

Short communication

SPPSU-based hybrid proton conducting polymeric electrolytes for intermediate temperature PEMFCs

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Abstract

Polyphenylsulfone (PPSU) was reacted with SiCl_4 to afford silylated telechelic polymers having different inorganic content, which were sulfonated to different degrees ($0.05 \leq \text{DS} \leq 2$) using H_2SO_4 or $\text{ClSO}_3\text{Si}(\text{CH}_3)_3$. A class II organic–inorganic hybrid polymer was then synthesized *via* cross-linking through Si–O–Si bonds generated by non-hydrolytic sol–gel reactions. The physicochemical properties of the hybrid were suitable for the preparation of self-standing, flexible and homogeneous membranes which were characterized ATR/FTIR spectroscopy demonstrating the formation of covalent bonds between the organic and inorganic components and the absence of dispersed inorganic silicon. The electrochemical performance was analyzed by electrochemical impedance spectroscopy which showed adequately high conductivity values to make the hybrid polymer a suitable candidate for application as electrolyte in PEMFCs operating at $T > 100^\circ\text{C}$.

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1. Introduction

Organic–inorganic hybrids have been investigated for a variety of applications since they offer the possibility of combining the properties of two components in a unique material, hence to develop functional materials with tuned properties. It is widely accepted that hybrids where interactions occur at molecular level allow a much finer tailoring of the final material properties than that obtained in the formation of a composite system [1].

The peculiar features of hybrid systems can be applied in the development of innovative materials to be used as proton conductors in polymer electrolyte membranes fuel cells (PEMFCs) [2,3]. New generation electrolytes must in fact meet several requirements: among them most important are high proton conductivity, sufficient flexibility to make good contacts with electrodes and, at the same time, enough rigidity to sup-

port the membrane electrode assembly (MEA), high hydrolytic stability, and low permeability to gaseous or liquid fuels. Furthermore, such performances should be maintained above 100°C to increase CO tolerance, enhance fuel oxidation kinetics, and ease thermal balance [4,5].

Among the numerous approaches that have been proposed to achieve the correct electrochemical and mechanical properties, in our laboratory attention has been focused on possible modifications that can be introduced in sulfonated arylene main chain polymers. These polymers show rather large conductivity when sulfonated, but their mechanical, morphological and solubility properties progressively deteriorate with the degree of sulfonation (DS) because acid groups directly linked to the aromatic hydrophobic backbones cannot assemble in phase separated domains as well as perfluorinated systems with more hydrophobic flexible side chains. The preparation of composite systems and synthesis of silylated polymers allowed to obtain membranes with enhanced thermal stability, reduced swelling and high conductivity values ($\sigma > 0.01 \text{ S cm}^{-1}$ at 120°C) [6–8].

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The strategy chosen in the present work was to prepare a covalent hybrid sulfonated polymer, where cross-linking via Si–O–Si units was expected to enhance morphological stability modifying the separation between the hydrophobic and hydrophilic regions, thus modulating the requirements of high conductivity and low permeability.

2. Experimental

Polyphenylsulfone (PPSU, $M_w = 46,173$) was obtained from Victrex in the form of powder. All other chemicals (Aldrich) were reagent grade and were used as received.

PPSU was dried at 100 °C for 1 h. Anhydrous THF and CH_2Cl_2 were prepared according to literature procedures [9].

2.1. Synthesis of $\text{Si}_{0.2}\text{S}_2\text{PPSU}$

PPSU (5 g, 12.5 mequiv.) was added, under nitrogen, to anhydrous THF (150 mL). The solution was stirred at room temperature for 1 h, then cooled to –60 °C. After 1.5 h an excess of BuLi (2.5 M in hexane, 25 mL, 62.5 mmol) was added, and the red solution was stirred for 2 h at –60 °C. SiCl_4 (0.29 mL, 2.5 mmol) was then added and the solution was slowly warmed to RT, then kept at reflux overnight. After cooling to RT, the precipitate formed was filtered and washed with absolute ethanol, then with cold water until no chlorides were detected. The product ($\text{Si}_{0.2}\text{PPSU}$) was added to concentrated H_2SO_4 (500 mL) and the mixture was kept stirring at 50 °C for 5 h, then poured in 2 L of ice-cold water obtaining a precipitate which was filtered, washed with water to neutral pH and dried under vacuum for 5 h.

