Cross-linked sulfonated aromatic ionomers via SO₂ bridges: Conductivity properties

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Highlights

- Proton conductivity of SPEEK optimized by hydration, possible only for cross-linked polymer.
- Plot of proton mobility vs hydration number λ indicates conditions for an optimal conductivity.
- At λ > 20, proton conductivity > 0.1 S/cm predicted at 100 °C; measured value 0.16 S/cm at λ = 60.

Abstract

The proton conductivity of SPEEK membranes in situ cross-linked by thermal treatment at 180 °C for various times was investigated by impedance spectroscopy. The conductivity measurements were made on fully humidified membranes between 25 and 65 °C and on membranes exposed to different relative humidity between 80 and 140 °C. The Ionic Exchange Capacity (IEC) was determined by acid-base titration and the water uptake by gravimetry. The proton conductivity was determined as function of temperature, IEC, degree of cross-linking and hydration number. A curve of proton conductivity vs. hydration number allows predicting that in order to reach a value of 0.1 S/cm at 100 °C a hydration number above 20 is necessary. The measured conductivity at this temperature is 0.16 S/cm for a hydration number of 60.

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1. Introduction

Sulfonated aromatic polymers (SAP) are promising alternative materials to perfluorinated membranes working in fuel cells at 80–90 °C [1–6]. However, it is desirable to operate in a higher range of temperature, around 120 °C, to enhance the conductivity of membranes, reduce anode poisoning and improve the fuel oxidation kinetics [7–9]. One of the best-known examples of SAP is sulfonated poly(ether ether ketone) (SPEEK) with high degree of sulfonation (DS) required for an appropriate proton conductivity [10–16]. However, highly sulfonated SPEEK has low mechanical and morphological stability and is a highly swellable or even water-soluble product, especially when used at a temperature higher than 100 °C [17,18].

A powerful method to improve the solvent resistance, dimensional stability and mechanical strength of polymers, maintaining a locally high density of functional groups, such as sulfonic acid groups, is the formation of covalent cross-links between macro-molecular chains [19–23]. A direct cross-linking (XL) reaction performed in situ during the casting procedure is certainly an interesting and promising methodology to obtain stable and long-life membranes [24]. Furthermore, the introduction of covalent bonds between adjacent polymeric chains by thermal treatment of cast membranes is really economic and due to its simplicity, this method is very suitable for industrial preparation, because the procedure can be easily up-scaled.

In our recent articles [24–26], we have reported the reaction mechanism for the formation of XL-SPEEK via sulfone bridges, together with the membrane properties such as hydrolytic stability, mechanical, thermal, and permeability behavior. All these results showed that XL polymers are adequate candidates to replace Naflon.
in H₂ fuel cells. An important aspect not yet well defined is the conductivity of these membranes. Given that a part of sulfonic acid groups is consumed during the cross-linking reaction, a decrease of conductivity should be expected with an increase of XL density (Degree of XL, DXL). The proton conductivity of ionomer membranes has been measured and discussed as a function of different parameters including ion exchange capacity (IEC) [13,27], water uptake [28], polymer fraction [29,30], hydration number [8,31,32] and proton concentration [33,34]. Holdcroft and coworkers specifically discussed the proton mobility in main-chain, statistically sulfonated polymers, including SPEEK, as a function of various parameters, such as IEC, water volume fraction and hydration number [35]. The advantage of using the hydration number and/or the proton concentration is that the amount of acidic groups and water molecules are simultaneously taken into account. The ionomer conductivity depends also on the proton mobility, which can be related to the membrane tortuosity and the connectivity and percolation of hydrated channels [36-40].

In this paper, the proton conductivity of XL-SPEEK with different DXL will be discussed as a function of temperature and relative humidity (RH). The proton mobility will be evaluated and discussed as a function of the proton concentration and the maximum obtainable proton conductivity will be estimated as function of the temperature and hydration number.

