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ORIGINAL PAPER

Effect of functionalized silica particles on cross-linked poly(vinyl alcohol) proton conducting membranes

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Abstract A family of proton conducting membranes based on cross-linked poly(vinyl alcohol), PVA, has been synthesized and characterized. The influence of surface-functionalized silica particles on the membrane properties has been evaluated by means of ^{1}H-NMR, vibrational spectroscopy, thermal analysis and electrochemical characterization. The study revealed that the crystallinity of the polymer, the proton diffusivity and the water retention are strongly affected by the presence of the inorganic compound. Conductivity measurements and preliminary fuel cell tests agreed in determining the best PVA/silica ratio among the various compositions explored and demonstrated the potentiality of the selected membranes as electrolytes in fuel cell devices.

Keywords Composite membranes · Cross-linked poly(vinyl alcohol) · Functionalized silica · Fuel cell

1 Introduction

Proton conducting membranes are key components in the development of fuel cell devices to be used as power sources in both electric vehicles and portable electronics [1]. Therefore, great efforts are devoted to the optimization of the conventional perfluorosulfonic polymer membranes, such as Nafion-based systems, and to research of alternative membranes [2, 3]. In this view, "gel-type" systems, formed by confining a highly conductive acidic solution into a suitable polymer matrix, are attracting interest [4, 5]. One of the specific advantages of this type of membrane is related to the proton conduction mechanism which, in contrast with the Nafion case, is not strictly dependent on the relative humidity level [6].

In virtue of its hydrophilic properties and good swelling ability, poly(vinyl alcohol) is a cheap polymer widely used in the formation of membranes for alkaline batteries [7] as well as polymer electrolyte membrane fuel cells. In the latter case, PVA-based membranes have been tested both as proton conductors, by the addition in the polymer matrix of strong acids such as phosphomolybdic and phosphotungstic acids [8, 9], and as anionic conductors, by blending PVA and potassium hydroxide [10]. The presence of functional –OH groups in the PVA chain allows the reaction with aldehydes to form chemical cross-links, resulting in an extended thermal and mechanical stability of the polymer matrix [11]. Another approach aimed at improving the properties of the membrane consists of the formation of polymer-ceramic composites. The inclusion of inorganic compounds in the gel-type membranes is fundamental in promoting the absorption and retention of the conducting solution [12]. Moreover, on the basis of their size, their surface properties and functionalization, the filler particles, besides acting as reinforcing components, have a significant impact on both ion conduction and membrane morphology, by promoting amorphous or crystalline phases [13, 14].

PVA-based proton conducting membranes have recently been studied in our laboratory and the influence of cross-linking reaction, combined with the dispersion of selected ceramic powders, has already been demonstrated [15, 16]. The present paper represents a continuation of the study,

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aimed at highlighting the specific role on the membrane properties of a unique non-inert inorganic additive, having $–SO_3H$ terminal groups anchored to its surface. In addition, in order to prove the applicability of the proposed composite membranes, laboratory fuel cell prototype tests are reported and discussed.

2 Experimental

Poly(vinyl alcohol), PVA, 99+% hydrolyzed, with an average molecular weight of 130,000, was used as supplied by Sigma-Aldrich. The cross-linking agent was a 25 wt.% solution of glutaraldehyde in water, GLA (Sigma-Aldrich, St. Louis, MO, USA). The ceramic filler, 4-Ethyl benzenesulfonyl chloride-functionalized silica (Sigma-Aldrich) was stored in an inert atmosphere. The molecular structure of this functionalized silica is displayed in Fig. 1a. Before use, it was stirred in water and during this process chlorine was exchanged by an OH group, resulting in a $–SO_3H$ end-function, as shown in Fig. 1b. The replacement of –Cl with –OH was proved by detecting with $AgNO_3$ the presence of chlorides in the washing water; this treatment in water was repeated until the $AgNO_3$ test showed that chlorides were no longer present. Nominal particle size and functional groups concentration are 40–65 microns and ca. 1 mmol g^{-1}, respectively.