The degree of sulfonation (DS) was determined by elemental analysis and was DS = 2.

2.2. Synthesis of $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$

PPSU (5 g, 12.5 mequiv.) was added, under nitrogen, to anhydrous CH_2Cl_2 (400 mL). The yellow solution was stirred at reflux for 1 h, then a solution of $\text{ClSO}_3\text{Si}(\text{CH}_3)_3$ (2 mL, 12.8 mmol) in anhydrous CH_2Cl_2 (8 mL) was added dropwise. After 5 h a light brown precipitate separated from the solution. The mixture was kept at reflux for a total of 2 days. After cooling to –60 °C, BuLi (2.5 M in hexane, 30 mL, 75 mmol) was added dropwise and the orange solution was kept stirring at –60 °C for 2 h. SiCl_4 (0.04 mL, 0.375 mmol) was then added and the solution was slowly warmed to RT, then kept at reflux for 2 h. CH_3OH (500 mL) was added and the mixture was kept stirring for 1 h at RT. The product was filtered, washed with methanol, then with water until no chlorides were detected. The product was dried under vacuum for 4 h. The degree of sulfonation (DS) was determined by elemental analysis and was DS = 0.05.

2.3. Synthesis of HSiPPSU

Equimolar amounts of $\text{Si}_{0.2}\text{S}_2\text{PPSU}$ and $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$ were reacted in dimethylacetamide (DMAc) at 120 °C for 2 days

in the presence of pyridine. The mixture was dried in vacuum and the residue was washed with water, then dried in vacuum.

HSiPPSU membranes were prepared by solution casting. In a typical procedure, the polymer (150 mg) was dissolved in DMAc (30 mL) and the solution was stirred for 24 h. After evaporation of most of the solvent the solution was cast onto a Teflon plate. The cast membranes were dried at 80 °C for 10 h, and then further dried under vacuum at 80 °C for 4 h. The hybrid membranes were activated in 5 M H_2SO_4 for 2 h.

ATR/FTIR spectra were collected in the range 4000–550 cm^{-1} , on a Nicolet 870 E.S.P. with a Golden Gate MK2 Diamond Specac cell. Spectra have been recorded positioning the samples on cell platform operating at room temperature (32 scans, 2 cm^{-1} resolution).

Electrochemical impedance spectroscopy (EIS) measurements, performed with a PARSTAT 2273A instrument with an applied voltage of 20 mV in the 1 MHz to 10 Hz frequency range, were used to determine the proton conductivity of each membrane. Membranes were sandwiched between commercial electrodes (E-Tek ELAT HT 140E-W with a platinum loading of 5 g^{-2}). The effect of relative humidity (RH) and temperature on proton conductivity was investigated. Controlled RH environments were obtained using a house-made double chamber apparatus. The two compartments were held at different temperatures T1 and T2, with $T1 \leq T2$. The compartment at T1 contained water, while the compartment at T2 housed the test cell [10]. T2 was kept constant whereas T1 was varied to achieve different RH values. Relative humidity was monitored by a humidity sensor (VAISALA HMP237) in the 20–100% RH range.

The resistance of the membranes, hence their conductivity, was calculated by a linear fit of the impedance spectra in their linear portion. From the resistance values we obtained the conductivity (σ) value using the following equation:

$$\sigma = \frac{d}{RA}$$

where R is the resistance, d the distance between electrodes and A is the electrode area.