2. Experimental

SPEEK was synthesized by reaction of PEEK (Victrex, MW = 38,300 Da) with concentrated sulfuric acid at 50 °C, as reported earlier [17,24]. The membranes were cast from dimethylsulfoxide (DMSO, Sigma-Aldrich) using a homemade Doctor Blade type equipment and dried at 120 °C for 24 h [41]. A thermal treatment at 180 °C for a time up to 24 h was applied to cross-link polymer chains. All membranes were regenerated at 25 °C in 3% H₂SO₄ for 1 h and in 5 M H₂SO₄ for 1 h before rinsing until neutral pH with pure water.

The Ionic Exchange Capacity (IEC in milliequivalents per g of dry polymer) of the ionomers was determined by acid-base titration. To remove remaining casting solvent DMSO after regeneration, the membranes were swelled in boiling water for 24 h. The membranes dried over P₂O₅ were then cation exchanged in 1.5 M NaCl solution for 24 h and the acidic solution was then back-titrated with 0.1 N NaOH solution. A potentiometric equivalent point detection was used.

The water uptake (WU) was measured either by immersion in water at 25, 80 or 100 °C or as function of RH and temperature in a homemade apparatus [42]. For the measurements by immersion, samples dried over P₂O₅ for 3 days were weighed (m_dry) and were then immersed 24 h in liquid water in a closed Teflon vessel at a constant temperature of 25, 80 or 100 °C. After the immersion, the membranes were equilibrated at 25 °C for 24 h. The excess of water was carefully wiped off and the membrane mass was determined (m_wet). This gave the water uptake:

\[
\text{WU} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}}
\]  

(1)

The hydration number was calculated as follows:

\[
\lambda = \frac{n(H_2O)}{n(SO_3H)} = \frac{\text{WU} \times 1000}{M(H_2O) \times \text{IEC}}
\]  

(2)

M(H₂O) is the molar mass of water.

The proton conductivity was measured by impedance spectroscopy (EG&C 6310 and Solartron 1260) in through-plane two-point configuration. The amplitude of the applied voltage was 20 mV and the frequency range was between 10 Hz and 1 MHz. The membrane resistance R was determined from the high frequency intercept with the real axis on a complex plane impedance plot. The proton conductivity σ was then calculated using the thickness d of the polymer sample, determined before and after the experiment, and the electrode area A:

\[
\sigma = \frac{d}{RA}
\]  

(3)

Two different measurement setups were applied in this work.

1. The measurements at full humidification were made in a Swagelok cell in presence of liquid water. Before the conductivity measurements, the membranes were immersed in water for 24 h at a fixed temperature (25, 80 or 100 °C) in a closed Teflon vessel to adjust their hydration number. The Swagelok was hermetically closed with fixed force so that the pressure applied on the stainless steel electrodes was reproducible. The cell was placed in a temperature-controlled oven operated between 25 and 65 °C. The working electrode area was 0.19 cm².

2. The conductivity measurements as a function of temperature between 80 and 140 °C or relative humidity (RH = 30–95%) were done in a homemade apparatus [42]. The relative humidity could be changed by variation of the temperature T_i of a water reservoir in contact with the sample held at a temperature T_e. The electrodes were ETEK ELAT HT 140EW with a platinum loading of 0.5 mg/cm². The relative humidity was monitored by a humidity sensor in the 20–100% RH range.

3. Results

3.1. Proton conductivity in fully humidified conditions from 25 to 65 °C

The IEC after cross-linking, the Degree of XL (DXL), the water uptake at the temperature of immersion T_{immersion} (expressed as hydration number λ) and the proton conductivity at 25 °C of fully humidified SPEEK membranes are reported in Table 1.

The proton conductivity for an equivalent IEC depends very strongly on the hydration number, which can be tuned by the temperature of immersion using the memory effect of the membranes. This means that once established at high temperature the hydration number does not change at lower temperature. It is thus possible to get quite high hydration numbers and to boost in this way the proton conductivity of XL membranes. One should emphasize that hydration at 80 or 100 °C is possible only for XL-