The PVA-based membranes were prepared by dissolving PVA, or PVA/SiO_x in an appropriate ratio, in distilled water. Then, diluted GLA was gradually added (1,5 mL for each gram of PVA or PVA/SiO_x) together with a small amount of sulfuric acid, acting as catalyst for the cross-linking reaction. The viscous solution was then cast on a Petri-glass dish, undergoing freeze-thaw cycles in order to gain high mechanical strength and elasticity. This freeze-thaw procedure is widely used for PVA-based membranes and is described in depth elsewhere [11]. As a result of this treatment the membranes became dense and self-standing, with a final thickness varying from 200 to 300 µm. More details on the preparation procedure are reported in our previous work [16].

Table 1 summarizes the polymer/filler relative composition for the four cross-linked PVA-based membranes investigated in this work. The membranes are named as *PVA_xSiO*$_x$ where "*x*" is a number indicating the weight percent of functionalized silica in the sample. At the end of the preparation procedure the membranes still contained a large amount of water (between 70 and 90 wt.%). Proton conductivity is achieved by confining a 2 M sulfuric acid solution in the polymer matrix through a simple dipping procedure.

Table 1 Composition of the PVA-based membranes

Membrane	PVA (wt.%)	SiO_x (wt.%)
PVA_0SiO_x	100	–
PVA_10SiO_x	90	10
PVA_14SiO_x	86	14
PVA_25SiO_x	75	25

^{1}H NMR pulse gradient spin-echo (PGSE) method was applied for the determination of the proton self-diffusion coefficients. The experiments were performed on a Chemagnetics CMX-300 spectrometer with a ^{1}H Larmor frequency of 301.0 MHz, using the Hahn spin-echo pulse sequence ($\pi/2$-τ-π) [17].

Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) experiments were carried out with a DSC 821 Mettler-Toledo and with a TGA/DTA 851 Mettler-Toledo instrument, respectively. The scanning rate during the experiments was 10 °C min^{-1}, in nitrogen flux for DSC and in air flux for TGA.

Raman experiments were performed at room temperature on a Bruker IFS-66v instrument equipped with a FRA 106 FT-Raman module. The 1,064 nm line of a Nd : YAG laser was used as the excitation source. Spectra were averaged over 1,000 scans. Infrared (IR) experiments were carried out in an Ar-filled dry box on a Bruker spectrometer. A Specac Attenuated Total Reflection (ATR) device equipped with a single reflection diamond crystal was used to record spectra, averaged over 32 scans. The resolution was 2 cm^{-1} for both Raman and IR measurements.

Ionic conductivity was determined from impedance spectra, recorded by a 1255B Solartron Frequency Response Analyzer (FRA) with samples (surface geometrical area: 0,3 cm^2) sandwiched between two platinum electrodes in a spring-loaded cell. A signal of 10 mV amplitude was applied and a frequency range of 100 kHz–1 Hz was explored. Impedance measurements were performed on membranes soaked at room temperature in 2 M H_2SO_4 solution. Conductivity time-tests in the temperature

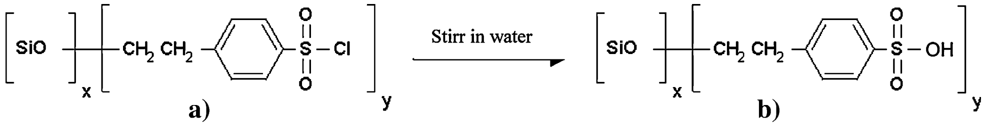

Fig. 1 Molecular structure of the 4-Ethyl benzenesulfonyl chloride-functionalized silica as supplied (**a**) and of the corresponding compound, SiO_x, after stirring in water (**b**)

range 25–80 °C were executed in presence of water (by keeping the cell in a water-saturated container).

H_2/air fuel cell tests were carried out with a Teledyne Medusa^{TM} Rd, fuel cell test system 890C (Scribner Associates Inc.), under computer control. Catalyst ink preparation followed a procedure established elsewhere [18]. Accordingly, a commercial solubilized Nafion solution (5% solution, Fluka) was mixed with the supported platinum catalyst (20% Pt on Vulcan XC72, De Nora North America), with some glycerol (Fisher Chemicals) and with tetra-butyl ammonium hydroxide (TBAOH, Aldrich). The catalyst ink was then painted on a gas diffusion layer, GDL, carbon cloth backing (E-TEK) to finally obtain an electrode with a catalyst loading of 0.4 mg Pt/cm^2. The desired H^+ form of the perfluorosulfonic ionomer present in the catalyst layer was assured by treating the electrodes in boiling hydrogen peroxide, water and sulfuric acid solutions. The membranes under investigation, activated by a 2 M H_2SO_4 solution, were tested as electrolytes by putting them between two of the realized catalyst-diffusion electrodes. The obtained “sandwich” was directly inserted in a cell fixture of 5 cm^2 active area connected to the fuel cell test station. Performances were monitored at two different cell temperatures, 50 and 80 °C, under 100% relative humidity (RH) and atmospheric pressure conditions. Hydrogen was fed to the anode and air to the cathode, both at a fixed flow rate of 0.1 L min^{-1}.

