NAFION® MEMBRANES: MOLECULAR DIFFUSION, PROTON CONDUCTIVITY AND PROTON CONDUCTION MECHANISM

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ABSTRACT

^{1}H-PFG-NMR diffusion and proton conductivity data for NAFION® 117 is presented as a function of temperature and water content. From this, H_2O diffusion on a molecular scale is concluded to be similar to the one in bulk water. But "geometrical" restrictions of diffusion lead to a decreasing pre-exponential factor, i.e. decreasing macroscopic diffusion coefficient with decreasing water content. It is shown that proton conductivity is correlated with water diffusion for low degrees of hydration (vehicle mechanism). With increasing hydration there is an increasing contribution from "structure diffusion" culminating in an amplification factor of $A = 2.5$ for fully hydrated protonic NAFION® 117 at room temperature. The bonding of water in NAFION® as well as the local environment (hydration) of the acidic proton are concluded to be similar as in acidic aqueous solutions.

INTRODUCTION

Due to their unique mechanical, chemical and electrical properties, perfluorinated polymers are the technologically most relevant ion conducting membrane materials. The most prominent of that family is NAFION® which consists of a tetrafluoroethylen backbone with a perfluorinated ether side chain terminated by an SO_3^- ion exchanging group.
Although many properties of this material have been extensively investigated (see [1, 2] and refs. therein) reliable proton conductivity data as well as details of the proton conductivity process of the protonic form are hardly available. But it is certain that proton conductivity is strongly related to the water content as is observed for any hydrous proton conductor so far.
It has recently been shown that proton conductivity in hydrous systems (acidic aqueous solutions and solid hydrates) can be described by one common proton conduction mechanism, namely "structure diffusion triggered by molecular diffusion" [3]. However, from IR-spectra Falk concluded significantly weaker hydrogen bonding of water in NAFION® compared to this in bulk water [4]. He anticipates physical properties widely different for the water in the two enviroments which was later supported by NMR and DSC studies [5]. As proton conductivity in aqueous systems is highly related to the properties of the water therein it appears interesting to investigate whether proton conductivity in NAFION® fits into the general understanding of proton conductivity in aqueous systems or if different processes are taking place on a molecular level.

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For this reason the comparison of temperature dependent data on molecular diffusion and proton conductivity have already shown to be helpful [3, 7, 8]. A recent study on the role of water in NAFION® provided such data for one temperature (303K) [6]. This contribution adds temperature dependent data which are interpreted on the background of the available model of proton conductivity.

The results may also be helpful for the design of new proton conducting membrane materials based on a different chemistry but likewise for an improved water management of NAFION® membranes as separators in H_2/O_2–fuel cells under operating conditions.

EXPERIMENTS

Sample preparation

Yellowish NAFION® 117 (equivalent weight 848 g/mol dry polymer) membranes supplied by DuPont de Nemours (U.S.A.) in 1979 have been treated in a stirred solution of 5M HNO_3 at 373 K for 2 hours and kept in the solution at room temperature for another two days. The colorless membranes were then washed with pure H_2O at 323 K until the solution remained neutral. In this form they have been stored in pure water at room temperature. Before use the samples have been kept under the constant water vapour pressure of either pure water or saturated aqueous solutions of different salts at 303 K in a closed thermostated container for at least 4 days.

The samples were immediately transferred into a gas–tight glass tube for NMR–measurements. The identical samples were then used in an gas–tight, fiber–reinforced, PEEK (provided by ICI) sample holder for impedance measurements. After filling, the containers of both experiments had a negligible residual volume thus enabling measurements at constant water contents and at water contents determined by the saturation vapour pressure of pure water at each temperature. The water contents $n = [H_2O]/[SO_3^-]$ given in the figures were determined from the magnetisation observed in the NMR-experiment using a defined amount of liquid water as a reference. The results were slightly higher ($\Delta n \approx 0.5$) than those obtained by weighting the same sample before and after transforming it into the sodium form (this has a lower heat of hydration [9]) and subsequent drying over P_2O_5 for at least 4 days at 323 K.