Table 1

<table>
<thead>
<tr>
<th>IEC (mg g⁻¹)</th>
<th>DXL</th>
<th>T_{immersion} (°C)</th>
<th>λ</th>
<th>σ (25 °C) (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.70</td>
<td>0</td>
<td>25</td>
<td>103</td>
<td>0.014</td>
</tr>
<tr>
<td>2.30</td>
<td>0.15</td>
<td>100</td>
<td>910</td>
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<tr>
<td>2.10</td>
<td>0.22</td>
<td>100</td>
<td>81</td>
<td>0.016</td>
</tr>
<tr>
<td>2.07</td>
<td>0.23</td>
<td>100</td>
<td>100</td>
<td>0.024</td>
</tr>
<tr>
<td>2.05</td>
<td>0.24</td>
<td>25</td>
<td>18</td>
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</tr>
<tr>
<td>2.02</td>
<td>0.25</td>
<td>80</td>
<td>61</td>
<td>0.010</td>
</tr>
<tr>
<td>2.02</td>
<td>0.25</td>
<td>25</td>
<td>18</td>
<td>0.002</td>
</tr>
<tr>
<td>1.84</td>
<td>0.32</td>
<td>25</td>
<td>9</td>
<td>0.001</td>
</tr>
<tr>
<td>1.80</td>
<td>0.33</td>
<td>25</td>
<td>9</td>
<td>0.006</td>
</tr>
</tbody>
</table>
SPEEEK; uncross-linked membranes dissolve in water at such high temperature.

The temperature dependence between 25 and 65 °C of the proton conductivity of SPEEK (DXL = 0.25, IEC = 2.02 meq/g) equilibrated in water at 80 or at 100 °C is reported in Arrhenius representation in Fig. 1. One can clearly observe the enhancement of the proton conductivity with increasing hydration number. The memory effect of the membranes allows working at constant hydration number, i.e. constant proton concentration, once the membranes are hydrated at temperatures higher than 65 °C, so that the temperature dependence of the proton mobility can be determined (the small temperature dependence of the solution density is neglected). Below the glass transition temperature of the ionomer (which is above 200 °C for XL-SPEEK), the activation energy of proton conduction can be calculated using an Arrhenius-type equation:

\[ \sigma = \sigma_0 \exp \left( \frac{-E_a}{RT} \right) \]  

(4)

\( \sigma_0 \) is the prefactor, \( R \) is Boltzmann’s constant and \( T \) is the absolute temperature. The activation energy of proton conduction amounts to (21 ± 3) kJ/mol (0.22 eV), which is a typical value for SPEEK in fully humidified conditions, where a Grotthuss-type mechanism is observed [43]. The highest conductivity at 25 °C amounts to 0.024 S/cm (Table 1 and Fig. 1) for an ionomer with relatively high IEC and DXL is compared as function of RH in Fig. 4. As expected, the conductivity decreases with increasing DXL; the conductivity increase with RH is again related to the increasing proton mobility with hydration number. The temperature dependence of the proton conductivity at RH = 90% is shown in Fig. 5. The proton conductivity of a heavily cross-linked SPEEK with IEC = 1.5 meq/g (DXL = 0.4) is actually higher (0.02 S/cm at 100 °C) than that of an uncross-linked membrane (DXL = 0) with the same IEC (0.01 S/cm at 100 °C).

3.2. Proton conductivity as function of relative humidity from 80 to 140 °C

The water uptake at 100 °C of a cross-linked SPEEEK membrane (IEC = 1.9 meq/g, DXL = 0.24) is represented as function of RH in Fig. 2. The temperature dependence of the proton conductivity at 90% RH is shown in Fig. 3. A difference of conductivity can be observed between the first heat-up and the following heating—cooling cycles; this behavior is classically observed for hydrated acidic ionomers [42] and is related to the slow kinetics of the hydration, because the membranes are initially not fully hydrated. The proton conductivity for this cross-linked membrane at 140 °C is as high as 0.082 S/cm under 90% RH: the conductivity under 100% RH corresponding to full hydration would be even higher. In fact, the conductivity at 100 °C and 100% RH of a cross-linked membrane (IEC = 2.0, DXL = 0.20) attains the very high value of (0.16 ± 0.03) S/cm for a hydration number \( \lambda = 60 \).

Furthermore, the conductivity remains stable even at 140 °C and no swelling-related degradation is observed with time, emphasizing the positive effect of polymer cross-linking (Fig. 3).