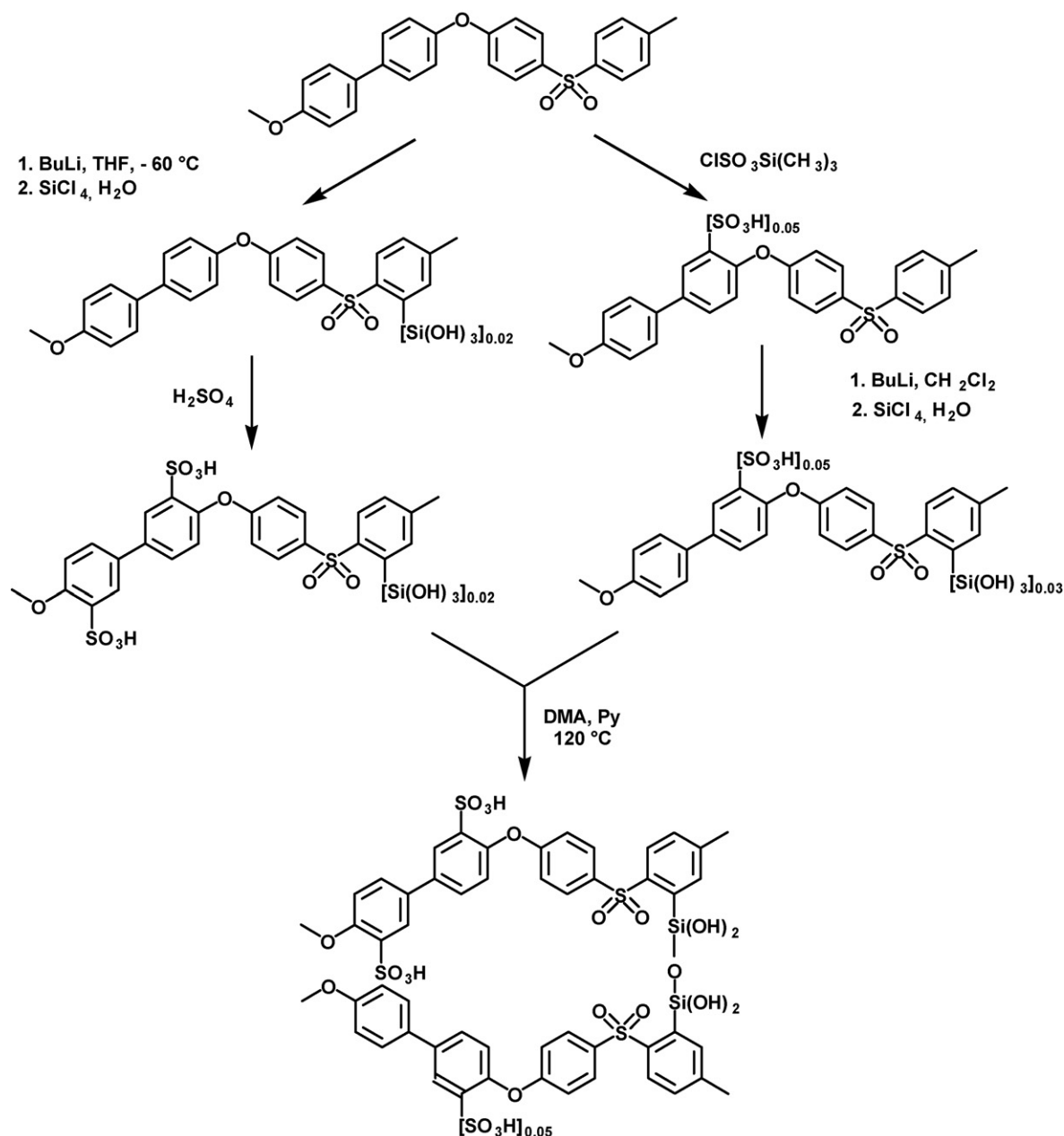
3. Results and discussion

The formation of a class II hybrid where inorganic moieties are covalently bound to the organic backbone of PPSU was the strategy that we choose to match the requirements needed for a protonic conductor to be used as electrolyte in PEFCs. Polyphenylsulfone (PPSU) is a fully aromatic polymer with good thermal stability, and oxidation resistance which may act as proton conductor when sulfonated [11]. It was here chosen as starting material because of its solubility in organic solvents that allows to control functionalization reactions in homogeneous conditions, a condition that is seldom met by other polymeric systems. Thus, in a first synthesis silylation was achieved by reaction with SiCl_4 in anhydrous conditions, and the product was then sulfonated in concentrated sulfuric acid. In a second synthesis sulfonation with a milder agent, $\text{ClSO}_3\text{Si}(\text{CH}_3)_3$, was the first step of the process, and the soluble product was reacted

with SiCl_4 , then hydrolyzed. The degrees of sulfonation of the two samples, identified as $\text{Si}_{0.2}\text{S}_2\text{PPSU}$ and $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$, were $\text{DS} = 2$ and $\text{DS} = 0.05$, while the degrees of silylation were $\text{DSi} = 0.2$ and $\text{DSi} = 0.03$, respectively.