Fully hydrated NAFION® in the sodium form has been obtained by ion exchanging the protonic form in 0.01 m NaOH and washing in H_2O at 323 K until pH-neutrality.

H–self–diffusion coefficient measurements

The ^{1}H–self–diffusion coefficient measurements have been performed on a home built NMR pulse spectrometer with a specially designed PFG equipment [10]. Details of the PFG–NMR technique have been reviewed by Stilbs [11].

The experiments were carried out at a resonance frequency of 52 MHz, a maximum field gradient strength of 25 Tesla/m, a maximum pulse length of 2400 μs and a diffusion time of 6 ms. Several heating and cooling runs in the temperature range 293 – 353 K have been performed to check the appearance of irreversible changes of the sample. Whereas these were negligible for high degrees of hydration, for low water content ($n = 3.5$) some hysteresis is observed. In contrast to measurements at constant water content, those for samples in contact with water required equilibration for half an hour after each temperature step (10 K). For the latter the contribution of the liquid water to the total signal was suppressed by using a special saturation pulse sequence.

The diffusion coefficient of each sample was found to be independent of the diffusion time 2τ ranging 2τ between 2 and 10 ms, indicating the absence of percolation effects (reduced dimensionality) for the corresponding diffusion lengths ($\approx 0.1 - 10\ \mu m$) and water contents ($3.5 - 14\ H_2O/SO_3^-$). All diffusion coefficients were recorded perpendicular to the membrane.

Proton conductivity measurements

The H^+-conductivity was measured by complex impedance spectroscopy using a frequency response analyser (Solartron 1174) and gold foils as proton blocking electrodes. The measurements were performed under the same conditions as those for the NMR-experiments. Heating and cooling rates were approximately 10 K/h.

PROTON CONDUCTION MECHANISM IN AQUEOUS SYSTEMS

Before discussing the proton conduction mechanism of NAFION® the principal features of this in other aqueous systems [3, 7] should be briefly outlined. As demonstrated in fig.1 the diffusion of hydronium ions (H_3O^+) as a whole (step 1) is highly correlated with intermolecular proton transfer (step 2). Each diffusional jump of a H_3O^+ into its first hydration sphere "triggers" a transfer of the excess proton into the second hydration sphere. Around the H_3O^+, formed in this way, new hydration spheres form by H_2O reorientation (step 3). This collective process results in a proton conductivity which is higher by factor A (A : amplification factor) than expected from H_3O^+ diffusion only. $A = D_{AH^+}/D_{H_2O}$ (D_{AH^+} is calculated from the equivalent conductivity of protons, and the diffusion coefficient of H_2O is assumed to be identical to the one of H_3O^+) is approximately equal to K^{+^2} where K^+ is the number of transient hydration spheres.

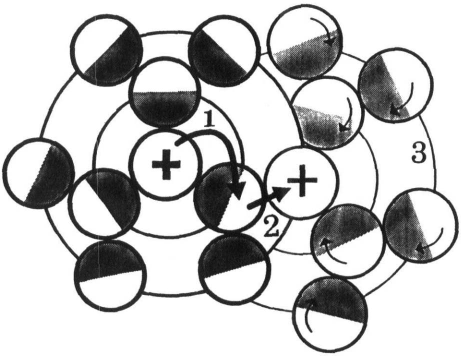

Fig. 1: Proton conduction mechanism in aqueous systems involving 1: molecular diffusion, 2: intermolecular proton transfer and, 3: hydration cluster reorganisation (according to refs. [3] and [7], see text).

For dilute aqueous solutions of acids the hydration cluster reorganisation (step 3) is rate limiting. This leads to a decrease of A with temperature ($A = 4.5$ at 300 K). In solid hydrates however, this has not yet been observed so far. Their H_3O^+ hydration cluster size is generally smaller and simply determined by the crystallographic structure. As a result A becomes practically temperature independent. It should be noted that for less than primary hydration ($K^+ \leq 1$) the mechanism merges into the vehicle mechanism [12], i.e. molecular diffusion of H_3O^+ and H_2O only. It is obvious that all three steps are affected by the strength of the hydrogen bonds involved.