4. Discussion

The proton mobility can be calculated from proton conductivity and water uptake data determined at the same temperature and RH. The proton concentration (in mol/L) is first calculated from IEC and water uptake WU according to:

\[ \lambda = \frac{\sigma}{\sigma_0} \exp \left( \frac{E_a}{RT} \right) \]

Fig. 1. Arrhenius plot of the proton conductivity of cross-linked SPEEEK with constant hydration number (memory effect). IEC = 2.02 meq/g, DXL = 0.25, \( \lambda = 60.5 \) (●) and IEC = 2.1 meq/g, DXL = 0.22, \( \lambda = 80.7 \) (○).

Fig. 2. Hydration number of a cross-linked SPEEEK membrane (IEC = 1.9 meq/g, DXL = 0.24) as function of RH at 100 °C.

Fig. 3. Proton conductivity of a cross-linked SPEEEK membrane (IEC = 1.9 meq/g, DXL = 0.24) as function of temperature at 90% RH.
and found values between 1.1 and 1.3 g/cm³ [44]. This variation is an approximation.

Our assumption is thus a reasonable below the uncertainty of good conductivity measurements, which is typically about 30%. The degree of cross-linking at 90% RH.

Fig. 5. Temperature dependence of the proton conductivity of SPEEK with different degree of cross-linking at 100 °C.

\[ c(H^+) = \frac{IEC \times d}{WU} \] (5)

For this calculation, we assume that all water in the polymer is inside the acidic solution, that all sulfonic acid groups are fully dissociated and that the density \( d \) of the acidic solution is equal to 1. The first assumption is reasonable given the strong interactions between protons and water molecules. An incomplete dissociation of sulfonic acid groups will actually be observed in the proton mobility plots. Concerning the density of the acidic solution, Alberti et al. reported data inside Na⁺/CI⁻ mobility plots. The density of the acidic solution is equal to 1.

The proton mobility can then be calculated according to:

\[ u(H^+) = \frac{\sigma}{F c(H^+)} \] (6)

The advantage of this description is that all hydrated acidic polymers, including NaFon and SAP, show similar laws as function of the proton concentration above the percolation threshold [33,34]. The variation of the dissociation degree of sulfonic acid groups is included in the variation of the proton mobility. Furthermore, morphological characteristics of the ionomers, such as membrane porosity and tortuosity, or the percolation threshold of hydrated channels, can be estimated.

Fig. 6 shows a plot of proton mobility vs square root of proton concentration for the studied SPEEK membranes at 25 and 100 °C. The percolation threshold is observed at a proton concentration around 10 mol/L, which corresponds to a hydration number between 5 and 6. Recent molecular dynamics simulations gave similar values for the percolation threshold of hydrated domains in SPEEEK. Mahajan and Ganesan [45,46] obtained percolating water domains above 10 wt% of water in a SPEEK with degree of sulfonation DS = 0.5; this corresponds to a hydration number \( \lambda > 4 \). Komarov et al. used dynamic density functional theory and found percolation at \( \lambda = 7 \) [47]. In their analytical model for the calculation of SPEEK conductivity, Pisani et al. used a percolation threshold at a volume fraction of acidic solution phase of 0.22, corresponding also to a hydration level around 7 [48].

The relation between proton conductivity and proton concentration can be described by a cubic power law above the percolation threshold [34]. The concentration dependence of the proton mobility is strong in acidic solutions inside nanometric hydrated channels, because of important electrostatic interactions between solvated protons and ionized sulfonate ions on the channel walls, which reduce the proton mobility. Another view of the same phenomenon is to say that the sulfonic acid dissociation is reduced with increasing proton concentration so that the protons are “trapped” near the sulfonate anions. Very similar mobility plots can be found in solutions of weak electrolytes, where the electrolyte dissociation is incomplete.

The presence of the solid polymer prohibits a fraction of the volume to the conductive acidic solution phase and extends the distance that the moving protons must cover to cross the tortuous medium. These two effects can be described by the introduction of the porosity, \( \epsilon \), and the tortuosity, \( \tau \), as topological parameters and by rescaling the mobility, according to the phenomenological relation:

\[ u(H^+) = \frac{\epsilon \tau}{u(H^+)} \] (7)

The extrapolated value of proton mobility at infinite dilution and 25 °C in SPEEK (Fig. 6) is found to be \( 3 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \), which is in excellent agreement with the value reported by Peckham et al. \((3.2 \pm 0.4) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} \) [35] and only slightly below the proton mobility in pure water [49], which indicates a low tortuosity in XL-SPEEK.