3 Results and discussion

A preliminary test to establish the influence of the functionalized silica was carried out on the cross-linked membranes by ^{1}H NMR self-diffusion measurements. Interesting results were achieved by comparing a ceramic-free sample (PVA_0SiO$_x$) with a ceramic-added one (PVA_10SiO$_x$), both activated by absorbing a 2 M H_2SO_4 solution. The measurements were performed upon heating from 25 to 90 °C and subsequently cooling to 25 °C. The results obtained in terms of proton self-diffusion coefficients are shown in Fig. 2. In both samples the diffusion is activated by the temperature but, noticeably, the values related to the silica-loaded membrane are higher for all temperatures. In addition, a decrease of the values is generally detected in the cooling scan, implying a thermal removal of proton diffusing species, presumably water. This kind of hysteresis is considerably more evident in the silica-free sample (triangles in Fig. 2). Here, in fact, the diffusion coefficient, D, decays above 80 °C, underlining a faster liquid release at high temperatures in PVA_0SiO$_x$ membrane and highlighting, in turn, the role of SiO$_x$ in promoting the water retention. The *D*-values observed for the monitored membranes are fairly close to those of pure water at room temperature (ca. 2×10^{-5} cm^2 s^{-1}), suggesting that diffusivity in our polymer matrices recalls a liquid-like behavior.

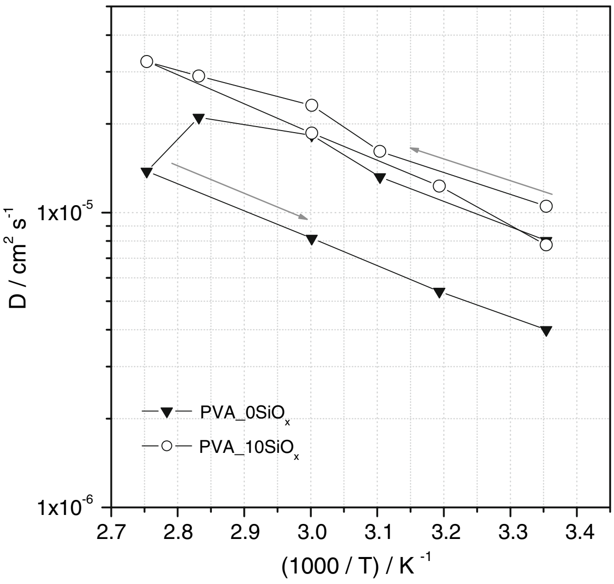

Fig. 2 ^{1}H Self-Diffusion Coefficient as a function of temperature in PVA_0SiO$_x$ and in PVA_10SiO$_x$ membranes, activated by the absorption of 2 M H_2SO_4

Figure 3 shows the thermal gravimetric, TG (a) and the derivative thermal gravimetric, DTG (b) analyses of the four cross-linked pristine membranes, before activation in sulfuric acid. Two main thermal processes are evident, in the temperature region 25–125 °C and above 240 °C, respectively. The first one, in the lower T-range, is due to the release of water and, from the shape of the derivative curves (Fig. 3b), it is expected to occur in more than one step, related to different strengths of water coordination in the matrix. The weight loss shifts to higher temperatures with higher amounts of added silica in the membranes. The second process, above 240 °C, is due to decomposition of the polymer. This is strong in the silica-free sample (PVA_0SiO$_x$) but it becomes progressively weaker with addition of the ceramic. This suggests a positive effect of SiO$_x$ on the thermal stability of the membranes. We do not discuss the relative values of total weight loss, this being a compromise between the initial water content (depending, in turn, on several parameters, such as aging effects and storage) and the retention ability of the membrane. Actually, the PVA_25SiO$_x$ sample, i.e., the most concentrated in silica, shows a unique behavior with a total weight loss of only 10–12%, most likely due to a reduced amount of water in the starting sample.