Fig. 1 shows the ATR/FTIR spectra of the two silylated polymers (traces a and b for $\text{Si}_{0.2}\text{S}_2\text{PPSU}$ and $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$, respectively) compared with those of a sample sulfonated in sulfuric acid but without the introduction of the silicon residues (S_2PPSU , Fig. 1c), and that of the starting material (PPSU, Fig. 1d). All spectra are dominated by PPSU infrared signals, thus, to highlight the differences between products deriving from silylation and sulfonation processes, Fig. 1e shows the spectrum obtained subtracting signals of S_2PPSU from those of $\text{Si}_{0.2}\text{S}_2\text{PPSU}$. The main positive bands, due to new absorp-

tions generated by the silylation process, are located at 1175, 1138, 1112 (w), 1082 and 1018 cm^{-1} . The signal at 1175 cm^{-1} is due to two contributions: $-\text{SO}_3^-$ group and ring modes of 1:2-substituted benzene, while the absorptions at 1138 and 1082 cm^{-1} could be attributed to ring modes of 1:4- and 1:2:4-substituted benzene. The band at 1018 cm^{-1} is due to 1:3:4-substituted benzene rings. The presence of covalently linked silicon is confirmed by the weak signal at 1112 cm^{-1} which is typical of Ph–Si stretching mode [12]. The absorption due to vibrations of the Si–OH groups is observed at about 960 cm^{-1} [13], while the absence of bands at 1220 and 1090 cm^{-1} confirms the lack of inorganic silicon [14]. Similar features, although with decreased intensity given the much lower DS and DSi, were observed in the spectrum of $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$



Scheme 1. Synthetic pathway for the preparation of silylated and hybrid polymers.

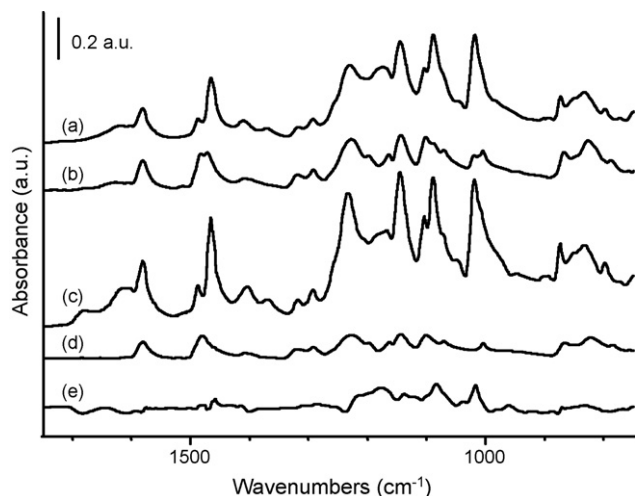


Fig. 1. ATR/FTIR spectra of (a) $\text{Si}_{0.2}\text{S}_2\text{PPSU}$, (b) $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$, (c) S_2PPSU , (d) PPSU and (e) = (a) – (c) subtraction spectrum.

(Fig. 1b). The presence of sulfonic groups in $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$ is demonstrated by the band at 1165 cm^{-1} . Its lower position and intensity with respect to the bands observed in the spectrum of $\text{Si}_{0.2}\text{S}_2\text{PPSU}$ are indicative of a lower sulfonation degree, in agreement with the milder synthetic conditions and with elemental analysis results. The main spectral differences between the two sulfonated and silylated polymers were observed in the region $1150\text{--}1000\text{ cm}^{-1}$: the signals are due to ring modes of polysubstituted benzene and their position and intensities reflect the lower substitution degree of $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$ with respect to $\text{Si}_{0.2}\text{S}_2\text{PPSU}$.

The association of the two polymers was then realized through non-hydrolytic sol–gel reaction. Scheme 1 shows the complete synthetic procedure.