Fig. 5. Relative humidity dependence of the proton conductivity of SPEEK with different degree of cross-linking at 100 °C.

\[ u(H^+) / (\text{cm}^2 \text{V}^{-1} \text{s}^{-1}) \]

T /°C

RH %

\( 1E-4 \)

\( 1E-3 \)

\( 1E-2 \)

\( 1E-1 \)

\( 10 \)

\( 20 \)

\( 30 \)

\( 40 \)

\( 50 \)

\( 60 \)

\( 70 \)

\( 80 \)

\( 90 \)

\( 100 \)

Fig. 6. Proton mobility in cross-linked SPEEK vs. square root of proton concentration at 25 °C (○) and 100 °C (●).
The cross-linking of ionomer membranes can have conflicting influence on the proton mobility. On the one hand, the proton mobility might be reduced by a reduction of the membrane porosity, due to a loss of free volume by the formation of cross-linking sulfone bonds, which distance (0.26 nm) is clearly shorter than the average distance between macromolecular chains in uncross-linked polymers [26]. On the other hand, a reduction of the channel tortuosity by the formation of covalent sulfone bridges, straightening the hydrated channels, is expected to enhance the proton mobility. The better conductivity observed in Fig. 5 for a cross-linked SPEEEK possessing a comparable IEC than an uncross-linked one indicates that the decrease of tortuosity is probably the predominant effect, so that surprisingly high conductivity values can indeed be observed for cross-linked materials.

As the proton mobility decreases with increasing proton concentration, the proton conductivity, which is the product of both, must show a maximum for an intermediate value of hydration number. Pisani illustrated this maximum for the case of perfluorinated ionomers (Nafion and Dow membranes), where it can be observed at a hydration number around 40 (Fig. 1 in ref. [48]). Fig. 7 shows the calculated dependencies for SPEEEK at 25 °C and at 100 °C (full lines) and experimental data for both temperatures (closed symbols). At 25 °C, a maximum of conductivity around 0.02 S/cm is predicted and experimentally observed for a hydration level \( \lambda = 90 \), corresponding to a molar proton concentration of about 0.6 mol/L. The interest of this figure is also to predict which proton conductivity can be obtained for a certain hydration level. In order to obtain a conductivity above 10^{-2} S/cm at 25 °C, for example, a hydration number above 35 is necessary.

At 100 °C, proton conductivity values above 0.2 S/cm are predicted for hydration numbers between 70 and 120. At \( \lambda = 60 \), the experimental value (0.16 S/cm) is near the prediction (Fig. 7). Although such hydration numbers might be too high in practice, since membrane swelling must be avoided, a conductivity of 0.1 S/cm, which is the level generally required for application, can be attained at a very reasonable hydration level above 20.

In conclusion, it is thus possible to improve the proton conductivity of XL-SPEEK by hydrating the cross-linked membranes at high temperature, under conditions that uncross-linked SPEEEK would not support, so that quite good electrical properties can be obtained, compatible with fuel cell requirements.

5. Conclusion

The proton conductivity of various cross-linked SPEEK membranes was determined by complementary two-point measurements: in fully humidified conditions between 25 and 65 °C and as function of RH between 80 and 140 °C. The data are consistent and allow calculating the activation energy of proton conduction (21 ± 3 kJ/mol). The presented plot of conductivity vs hydration number allows estimating proper hydration conditions for a particular conductivity.

At 100 °C, thermally cross-linked SPEEK membranes show conductivity as high as 0.16 S/cm and the value of 0.1 S/cm, required for application, can be reached at hydration numbers above 20, which are compatible with non-swelled membranes. Based on these results, cross-linked SPEEEK can definitely be proposed for use especially in intermediate temperature fuel cells working above 100 °C, if sufficient hydration levels are provided and maintained during operation.

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References