The thermal properties of the four cross-linked pristine membranes were also investigated by Differential Scanning Calorimetry (DSC). The samples were cooled from 25 to −20 °C and then heated up to 240 °C, to finally be cooled

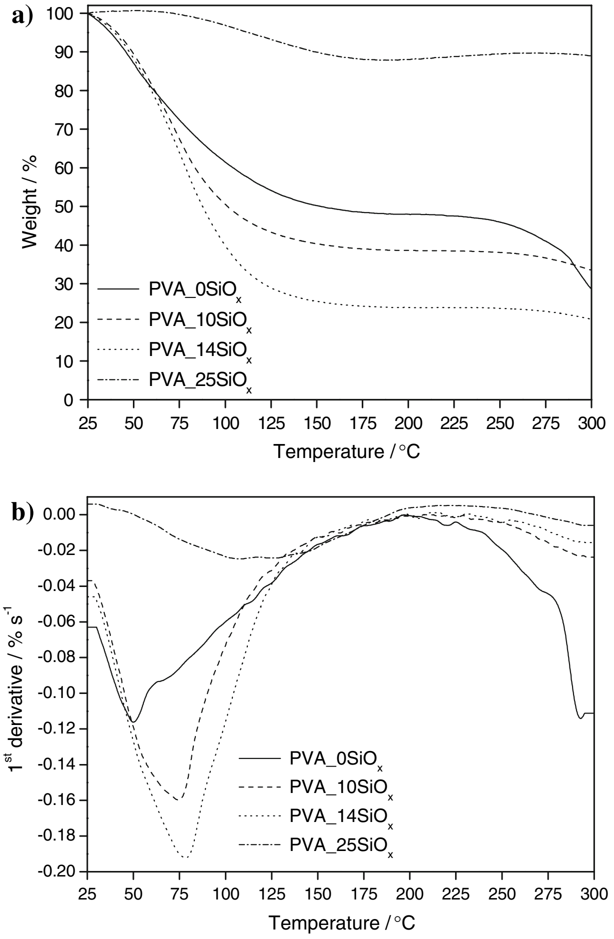

Fig. 3 TG (**a**) and DTG (**b**) responses of the four cross-linked PVA-based pristine membranes

back to 25 °C. The upper limit was chosen to avoid decomposition of the polymer matrix, occurring above 240 °C (see the TG analysis of Fig. 3). In Fig. 4 we show a typical DSC response. The melting of water, crystallized during the initial cooling, is observed between 0 and 10 °C. A second endothermic peak is present around 160 °C and is related to the vaporization of water from the membrane. When magnifying the dashed-marked area of Fig. 4a, we also notice the presence of a reversible thermal transition due to the melting and the crystallization of PVA (Fig. 4b). By analyzing the area of the corresponding peaks in the four membranes, we can compare the enthalpy of the related transition in each sample, evaluated for the exothermic crystallization process. The enthalpy of crystallization values of the polymer, H_c, in the four membranes are reported in Table 2. Interestingly, we observe a decrease in H_c with the amount of SiO_x in the membranes. This means that the selected functionalized inorganic compound promotes the amorphous phase in the polymer matrix.

The issue of crystallization of PVA was also investigated by Raman spectroscopy, exploiting the vibrational bands due to the amorphous and the crystalline phases found at 1,126 and 1,147 cm^{-1}, respectively [19]. Figure 5a shows the dehydration process of sample PVA_25SiO_x, containing 25 wt.% of functionalized silica. The Raman spectra, normalized to the C-C stretching mode at 916 cm^{-1}, show the evolution from the wet to the dry state of the membrane and the concomitant increase of the crystalline band (1,147 cm^{-1}) relative to the amorphous one (1,126 cm^{-1}). This trend is in common for all the investigated membranes, as also proved by IR spectra (not shown here). In Fig. 5a the bands arising from the SiO_x itself have been indicated with an "*X*". Taking the SiO_x Raman contribution into account, the spectral range 1,050–1,200 cm^{-1} has been fitted with Gaussian bands, in order to detect the amorphous and crystalline contributions. Figure 5b shows the evolution of these two contributions for the dry membranes with different SiO_x concentrations. It is clear that, although the crystalline phase increases as a result of dehydration, this increase is counteracted by the presence of SiO_x and the degree of crystallization is found to be gradually lower for higher silica contents. Hence, the crystallinity of PVA is determined by both the presence of the functionalized filler and the water content.