Fig. 2a shows the ATR/FTIR spectrum of the condensation product, HSiPPSU. The spectral features reflect the equimolar ratio of the two precursors. The inset in Fig. 2d shows

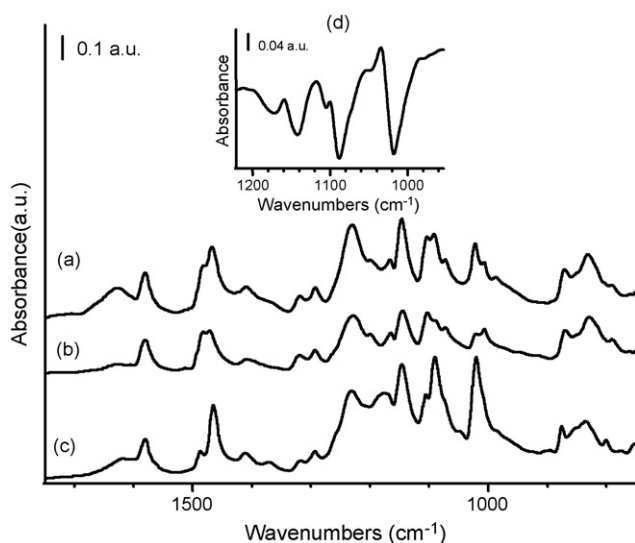


Fig. 2. ATR/FTIR spectra of (a) HSiPPSU, (b) $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$, (c) $\text{Si}_{0.2}\text{S}_2\text{PPSU}$ and (d) = (a) – (b) – (c) subtraction spectrum.

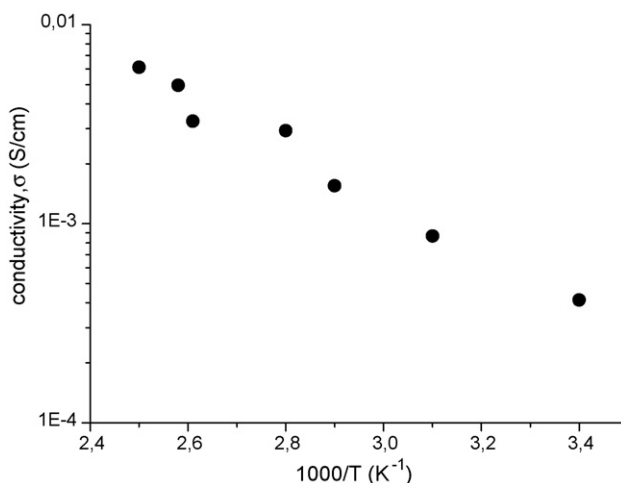


Fig. 3. Arrhenius plot for a non-hydrated membrane of HSiPPSU.

the difference spectrum obtained subtracting the spectra of the precursors (Fig. 2b and c) from that of HSiPPSU with a subtraction factor equal to 1. The presence of new components due to Ph–Si stretching signals together with the band at 1030 cm^{-1} , typical of Si–O–Si groups, indicate the formation of inorganic cross-linking between the two different polymers.

To verify their possible application as polymeric electrolytes, the solubility, water uptake and electrical behavior of the three polymers were analyzed. Membranes were successfully prepared by casting and activated in $5\text{ M H}_2\text{SO}_4$. Membranes of $\text{Si}_{0.2}\text{S}_2\text{PPSU}$ showed poor mechanical properties and excessive water swelling, while in the case of $\text{Si}_{0.03}\text{S}_{0.05}\text{PPSU}$, conductivity was almost negligible.

The room temperature conductivity of activated, non-hydrated HSiPPSU was $\sigma = 4.1 \times 10^{-4}\text{ S cm}^{-1}$, and stable values were recorded for several days. Fig. 3 shows the variation of conductivity of HSiPPSU as a function of temperature: conductivity increases with temperature up to $\sigma = 6.1 \times 10^{-3}\text{ S cm}^{-1}$ at $125\text{ }^\circ\text{C}$. The linear Arrhenius behavior and the value of activation energy calculated ($E_a = 0.28\text{ eV}$) agree with a hopping mechanism for proton transfer [15].

Moreover, the solubility and mechanical properties of HSiPPSU appeared to be suitable for its applications as a polymeric electrolyte: membranes prepared with the hybrid product were in fact insoluble in hot water and methanol. The water uptake from the liquid phase reached an asymptotic value of ca. 120%, corresponding to $\lambda = 10$, with λ expressing the number of water molecules per sulfonic acid group.

