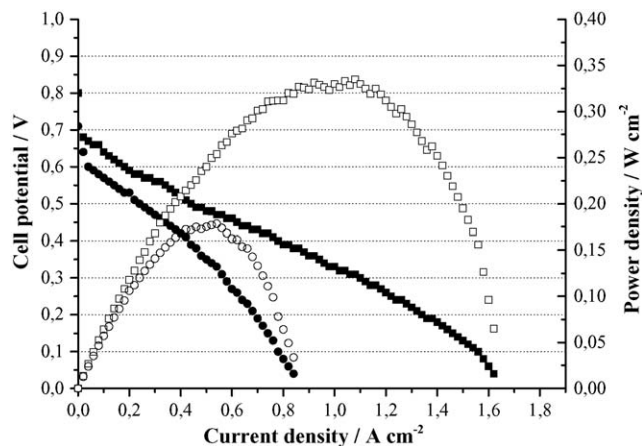
Fig. 10. Polarization and power density curves for the MEA containing 5 wt.% of mesoporous titania heated to 450 °C, measured at 145 °C in air and oxygen feed (2 M methanol). (●) cell potential in air; (■) cell potential in oxygen; (○): power density in air; (□): power density in oxygen.

with air and oxygen feed, prepared with the same membrane as in Fig. 9. In the presence of air feed the maximum power density of 178 mW cm^{-2} was reached at a current density of 0.54 A cm^{-2}, while for oxygen feed the maximum power density was 335 mW cm^{-2} at a current density of about 1.08 A cm^{-2}.

As previously observed for a DMFC based on a nanocomposite Nafion membrane including 5 wt.% of nano-sized TiO_2 particles, a DMFC based on a recast Nafion membrane containing 5 wt.% mesoporous TiO_2 was operated for 100 h without observing a decrement of the electrochemical performance.

3. Class II hybrid proton conducting membranes

Arylene main chain polymers have received a great deal of attention as possible alternative to perfluorinated systems mainly because of their lower cost and their ease of functionalization [20,21]. Among the different polymers, sulfonated polyetheretherketone (SPEEK) has been widely studied because, at high degree of sulfonation (DS), its conductivity is large enough to meet the requirements needed for appli-

cation in PEMFCs. However, its mechanical properties tend to progressively deteriorate with sulfonation. It is known, in fact, that in polyaryletherketone-based systems, such as SPEEK, the absence of significant hydrophilic-hydrophobic separation results in very narrow and poorly connected water channels and large separation between the sulfonic acid groups [21,22].

The approach we followed to attain the correct balance between the hydrophilic and hydrophobic components was to prepare Class II hybrid polymers where the organic and inorganic moieties were linked through strong covalent bonds [23].

Although composite Class I hybrids gave satisfactory results, it is very hard to achieve homogeneity in systems where the fillers may be, at best, finely dispersed in the polymeric matrix. On the contrary, in Class II hybrid materials control at a molecular level of the dosage and dispersion of inorganic clusters may be reached, thereby resulting in an improvement of electrochemical performance. We thus prepared an organic/inorganic hybrid containing sufficient amount of inorganic component (as –Si(OH)$_3$ moieties) to improve SPEEK mechanical properties without significantly alter its conductivity. Despite its poor mechanical properties and difficulties in manipulation, it was chosen to use SPEEK with a high degree of sulfonation (DS = 0.9) to enhance conductivity, since solubility can be modulated by proper dosage of the inorganic component.

SPEEK was reacted with butyllithium at low temperature, in the presence of N,N,N',N'-tetramethylethylendiamine (TMEDA), which is known to promote the aromatic substitution reaction and subsequent reaction with $SiCl_4$, followed by hydrolysis. Scheme 1 shows the reaction sequence for the preparation of SiSPEEK.

The presence of silicon moieties, covalently bound to the polymer main chain was demonstrated by elemental analysis (% Si = 1.3 ± 0.1, corresponding to a ratio 100:17 monomeric unit:silicon), ^{29}Si NMR, and ATR/FTIR spectroscopies.

