



Short communication

The limits of proton conductivity in polymeric sulfonated membranes: A modelling study

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ABSTRACT

In this work, the conductivity limits of sulfonated membranes are investigated through a model analysis. A recent analytical conductivity model has been modified by reducing the number of variables to only three parameters, representing the hydration level, the ion exchange capacity and the morphology of the membrane. The effects of these parameters on the conductivity are investigated through a parametric analysis, showing significant trends.

Particular values of the morphology parameter define ideal conditions, in which the model conductivities constitute upper limits for real membranes. In particular, the model conditions of “ideal isotropic membrane” and “ideal non-tortuous membrane” are compared with the experimental proton conductivity of a number of polymeric membranes in the literature. It appears that membranes such as Nafion and Dow are close to the condition of “ideal isotropic membrane”, and their conductivity can be improved only by decreasing their tortuosity. On the other hand, the conductivity of other sulfonated polymers as SPEEK is well below the limit and can be enhanced by improving the membrane percolation properties.

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1. Introduction

One of the challenges in current fuel cell research is the development of novel proton conductive membranes with high proton conductivity, low reactant permeability and good thermal stability. Most of the works in this field, concern the improving of existing membranes, e.g. by forming co-polymers or by incorporation of inorganic components. In this frame, rationalization of the factors affecting membrane conductivity can be crucial in the design of new successful membranes. A considerable amount of works improving the understanding of Nafion have been published [1,2]; however, a simple and general analysis of membrane conductivity is still lacking from the published literature.

In this work, a simple analytical model [3] is used to study the main factors limiting the conductivity of PEM and the possible strategies for improving the conductivity of existing membranes.

In the next section, a qualitative description of the model is given, pointing out the aspects relevant to the discussion and describing an important model improvement. In Section 3, the results of model analysis are presented and discussed. Finally, in Section 4, the main conclusions are reported.

2. Model

2.1. Proton conductivity in the bulk acid solution

Protons in an acid solution form hydronium ions H_3O^+ . Proton transport through the solution occurs by two main mechanisms: (i) migration of hydronium ions (vehicular diffusion); (ii) jumping of a proton from a hydronium ion to an adjacent water molecule (structure diffusion).

For low ionic concentrations, the protons move independently from each other, and the solution conductivity is proportional to the proton concentration. However, when the ionic concentration increases, some interactions between the charge carriers are unavoidable. In particular, the ions attract and polarize water molecules around them thus reducing both the translational and rotational degrees of freedom of the solvent water. Since vehicle diffusion encounters translational friction resistance, while activation of structure diffusion is mainly determined by the orientation of the hydronium ion and the adjacent water molecules, both mechanisms are affected by water rigidity. In particular, by associating the reduction of the translational degrees of freedom with the vehicle diffusion mechanism and the reduction of the rotational degrees of freedom with the structure diffusion mechanism, an expression for the proton conductivity of the bulk solution is obtained [3].

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Nomenclature

c_i	concentration of species i
d	pore diameter
EV	equivalent volume
F	Faraday constant
K	constant
n	number
r	radius
t	tortuosity parameter
T	temperature
V	volume

Greek symbols

α	shape factor
ε	volume fraction
λ	hydration level
μ	water viscosity
σ	conductivity
Σ	cross-section

Subscripts and superscripts

0	reference value
eff	effective
exp	experimental
$pol+$	water polarized by positive charges
S	structure mechanism
s	surface
sub	subtracted from bulk
V	vehicular mechanism

2.2. Proton conductivity in the membrane

The proton conducting membranes are formed by attaching acid groups to hydrophobic polymers. When the membrane is exposed to vapor, the water molecules attracted by the hydrophilic acid groups penetrate it and dissolve the acid protons. Therefore, the hydrated membrane can be described as an acid solution inside a porous media with the anions fixed on its surface. With respect to the bulk acid solution described in the previous section, there are two new conditions: (i) the anions are fixed; (ii) part of the volume is occupied by the porous medium. By taking into account the first condition, a modified bulk conductivity σ_0 is obtained [3]. The second condition is common to all phenomena of transport in porous media and is briefly reviewed below.