Fig. 4 shows the comparison between the complex impedance plots of HSiPPSU membrane measured at $110\text{ }^\circ\text{C}$ at two different relative humidity values, *i.e.* 20% and 50%. At RH values lower than 50%, the EIS plots consisted typically of a low frequency straight line and a high frequency arc, which did not intercept the real axis at high frequency. The diameter of the arc decreased with increasing RH and eventually vanished at $\text{RH} \geq 50\%$. Above such RH value only a linear spike was observed. The same trend was observed for the EIS measurements carried out at $130\text{ }^\circ\text{C}$.

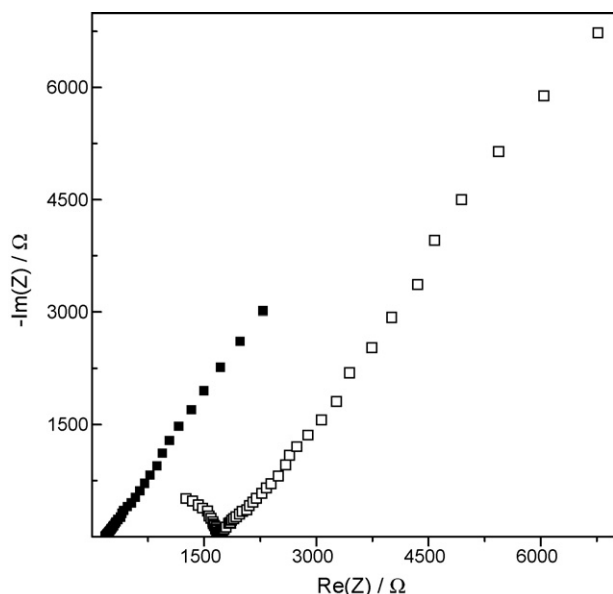


Fig. 4. Typical complex impedance plane plot for HSiSPPSU membrane measured at 110 °C and at 20% (□) and 50% (■) RH.

Fig. 5 shows the conductivity variation as a function of relative humidity, as derived from EIS plots, measured at 110 and 130 °C. In agreement with a water assisted conduction mechanism, conductivity increases with RH values. An increase of conductivity with temperature was also observed in the whole range of investigated RH, probably because of increased chain mobility favoring proton transfer. The conductivity at 130 °C and 100% RH reached $1.1 \times 10^{-2} \text{ S cm}^{-1}$, about one order of magnitude higher than the conductivity values at 100 °C.

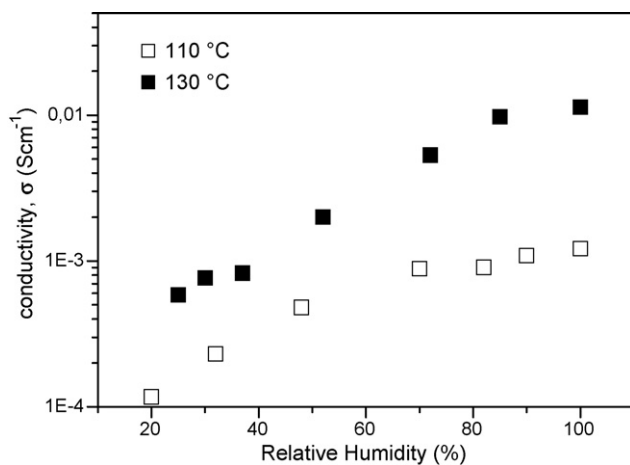


Fig. 5. Conductivity as a function of relative humidity (RH) of HSiSPPSU at 110 (□) and 130 °C (■).

4. Conclusions

Hybrid polymers where the organic and inorganic components are held together by means of covalent bonds were successfully prepared and characterized by ATR/FTIR. Non-hydrolytic condensation between Si(OH) groups present on the polymeric chain allowed to cross-link, via Si–O–Si bonds, polymers having different degrees of sulfonation to modulate their electrical and mechanical properties. The formation of the inorganic links between sulfonated PPSU chains allowed to reach conductivity values as high as $1.1 \times 10^{-2} \text{ S cm}^{-1}$ at 130 °C and 100% RH for the HSiSPPSU hybrid polymer thus identifying such material as a promising electrolyte in PEFMCs operating at intermediate temperature.

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