Fig. 11 shows the ^{29}Si NMR spectrum of SiSPEEK. The spectrum is characterized by two resonances (relative intensity 4:1), whose chemical shifts (−72.5 and −82.0 ppm) are typical of polyaryl-silicon T units [24] and were assigned to the two isomers shown in Scheme 1. No dispersed inorganic sil-
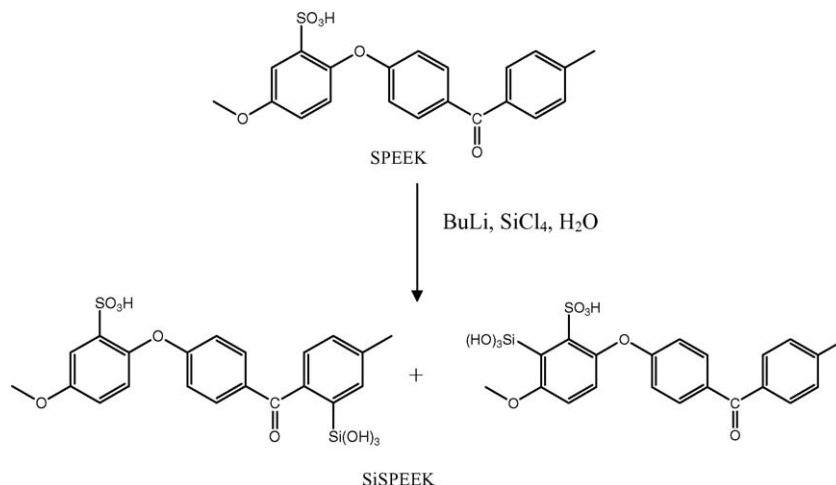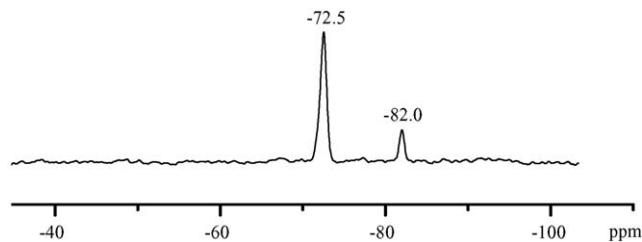

Scheme 1. Synthesis of sylilated SPEEK (SiSPEEK).

Fig. 11. ^{29}Si NMR spectrum of SiSPEEK in DMSO.

icon is present, as demonstrated by the lack of any peak at $\delta < -100$ ppm, characteristic of Q units [25].

The ATR/FTIR spectrum of the products showed bands, at 933 and 875 cm^{-1}, typical of aromatic silanols, together with a third band at 1127 cm^{-1}, attributed to the in-plane deformation of the ring with some contribution from the Si–C stretch. No bands due to Si–O–Si bonds were observed.

The thermogravimetric analysis of SiSPEEK showed no substantial difference with respect to the data relative to the parent SPEEK indicating that the formation of the hybrid did not alter the thermal stability of the polymeric structure.

Membranes of SiSPEEK were prepared by casting and activated in 5 M H$_2$SO$_4$. While SPEEK with elevated DS is soluble or form gel when immersed in water, SiSPEEK membranes showed an elevated water uptake still remaining flexible and easy to handle. The formation of covalently bound inorganic clusters increased then the level of water uptake, but did not result in excessive swelling or solubility in water of the membrane making conductivity measurements feasible.

Ionic conductivity was measured at room temperature by electrochemical impedance spectroscopy (EIS) using blocking Pt electrodes in the frequency range 1 Hz–100 kHz. Stable conductivity values were measured over a week, in the range 2×10^{-2}–1×10^{-2} S cm^{-1} (Fig. 12). No deviations from lin-
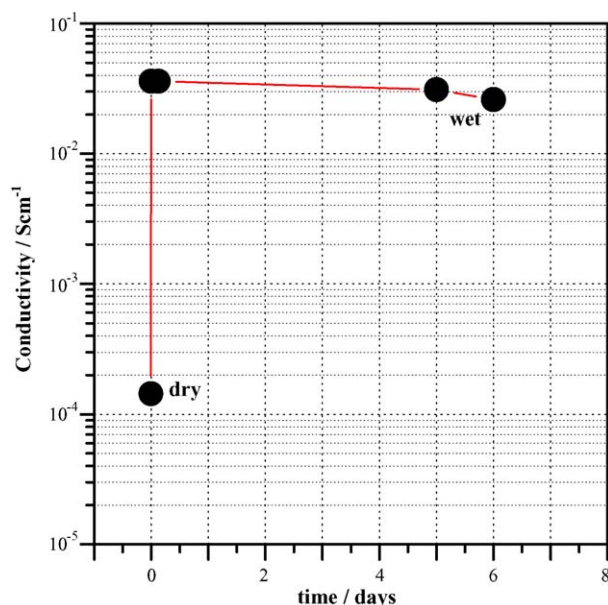