RESULTS AND DISCUSSION

Water diffusion

All PFG–NMR data could be fitted with a single diffusion coefficient indicating perfect averaging of the diffusion coefficient over all protons within the time scale of the experiment (ms). As the number of water protons is significantly greater than the number of acid protons and the diffusion coefficient of both are of the same order of magnitude (as shown later) the ^{1}H–PFG–NMR diffusion coefficients can approximately be considered to be the one of water in NAFION®. This is shown in fig.2a in an Arrhenius representation. For all water contents the curves are slightly bent, i.e. they cannot be described by single activation enthalpies. The observed temperature dependence (activation enthalpy) is only slightly dependent of the water content n and in particular similar to the one of pure water (see also fig.2a). Compared to the absolute value of D_{H_2O} for pure water, this is about one order of magnitude lower for fully hydrated NAFION® and dramatically decreases with decreasing water content.

This behaviour is distinctly different from that of ionic materials such as zeolites (e.g. [13, 14]) for which the activation enthalpy and entropy of water diffusion increases due to an increasing bonding strength and degree of ordering of the water with decreasing degree of hydration. If we assume that the activation enthalpy of diffusion reflects the heat of water bonding (hydrogen bonding), as recently suggested also for aqueous solutions [15], the bonding strength seems to be weak, similar to pure water and only slightly dependent on the water content of NAFION® especially for high degrees of hydration ($n \gtrsim 6$ corresponding to more H_2O than required for hydration of the ionic SO_3H–site [16]). This is in agreement with a thermodynamic study by Escoubes and Pinéri [16] who found -53.2 kJmol^{-1} for the heat of water sorption ($n = 12$, $T = 293$ K)) which is similar to -43.4 kJmol^{-1} for the heat of vaporization of liquid water at the same temperature.
However, the observed significant decrease of the pre–exponential factor probably reflects a decrease of the entropy of diffusion with decreasing water content. Considering the absolute values of the pre–exponential factors, which are significantly lower than that of water, the entropy of water diffusion is expected to be even negative in strong contrast to positive values for, e.g., zeolites. This behaviour is consistent with geometric constrains for the diffusion of water in the polymer. On a molecular scale, however, the water still may diffuse freely as in bulk water. Reductions of the effective number of water diffusion pathways with decreasing degree of swelling may thus give rise to a decreasing entropy of diffusion. In terms of percolation theory (see e.g. [17]) the diffusion process may have a