Motion of particles through porous media can be described using percolation theory. Transport coefficients as diffusivities or conductivities are rescaled, with respect to their values in void, as follows:

$$\sigma^{eff} = (\varepsilon - \varepsilon_0)^t \sigma_0. \quad (1)$$

The porosity parameter ε represents the ratio between the volume occupied by the liquid solution and the total volume; the percolation threshold ε_0 represents pore closures phenomena, which, at porosities lower than a characteristic threshold ($\varepsilon < \varepsilon_0$) can interrupt mass (and charge) passing through the pores; the parameter t is linked to the tortuosity of the medium. While Eq. (1) is widely used, including [3], it has a serious drawback being function of two parameters ε_0 and t , which are known only for simple model systems. In a recent paper [4], we derived an expression alternative to Eq. (1), by representing the porous medium as an assembly of solid objects with defined volume V , cross-section Σ

Table 1
Typical values of α .

$\alpha = 0$	No tortuosity
$\alpha \sim 0.6$	Packing of spheres
$\alpha > 1$	Percolation limits
$\alpha \sim 1.2$	Packing of cylinders

and radius r :

$$\sigma^{eff} = (\alpha \varepsilon^2 + (1 - \alpha) \varepsilon) \sigma_0 \quad (2)$$

where the only parameter α depends on the shape of the objects as:

$$\alpha = \frac{r \Sigma}{V}. \quad (3)$$

In general, associating values of α to real porous media is not a trivial task; however, some typical values of α can be defined, as reported in Table 1 [4]. It is worth to point out that reducing the structure parameters from two to one represents a substantial reduction of the “free” parameter space from two dimensional to one dimensional. In other words, a single number (the value of the parameter alpha) defines the structure instead of a pair of numbers (values of percolation threshold and tortuosity parameter). This has clear advantages in terms of: (i) interpretation of model results and (ii) model reliability (by using two fitting parameters it is much easier to obtain artificial agreement with experiment than by using only one). It is worth noticing that the proposed model modification can be applied not only to our previous model [3], but also to other conductivity models using Eq. (1) to represent the effects of membrane porous structure (see for example [5–7]).

The porosity ε can be easily expressed in terms of the hydration level λ , and the membrane volume per sulfonic group EV as:

$$\varepsilon \approx \left(\frac{1 + EV}{18\lambda} \right)^{-1}. \quad (4)$$

The final expression for the proton conductivity in the membranes is:

$$\begin{aligned} \sigma^{eff} &= \left(\alpha \left(\frac{1 + EV}{18\lambda} \right)^{-2} + (1 - \alpha) \left(\frac{1 + EV}{18\lambda} \right)^{-1} \right) \sigma_0 \\ \sigma_0 &= \frac{c_{H_2O}}{\lambda} (K_V f_V(\lambda) + K_S f_S(\lambda) e^{n_{pol+}/\lambda - n_{sub}}) \\ &\quad + \frac{1}{32\mu} c_{H_2O}^2 F^2 D_0^2 \sqrt{\frac{1}{n_s^4} + \frac{1}{(\pi\lambda)^4}} \end{aligned} \quad (5)$$

$$f_V(\lambda) = \max \left(0, 1 - \frac{n_{sub}}{\lambda} \right)$$

$$f_S(\lambda) = \max \left(0, 1 - \frac{n_{sub}}{\lambda} - \left(\frac{\lambda^4}{n_s^4} + 1 \right)^{-1/4} \right)$$

where the max functions indicates that only positive values of f should be considered. The bulk conductivity σ_0 , beside a misprint correction, has the same expression as in [3], while the structure pre-factor has been modified according to Eqs. (2) and (4).

2.3. Parameters

Eq. (5) contains a large number of parameters. In this section we give their values and briefly discuss them.

In Table 2, the values of water viscosity and water concentration are listed. The variations of viscosity with temperature should be taken into account when operating at temperatures different from 25 °C. In Table 3, the specific parameters of the model are listed.

Table 2
Water properties.