Fig. 12. Room temperature conductivity as a function of time of SiSPEEK membrane in dry and wet conditions (water uptake = 200%).

earity were observed in the impedance spectra of all samples after different storage periods, therefore implicating that the samples integrity was maintained over the examined period of time. Literature data for the room temperature conductivity of SPEEK membranes vary from 5.05×10^{-3} S cm^{-1} for DS = 0.85–8×10^{-3} S cm^{-1} for DS = 0.80. The values obtained for SiSPEEK membranes showed that while solubility properties were improved, conductivity values were not affected by the formation of the hybrid and values are suitable for performance as ion conducting membranes.

Another interesting material that we chose for the preparation of hybrid polymeric electrolytes is polyphenylsulfone (PPSU), a fully aromatic polymer with good thermal stability and oxidation resistance [26,27]. As for PEEK, the conductivity of PPSU is a function of the degree of sulfonation: conductivity values of about 10^{-3} S cm^{-1} have been reported for SPPSU with DS = 0.7, while larger sulfonation degrees lead to water soluble species, preventing possible application in fuel cells [5,28,29].

Among the reason considered to focus our attention on this polymer, prominent was its solubility in organic solvents that allowed to carry out functionalization reactions in organic solvents and in homogeneous conditions, a circumstance hardly met by other polymers. Once a hybrid is formed, proper conductivity can be achieved by introducing a large number of sulfonic acid groups or by mixing it, either in a blend or preparing copolymers, with a more conductive material. An interesting method to improve polymeric electrolyte performance is, in fact, to prepare physically cross-linked membranes by blending ionomeric polymers with different mechanical properties. The blending technique has the advantage of combining the positive features of each component while being very simple.

At variance with the procedure followed for the preparation of SiSPEEK, in the case of PPSU the formation of covalent C–Si bonds was carried out as the first synthetic step since the polymer is soluble in THF. Sulfonation was then carried out on the sylilated product in concentrated sulfuric acid. To enhance conductivity properties we aimed to reach a very high DS: in a first attempt we bound Si(OH)$_3$ moieties to PPSU, then sulfonated it up to DS = 2. With this material, we were successful in casting membranes that showed highly satisfactory electrical performance ($\sigma = 1.6 \times 10^{-2}$ S cm^{-1} at room temperature), but unfortunately combined with poor mechanical properties (excessive swelling). We have thus modified the synthetic strategy and used as sylilating agent PhSiCl$_3$, to verify if the extra phenyl substituents could decrease solubility in water of the final product (SiSPPSU) [30]. The synthetic procedure is illustrated in Scheme 2, where possible sulfonation on the silicon-bound phenyl ring is omitted for clarity. The product was characterized by elemental analysis (C, S and Si content) which confirmed the DS value, while the determined amount of silicon (% Si = 0.25 ± 0.05) corresponded to the stoichiometric ratio used for the synthesis, 1:0.05 monomeric unit:silicon, demonstrating the high efficiency of the preparative procedure.

Solubility properties were deeply modified and SiSPPSU resulted insoluble in water. Its plastic properties, however, were too poor to obtain a satisfactory membrane by casting, so it was decided to blend it with SPEEK having DS = 0.9. The
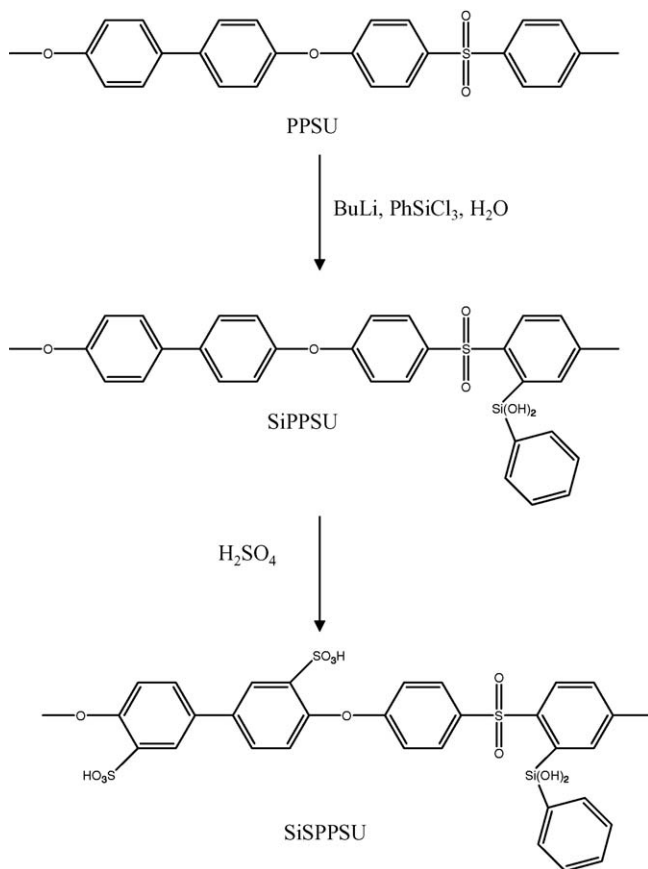
Scheme 2. Synthesis of sylilated and sulfonated PPSU (SiSPPSU).