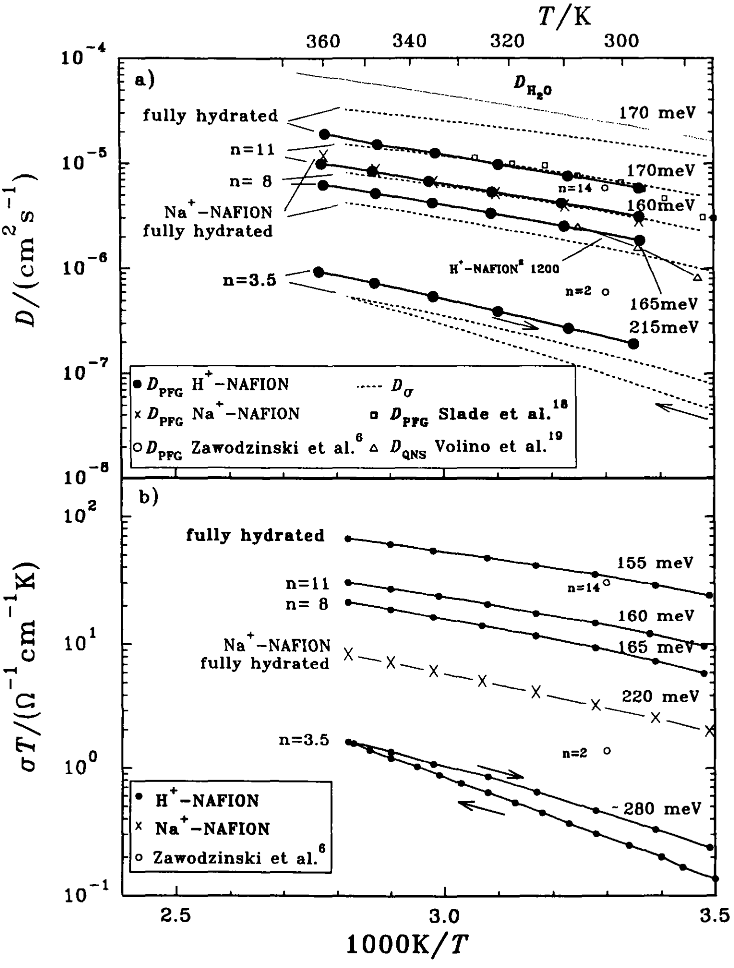

Fig. 2: a) H-diffusion coefficient obtained from ^{1}H-PFG-NMR and this calculated from ionic conductivity data via the Nernst-Einstein relationship for NAFION® 117 with the indicated water contents $n = H_2O/SO_3^-$. Diffusion coefficients from the literature and this for bulk water are given for comparison.

b) Ionic conductivity of hydrated NAFION® 117, data from the literature are given for comparison.

a) and b) The indicated activation enthalpies refer to the slopes at 300 K. Only data of cooling runs are shown if not indicated otherwise.

lower dimensionality on a microscopic scale. On a mesoscopic scale, however, the PFG-NMR data show perfect 3-dimensional diffusion, i.e. $t^{1/2}$ behaviour for the molecular displacement. It is important to note that all protons participate in the observed diffusion process, i.e. there are no microscopically isolated percolation clusters. This is even true for the sample with the lowest water content ($n = 3.5$). To some extent the H_2O obviously can form its own diffusion path within the "soft" polymer. The effect of restricted diffusion on a microscopic scale is demonstated in fig.3 together with the observation windows of the applied experimental techniques.

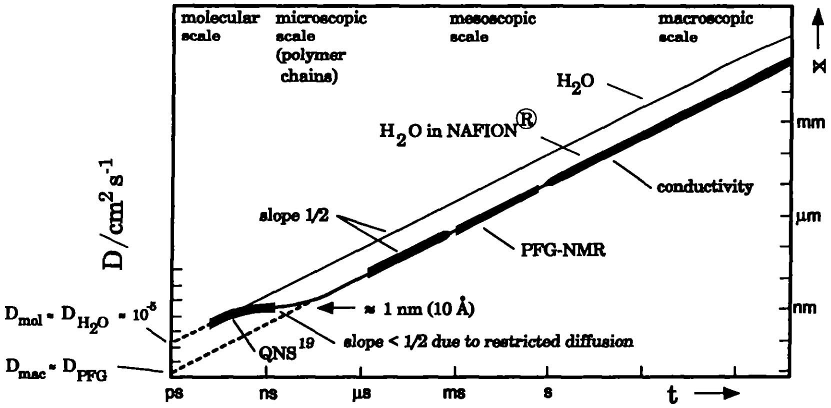

Fig. 3: Schematic comparison of molecular displacement x versus time t for water in NAFION® and bulk water. Hindered diffusion on a microscopic scale leads to a reduction of the macroscopic diffusion coefficient of water in NAFION® compared to this in bulk water.

Although the decrease of the water diffusivity in aqueous solutions of acids with decreasing solvent concentration is less severe [7], the basic behaviour is similar to the one in NAFION®.

This also includes the temperature dependence of the activation enthalpy. For solutions this recently has been ascribed to a decreasing hydrogen bond strength with temperature [15] rather than to an activated free volume. In solid proton conducting hydrates this has not yet been observed [3]. For these, the water bonding is obviously determined by the relatively rigid host structure interacting with the water. Thus the hydrogen bond interaction, which very much depends on the imposed O–O distance, becomes less temperature dependent and the diffusion coefficient of water, requiring breaking of hydrogen bonds, can be described by single activation enthalpies.