The nature of the interaction of the water was specifically investigated by IR spectroscopy. IR spectra of PVA membranes dried at 100 °C overnight are shown in Fig. 6 displaying the frequency range 1,520–1,780 cm^{-1} where the bending modes of the H–O–H groups are found, without interference from SiO_x bands. The two main bands at 1,650 and 1,712 cm^{-1} indicate the presence of water molecules of different coordination to the $–SO_3H$ groups, as also observed for poorly hydrated Nafion membranes [20]. These two bands are related to water molecules of the protonated $H_{2n+1}O_{2n}^{+}$ species, more specifically to the bending modes of water molecules in the solvating sphere (1,650 cm^{-1}) and of water molecules in the "inner" group (1,712 cm^{-1}), i.e., those more directly linked to the proton [21]. We observe that the higher frequency band is stronger in the silica-rich samples, indicating a stronger coordination of water to the sulfonic acid group and an effective proton transfer.

In Fig. 7 we compare the room temperature conductivities of the four membranes activated in 2 M H_2SO_4 solution. Conductivity values in a range of 3×10^{-2} – 2×10^{-1} S cm^{-1} are obtained. The highest conductivity is found in the silica-free sample (PVA_0SiO_x) while a kind of trend, where conductivity increases with SiO_x content, is established among the ceramic-added membranes. An explanation of the difference between silica-added and silica-free membranes is not immediate. If we go back to the discussion for ^1H self-diffusion coefficients and take into account the peculiarity of conductivity and diffusion measurements (the latter are species-specific but they are

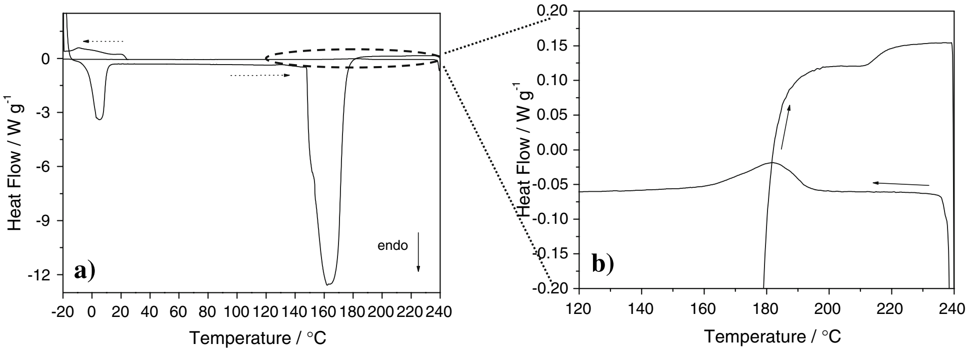

Fig. 4 Typical DSC response of the cross-linked PVA-based pristine membranes; **b** is the magnification of the dashed zone in **a**

Table 2 Enthalpy of crystallization of the polymer in the four cross-linked membranes

Membrane	H_c (J g^{-1}$_{polymer}$)
PVA_0SiO$_x$	1.64
PVA_10SiO$_x$	1.40
PVA_14SiO$_x$	1.04
PVA_25SiO$_x$	0.83

unable to differentiate between charged and neutral mobile species), we conclude that the contribution from a neutral proton component (i.e., water) is much stronger when silica is present, this resulting in a higher total diffusion coefficient but in a reduced conductivity. On the basis of other considerations (e.g., the agreement between fuel cell tests and conductivity measurements response at high temperature, see below), we exclude that the higher conductivity detected for the silica-free sample can be due to an additional contribution of negatively charged species. Finally, the small improvement of conductivities with silica loading among the ceramic-added membranes may be attributed to an increasing concentration of $-SO_3H$ filler end-functions in the samples.