Parameter	Description	Value
μ	Water viscosity	$0.89 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$
$C_{\text{H}_2\text{O}}$	Water concentration	$0.555 \times 10^5 \text{ mol m}^{-3}$

The first four parameters characterize the proton–water interaction and are obtained by fitting the experimental proton conductivity of hydrochloric acid solutions, as explained in [3]. The value of the parameter $n_{\text{pol}+}$ corresponds to the number of polarized water molecules around a hydronium. The next two parameters characterize the interaction between water and sulfonic groups; the number of water molecules on the surface of a sulfonic group n_0^s has been estimated from MD simulation results, while the value of d_0 comes from the assumption of cylindrical pore shape.

It is important to notice that all the above parameters characterize the interaction of water with protons and sulfonic groups, and, therefore, their values are common to all the sulfonated membranes.

Finally, the parameters characterizing the membrane, its hydration condition and pore structure are reported. These parameters are the variables of the model. The equivalent volume EV is related to the ion exchange capacity and to the membrane density, while the hydration level λ represents the membrane hydration condition. Physically, these two parameters represent the amount of the solid and liquid phases per unit sulfonic group in the hydrated membrane. The parameter α , as described above, represents the morphology of the porous membrane and depends on the shape of its solid components.

Except for λ , the other variable parameters appear only in the structure pre-factor. At fixed λ values, therefore, σ_0 is independent from the polymer type and morphology.

3. Results

3.1. Model validation

The validity of the model should be already assured by the experimental validation of bulk conductivity [3] and model validation of structure factor [4]. However, the specific validation of Eq. (5) can be beneficial to further enhance the reliability of the following analysis. In Fig. 1, the model conductivity of Nafion 1100, Dow 800 and SPEEK 700 membranes is shown as a function of λ and compared with the experimental conductivity data. It can be observed that:

- (1) A single α value is used in the whole hydration range of the membranes: from almost dry to fully humidified.
- (2) Similar membranes as Nafion and Dow, are described very well by the same α value.

Table 3
Model parameters.

Parameter	Description	Value
Specific model parameter		
n_{sub}	Proton–water	2.07
K_V	Proton–water	0.081 S cm^{-1}
K_S	Proton–water	0.251 S cm^{-1}
$n_{\text{pol}+}$	Proton–water	5
n_0^s	SO_3^- –water	12
d_0	SO_3^- –water	$1.2 \times 10^{-7} \text{ cm}$
Membrane properties		
EV	Equivalent volume	Variable
λ	Hydration level	Variable
Structure parameters		
α	Shape factor	Variable

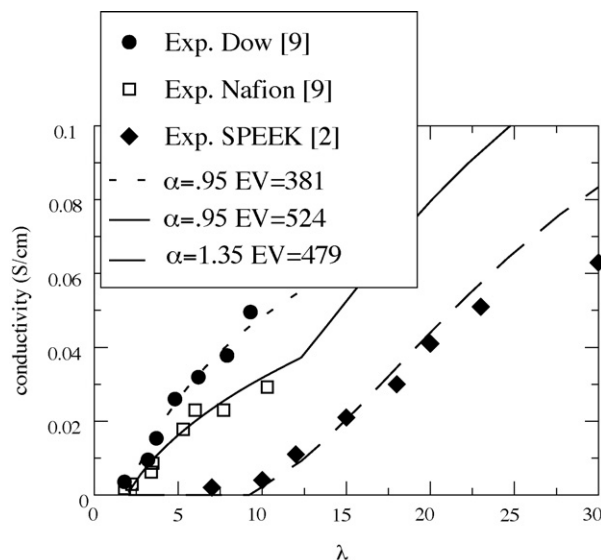


Fig. 1. Comparison of model conductivity with the experimental conductivity of Nafion 1100, Dow 800 and SPEEK 700 membranes.

- (3) The SPEEK membrane, which has a very different chemical composition and conductivity behavior, is still well described by just changing the value of α .
- (4) The obtained α values are reasonable and can be interpreted by comparison with the typical values given in Table 1.