Fig. 13. Arrhenius plot of the blend SiSPPSU/SPEEK containing 5 wt.% SiSPPSU.

very similar structure of the two polymers, both in terms of aromatic backbone and sulfonation, was expected to ease the formation of the blend via $\pi - \pi$, dipolar and electrostatic interactions. Homogeneous, transparent membranes containing 5 and 10 wt.% SiSPPSU in SPEEK were successfully cast from DMA solutions and their electrochemical performance compared with that of a pure SPEEK membrane. The formation of the blends modified the water absorption characteristics of SPEEK (which at DS = 0.9 shows excessive water swelling or even solubility in water): treatment in water for 1 h of the two blends and of the reference SPEEK resulted in water uptake values of 20% for the 10 wt.% blend, 50% for the 5 wt.% blend and 70% for pure SPEEK. The very low water uptake of the 10 wt.% blend suggested that a too strong interaction occurs between sulfonic acid groups, which may not be all available for proton transfer. This blend showed in fact poor electrochemical performance. On the contrary, the number of water molecules per sulfonic acid groups, $\lambda = 12$, calculated for the 5 wt.% blend was in the range expected to give high proton conductivity.

Fig. 13 shows the Arrhenius plot relative to the hydrated and activated (5 M sulfuric acid) membrane prepared with the 5 wt.% blend: high and stable conductivity values up to 6.4×10^{-2} S cm^{-1} at 120 °C were obtained, demonstrating thus that the material is suitable to be used as electrolyte in PEMFCs at intermediate temperatures.

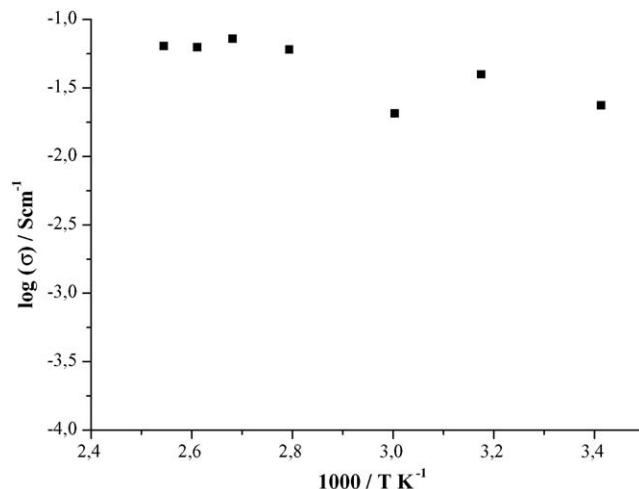Further studies are in progress aiming to improve the characteristics of hybrid polymers. It is foreseeable that such goal might be achieved by modulating the ratio between the organic and the inorganic components and/or or control, via sol/gel processes, the formation of an inorganic network embedded in the organic polymer network.

4. Conclusions

The use of Class I and Class II organic/inorganic hybrid membranes has been demonstrated to be effective in achieving good electrochemical performance of PEMFCs at temperatures above 120 °C, fed either with processed hydrogen, steam-reformed hydrogen, and methanol. Synthetic strategies for the preparation of hybrid polymers where the inorganic component is covalently linked to the organic one were designed and carried out. The strategy to covalently bonding inorganic moieties to all aromatic polymeric backbones to produce Class II hybrid membranes is very promising to further improve the ability to obtain highly-performant membranes operating in fuel cells above 120 °C. This route is open towards a systematic modulation of chemical and electrical characteristics. Tailoring materials at the molecular level offers promise to obtain unique electrochemical performances.

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