For NAFION® the observed temperature dependence of the activation enthalpy of the water diffusion coefficient may reflect a weakening of the hydrogen bond interaction between adjacent water molecules with temperature. But as this behaviour is still observed for the sample with the lowest water content ($n = 3.5$), this also seems to be true for the interaction of the water with its host, namely the SO_3H-site of the "soft" polymer side chain.

Altogether, at any water content the water of hydration in NAFION® may be considered to be similar to the one of liquid water on a molecular scale including the decrease of the hydrogen bond strengths with temperature. However, its diffusion becomes progressively restricted with decreasing degree of hydration within the polymeric host on a microscopic scale. This gives rise to a decrease of the pre-exponential factor and therefore to a decrease of the macroscopic diffusion coefficient.

This interpretation is in complete accordance with the one of an excellent QNS study by Volino et al. [19]. They were able to fit the quasielastic neutron scattering spectra of NAFION® 1200 with a H_2O diffusion coefficient close to the one of bulk water within a restricted spherical volume of ca. 1 nm (10 Å) in diameter and a macroscopic diffusion coefficient close to the one obtained from tracer diffusion experiments. The principal features of their model are also included in fig.2a.

Protonic concuctivity and proton conduction mechanism

The proton conductivity data compiled in fig.2b shows a similar dependence on water content and temperature as the water diffusion coefficient (fig.2a). But by directly comparing the diffusion coefficient D_σ obtained from the conductivity via the Nernst-Einstein relationship (that this can be done is demonstrated in ref.[8]) with D_{PFG} obtained by PFG-NMR (fig.2a) some distinct deviations become apparent. Whereas the two diffusion coefficients are almost identical for low water content ($n = 3.5$), $D_\sigma/D_{\mathrm{PFG}}$ increases with increasing water content. $D_\sigma/D_{\mathrm{PFG}}$ is nothing else but the amplification factor A which is shown in fig.4 together with its values for dilute aqueous solutions of hydrochloric acid and those of some solid protonic conductors. For fully hydrated H^+-NAFION® $A = 2.5$ at 300 K corresponding to an average hydration of the H_3O^+ of $K^+ \approx 1.5$ (see above). Like in aqueous solutions the amplification factor decreases with temperature for high water contents. In terms of the proton conduction mechanism outlined above the extent of proton hydration is decreasing with temperature. Moreover, the absolute values of A are practically identical with those for proton conductivity in aqueous hydrochloric acid (fig.4b). Both observations suggest that the H_3O^+ obviously forms its own isotropic hydration cluster like in aqueous solutions. In particular, this is not significantly influenced by the interaction of the H_2O with the polymer, especially for high degrees of hydration. For low water content ($n = 3.5$) D_σ is slightly smaller than D_{PFG} ($A < 1$, fig.4b). This might indicate incomplete dissociation of the SO_3H-group. It should, however, be noted that both, D_σ and D_{PFG} depend very much on the water content for low water concentration which gives rise to the large error bar in fig.4b. In any case, there is no indication for structure diffusion of the acidic proton for low degrees of hydration, i.e. hydrated protons diffuse as a whole (vehicle mechanism).

The observed hysteresis in the conductivity is probably due to a morpholocical change. This leads to less morphological restriction of molecular diffusion with increasing temperature. Its relaxation behaviour is slow especially for low degrees of hydration.

It is interesting that also Na^+-conductivity reflects the similarity with aqueous solutions.