By comparing Fig. 1 with Fig. 7 of Ref. [3], we observe that use of a single fitting parameter (Eq. (1)) instead of two parameters (Eq. (2)), increases the discrepancy between curve fitting and experimental results for the SPEEK membrane at λ higher than 25. However, as discussed in [3], at high λ values, the model is expected to overestimate the conductivity due to the model assumption of homogeneous proton distribution. Therefore, the better agreement observed in Fig. 7 of [3] may also be an artificial effect of over-fitting.

Overall, all the achievements listed above, are strong indications of model validity.

3.2. Parametric analysis

The effects of temperature on proton conductivity have been shown in [3]. All the results reported here are obtained at room temperature.

The membrane conductivity is represented as the conductivity of a bulk acid solution inside a solid porous matrix with the anions fixed on its surface. From this point of view, it is clear that optimal conditions are obtained when the presence of the solid polymer matrix has minimal effects on the proton transport properties while still keeping fixed the sulfonic groups, possibly in homogeneously distributed positions. Within such assumptions the optimal conductivity is represented by σ_0 .

In Fig. 2, the solid line represents σ_0 as a function of λ . It is seen that the maximum conductivity is obtained at a quite low value of λ corresponding to a high proton concentration, and reaches the very high value of 0.6 S cm^{-1} at room temperature. This curve is clearly quite far from real conductivity values as the solid matrix, in order to keep the sulfonic groups in fixed positions, must occupy a non-negligible fraction of the total volume. This effect is characterized by the EV parameter, which represents exactly the volume of solid polymer matrix per sulfonic group.

The presence of the solid medium, beside to preclude a fraction of the volume to the conductive liquid phase, extends the path that the moving particles should walk to cross the tortuous medium.

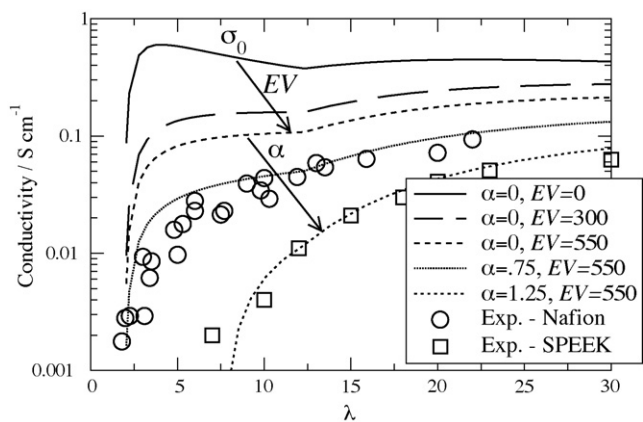


Fig. 2. Effects of model parameters on conductivity. The experimental conductivities of Nafion and SPEEK are reported for comparison.

While the first effect is unavoidable, the second depends strongly on the pores structure and can be ideally reduced to zero for straight pores in the direction of motion. Thus, a second series of ideal curves (one for each EV) can be drawn by considering non-tortuous pores ($\alpha=0$). In Fig. 2, the curves obtained for $EV=300$ and 550 (corresponding roughly to the EV of Nafion) are reported as dashed lines. It is seen that the effect of EV on conductivity is very important and that the maximal conductivity is now shifted toward higher λ values.

Finally, for $EV=550$, two additional curves are drawn for different α values: the first one, at $\alpha=0.75$, corresponds to a porous media made assembling spherical objects while the second one, at $\alpha=1.25$, corresponds to a porous media with percolation limits (see Table 1). The experimental conductivities of Nafion and SPEEK membranes are also reported for comparison. It is seen that the value of α affects considerably the conductivity and that, when increasing α , larger water contents are required to reach sufficiently high conductivities.