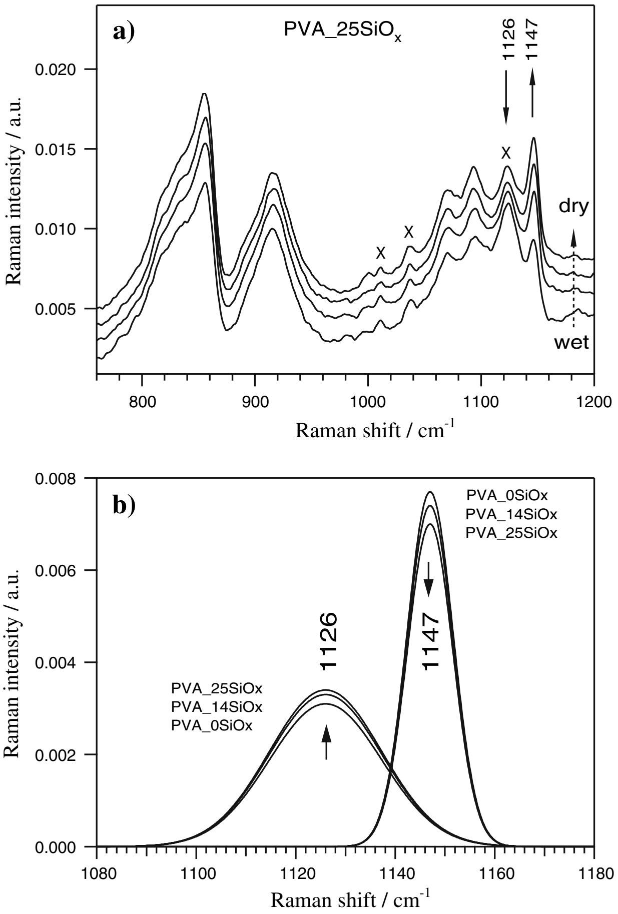

Fig. 5 (**a**) Raman spectra of sample PVA_25SiO$_x$ from the wet to the dry state shown with an arbitrarily vertical offset. Raman contributions from SiO$_x$ are indicated by an "X"; (**b**) Gaussian bands as from the fitting procedure on Raman spectra of dry samples with different SiO$_x$ contents

In order to investigate the effect of time and temperature on the conducting properties, the four activated samples were kept in their measurement cells in the presence of saturated water vapor and the conductivities were followed in time (ca. 2 months) at three different temperatures (25, 50, and 80 °C). Under these conditions, the retention ability of the matrix toward the absorbed acid solution is expected to play a key role. Figure 8 reports the trends of the four membranes. Each point is the average of several measurements performed in time at a given temperature. The conductivity of the silica-free sample (PVA_0SiO$_x$) slowly decreases in the monitored temperature range while the conductivities of PVA_10SiO$_x$ and PVA_14SiO$_x$ remain almost constant, with particular interest to the values shown by PVA_14SiO$_x$ membrane. In contrast, in the most concentrated silica sample (PVA_25SiO$_x$), the conductivity decays really fast, in such a manner that at 80 °C it is practically negligible. This means that the silica, up to a certain concentration, stabilizes, and enhances the properties of the final conducting membrane. The negative effect revealed by the highest ceramic amount could be related to a non-optimized morphology (a preliminary SEM investigation, not discussed here, showed the presence of huge particle aggregates in PVA_25SiO$_x$), which

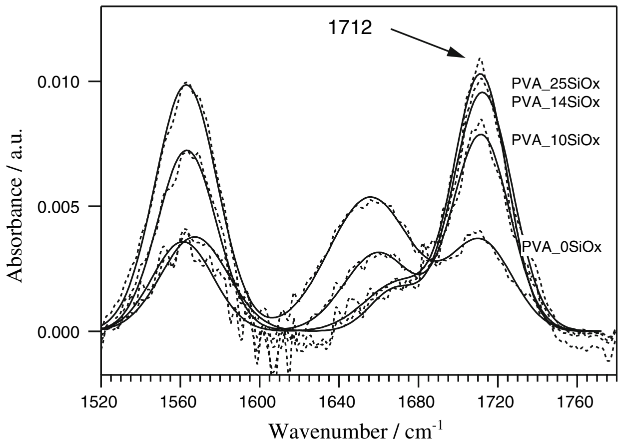

Fig. 6 Infrared spectra of dry samples treated at 100 °C overnight. The experimental traces (*dashed lines*) have been fitted with Gaussian bands (*solid lines*) to discriminate the contributions from water of different chemical environments