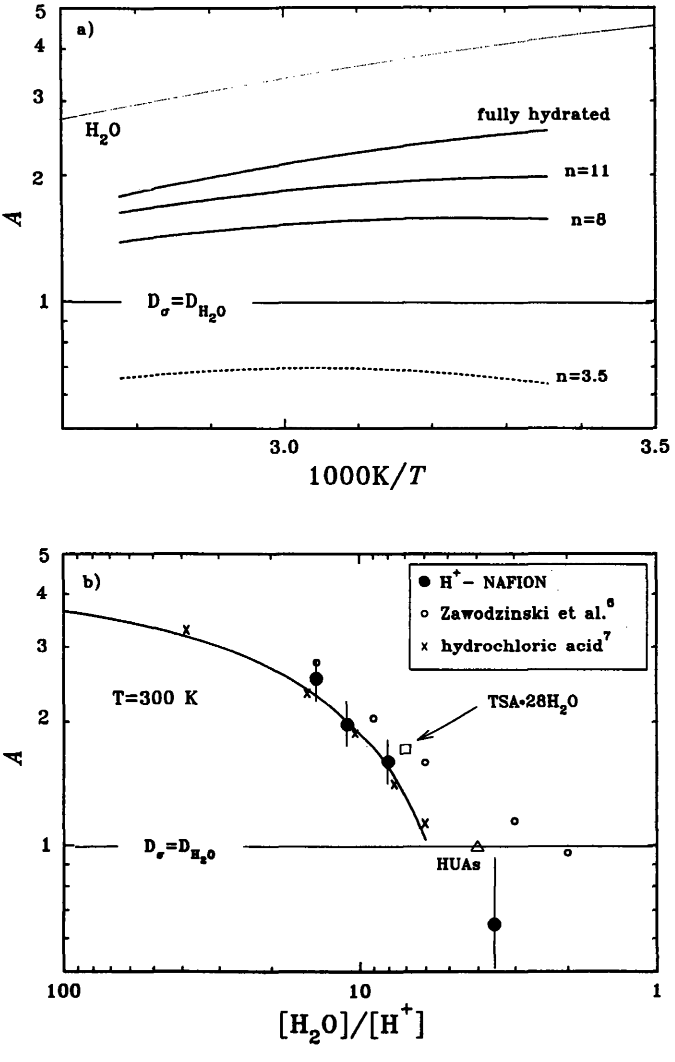

Fig. 4: a) Amplification factor $A = D_\sigma/D_{H_2O}$ as a function of temperature for protonic NAFION® 117 with different water content $n = [H_2O]/[SO_3^-]$. This for bulk water is given for comparison.
b) Amplification factor A as function of water content n. Corresponding values calculated from literature data this for aqueous hydrochloric acid [7] and this for the solid proton conductors $TSA \cdot 28H_2O$ □ and HUAs △ [3] are also included.

For Na^+-NAFION® $D_{\sigma Na^+}/D_{H_2O}$ is ≈ 0.5 (fig.2a) compared to 0.6 for the equivalent conductivity of Na^+ in dilute aqueous solution and this ratio is almost independent of temperature.

SUMMARY

According to the above discussion, molecular diffusion, proton conductivity and the enthalpies involved in these processes are similar for hydrated protonic NAFION® and acidic aqueous solutions on a molecular scale ($\lessapprox$ 1 nm). Restrictions for the transport pathways with decreasing water content on a microscopic scale ($\gtrapprox$ 1 nm), however, lead to an increasing negative entropy of water diffusion, a decrease of the pre–exponential factor and therefore a decrease of the macroscopic diffusion coefficient. For low water contents the protonic conductivity is correlated with molecular diffusion ($A = D_\sigma/D_{H_2O} \approxeq 1$, vehicle mechanism). But with increasing water content there is an increasing contribution from structure diffusion and the amplification A continously increases up to $A = 2.5$ for fully hydrated H^+-NAFION® at room temperature corresponding to 1.5 hydration shells of the H_3O^+ on the average. The local environment of the H_3O^+, which is thought to determine the amplification factor of the proton conductivity, is concluded to be dominated by the H_3O^+/H_2O interaction with very little influence from the polymer chains (especially for high degrees of hydration).

TECHNOLOGICAL IMPLICATION

From the viewpoint of the engineer using the material as a separator membrane in electrochemical cells, NAFION® basically behaves like a strong acidic aqueous solution, however, without convection phenomena. In particular, NAFION® is not expected to act as a better diffusion barrier. This requires reduced dimensionality for the diffusion process also on a macroscopic scale. In fact, this is in accordance with the observed high chemical diffusion coefficient of small water soluble molecules such as methanol. Appart from the fact that the non–crosslinked polymer NAFION® slowly dissolves in hot methanol this also prevents the application of NAFION® in direct methanol fuel cells.

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