3.3. Analysis of the membrane conductivities

Direct comparison of membranes conductivities with the theoretical limits is complicated by the fact that each membrane has its own EV value. However, since EV appears only in the structure pre-factor, we can assume ideal values of α , normalize the membrane conductivity for the structure factor and compare the results with the theoretical σ_0 :

$$\sigma_{\text{norm}} = \frac{\sigma_{\text{exp}}}{\alpha \varepsilon^2 + (1 - \alpha) \varepsilon} \Leftrightarrow \sigma_0. \quad (6)$$

Through such comparison, the distance between the real membranes and the ideal conditions corresponding to the chosen α value can be observed. Two interesting conditions can be tested: $\alpha=0$ corresponds to the ideal case of no tortuosity, while $\alpha=0.6$ corresponds to the packing of spheres and hence to the minimal tortuosity achievable by isotropic media [4].

In Fig. 3, the theoretical curve is presented together with the normalized experimental conductivities by assuming the ideal case of optimal isotropic membranes ($\alpha=0.6$ in Eq. (6)). A large number of different sulfonated membranes is considered: Dow [8,9], Nafion [2,8,9], sulfonated polyimides (SPI) [10], sulfonated polyetherether ketone (SPEEK) [2], sulfonated polyphenylene (SDAPP) [11] sulfonated polysulfone (SPSU) [12], SPEEK containing 50 wt% of hydrated tin oxide (SPEEK-Sn50) [13] and Nafion doped with ZrP (Nafion-ZrP) [14]. It should be noted that except for the cases of Nafion, Dow and SPEEK membranes, each point in the figure corresponds to a differ-

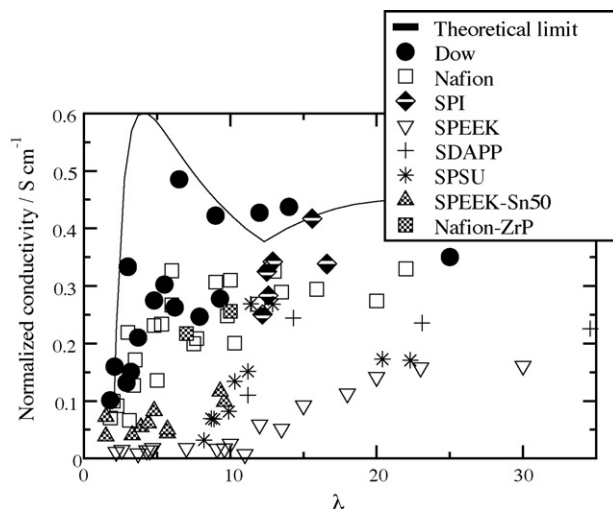


Fig. 3. Normalized proton conductivity of various sulfonated membranes as a function of the hydration level λ compared with the theoretical limits for isotropic membranes.

ent membrane with its own EV and, possibly, with different structures.

It appears that membranes such as Nafion and Dow are already very close to the theoretical conductivity limit. On the other hand, the conductivity of other sulfonated polymers as SPEEK is well below the limit and can be enhanced by improving the membrane percolation properties.

This can be achieved for example, by including inorganic particles acting like “proton bridges” between the isolated water clusters. An example is provided by the SPEEK – tin oxide membrane (triangles up) [13], which conductivity, still below the limit, is well above the pure SPEEK points (triangles down).

In Fig. 4, the theoretical curve is presented together with the normalized experimental conductivities by assuming the ideal case of non-tortuous membranes ($\alpha=0$ in Eq. (6)).

In such conditions, the theoretical curve represents an upper limit for the experimental values, and we observe that all the measured points are well below it. In particular, it appears that the conductivity of membranes such as Dow and Nafion can still be improved by decreasing their tortuosity. By comparison with Fig. 3, it appears that this can be achieved only realizing non-isotropic pore orientations. An example of this situation, shown in Fig. 4 as dark squares, is a Nafion-ZrP membrane pressed between the elec-

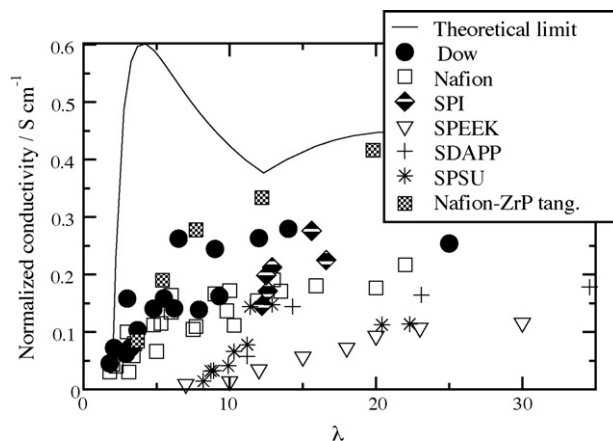


Fig. 4. Normalized proton conductivity of various sulfonated membranes as a function of the hydration level λ compared with the theoretical limits for non-tortuous membranes.