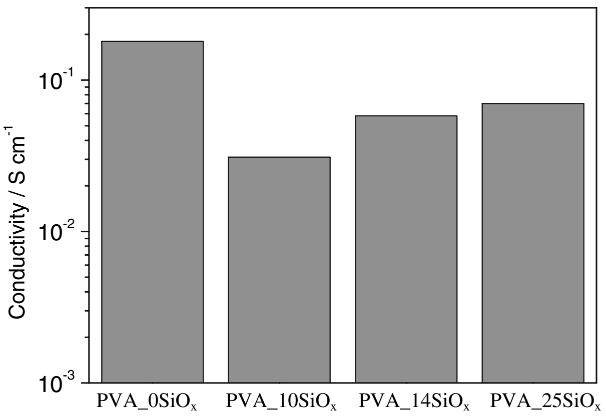

Fig. 7 Room temperature conductivity of the four cross-linked membranes activated by the absorption of a 2 M H_2SO_4

does not allow the expected long-term retention of the absorbed acid solution in the membrane.

Figure 9 summarizes the fuel cell test responses obtained using H_2SO_4-activated PVA membranes as electrolytes. The polarization and power-current curves at 50 °C (Fig. 9a, b, respectively) and the polarization and power-current curves at 80 °C (Fig. 9c, d, respectively) are reported. The open circuit voltages detected in these measurements are relatively high, about 0.9 V (see Fig. 9a, c). Even though a small contribution of activation losses and fuel crossover can not be excluded in the lowest current region, we attribute the initial voltage drop also to an instrumental problem. In fact, similar drops were found with different membranes, electrodes and MEA fabrication procedures when using the same instrumental apparatus (a loss of 150–200 mV was always observed immediately after applying a load). By looking at the general response of each membrane, we can establish a qualitative correlation

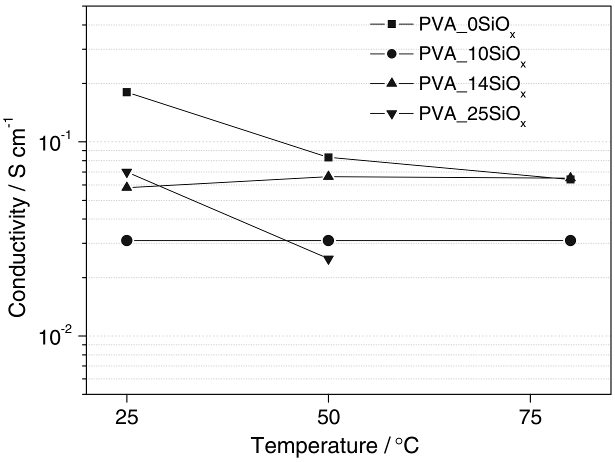

Fig. 8 Conductivity as a function of temperature of the four cross-linked membranes activated by the absorption of a 2 M H_2SO_4

with the conductivity measurements discussed above. The cell with the silica-free membrane (PVA_0SiO$_x$) seems to perform best at 50 °C, achieving a power density of 125 mW cm^{-2} for a current density of 370 mA cm^{-2}. The worst response is obtained with the most concentrated silica membrane (PVA_25SiO$_x$). The behavior of this membrane becomes even more drastic when the temperature is increased to 80 °C. Its performance is strongly reduced with respect to the other samples, in accordance with the conductivity results, which showed that, by keeping the PVA_25SiO$_x$ membrane at 80 °C for some days, it became almost non-conducting. Interestingly, at 80 °C the cell involving PVA_14SiO$_x$ membrane as electrolyte shows the best response. This reveals that the optimized composition among the four studied is that in the membrane having a PVA/SiO$_x$ ratio of ca. 6/1 (i.e., PVA_14SiO$_x$ membrane).

Unfortunately, the overall cell performance decreases with temperature increase from 50 to 80 °C. A prolonged time test (1 or 2 days for the fuel cell measurements here discussed), together with the increased temperature, caused a decrease in acid concentration absorbed in the membranes, this being monitored by a direct acid-base titration of the samples before and after each fuel cell test. The effect of both time and temperature on the acid-retention capacity of our membranes and, in turn, on their conducting ability is stressed in an operating fuel cell, where the membrane is in contact with dynamically flowing gases and liquid (i.e., water produced by the cathodic reaction).