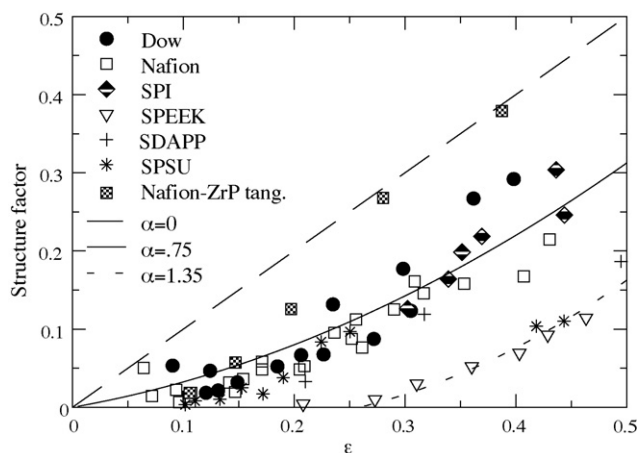


Fig. 5. Structure factors of various sulfonated membranes as a function of the porosity ε compared with typical theoretical curves.

trodes [15]. The conductivity of this membrane, when measured in a direction tangential to the membrane plane, comes quite close to the theoretical limit, evidencing a very low tortuosity in that direction. Silva et al. [16] observed that the difference between tangential and normal Nafion conductivity decreases while increasing the membrane thickness. Such behavior can be interpreted by the present model, by supposing the presence of non-tortuous proton paths on the membrane surfaces.

The same data can be analyzed in a different way: dividing the experimental data by σ_0 and representing the resulting values as a function of ε , we obtain a representation of the structural factor, which can be compared with the model:

$$\frac{\sigma_{\text{exp}}}{\sigma_0} \Leftrightarrow (\alpha\varepsilon^2 + (1 - \alpha)\varepsilon). \quad (7)$$

In Fig. 5 the experimental structural factors are reported, together with three theoretical curves. It is seen that most of the membranes behaves as porous media with isotropic tortuosity, while exceptions are, as discussed earlier, the SPEEK membrane and the tangential conductivity of Nafion-ZrP. The difference between the α of SPEEK and most of the other membranes, can be interpreted [4] in terms of the different shapes taken by the hydrated polymers, being the sulfonic groups attached to the “body” of PEEK rather than to the flexible “lateral chains” of Dow and Nafion.

4. Conclusions

The model conductivity is expressed as the product of two terms: a bulk conductivity, representing the conductivity of a liquid proton solution with fixed anions, and a “structure factor”. The bulk conductivity expression is quite complicated, but is common

to all sulfonated membranes. On the contrary, the structure factor is a simple expression of three characteristic parameters: λ and EV express the amounts of liquid and solid phase per unit proton, while the membrane morphology is described by the sole parameter α .

The effects of these parameters on the conductivity have been studied.

While λ and EV can be easily measured, α depends on the shape of the hydrated polymers and is difficult to evaluate. However, following its value, some reference situations can be defined and compared with the real membranes. In particular the conditions of “ideal non-tortuous membrane” and of “ideal isotropic membrane” have been considered and discussed. It appears that Nafion and Dow membranes are quite close to the limit of “ideal isotropic membrane” and their conductivity can be improved only by introducing anisotropy to reduce the tortuosity in the direction of proton transport. On the contrary, other membranes as SPEEK, are far from the theoretical limit and can be improved by enhancing their percolation properties.

Overall, the presented model is an effective and easy to use instrument to analyze conductivity data.

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