4 Conclusion

The effect of a functionalized silica filler, having a –SO_3H end-group, on cross-linked PVA membranes has been investigated and discussed. The thermal analyses demonstrated the role of the inorganic compound in improving the

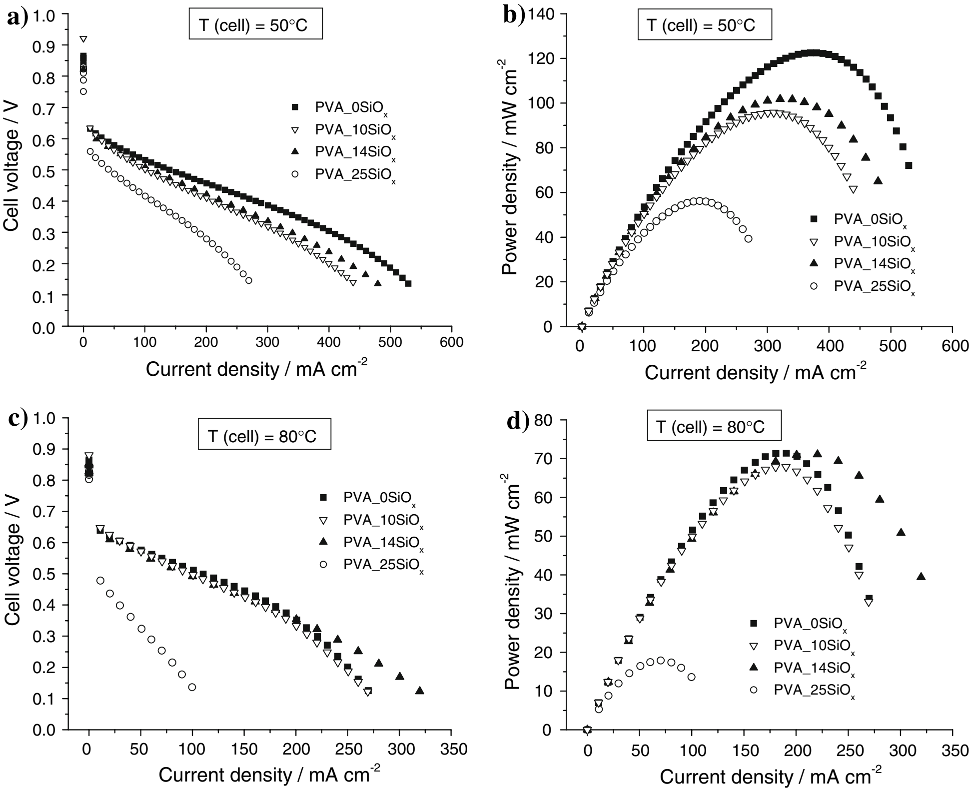

Fig. 9 Polarization and power-current curves at 50 °C (**a** and **b**, respectively) and polarization and power-current curves at 80 °C (**c** and **d**, respectively) obtained using as electrolytes the four PVA-based membranes activated by the absorption of 2 M H_2SO_4

stability of the membranes and in reducing the crystalline phase of the polymer matrix. Similar conclusions about the crystallinity issue were obtained by Raman spectroscopy, which revealed a higher amorphous/crystalline phase ratio in the polymer with increasing SiO_x content in the membranes. In addition, silica particles have a positive effect on the retention of the absorbed liquid phase (i.e., water is supposed to coordinate to the functional group of the filler), as shown by IR spectroscopy and ^{1}H-NMR. Self-diffusion coefficient measurements have also revealed that the proton diffusivity is enhanced by the presence of SiO_x in the polymer matrix. Conductivity values of the membranes activated by the absorption of 2 M H_2SO_4 were found to be in the order of $10^{-2} – 10^{-1}$ S cm^{-1}, with dependence on the composition of the membrane. Fuel cell tests on laboratory prototypes using our membranes as electrolytes have shown current and power levels which are comparable with those obtained in the same working conditions by adopting conventional membrane separators (i.e., Nafion 117). Conductivity and fuel cell measurements agreed in revealing the best membrane composition among the four investigated (i.e., PVA_14SiO$_x$).

Although further work is certainly necessary to fully ascertain the real practical impact of the membranes developed in this work, especially in terms of durability, the results obtained demonstrated that these gel-type membranes, also considering their intrinsic advances in terms of cost, can be considered as promising alternatives to the existing systems.

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