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Abstract
A quasielastic neutron scattering investigation, to study the single particle dynamics of water absorbed in a Nafion/zirconium phosphate composite membrane hydrated at a saturation value, is herewith presented. The measurements were done on samples hydrated with both H_2O and D_2O to properly select the spectral contribution of the confined water. Both the elastic incoherent structure factor (EISF) and the linewidth of the quasielastic component are evaluated as a function of the momentum transfer. Their trend suggests that the motion of the system hydrogen atoms can be schematized as a random jumping inside a confining spherical region, which can be related to the boundaries of the cluster that water molecules form around the sulfonic and phosphate acid sites. The size of such a region, the characteristic time necessary to explore the region and the number of mobile protons involved in this motion are similar to those estimated for water absorbed in a simple Nafion membrane at a saturation water content. Also the calculated jump diffusion coefficient resembles that of water confined in a simple Nafion membrane, and both are consistent with the value of bulk water. The results indicate that the dynamical behaviour of water in Nafion membranes is nearly unaffected by the presence of zirconium phosphate nanoparticles.

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1. Introduction

Fuel cells offer the promise of a low-polluting, highly efficient energy source. In polymer–electrolyte fuel cells, that are receiving most of the attention for automotive and small stationary applications, the electrolyte milieu is a polymer membrane, the so-called polyelectrolyte membrane (PEM), which is able to conduct protons [1, 2]. Polyperfluorosulfonic acid (PFSA) membranes such as Nafion (Du Pont de Nemours & Co.) have given an unquestionably substantial boost to the development of fuel cells. These polymers consist of a polytetrafluoroethylene backbone with pendant side-chains terminating with $-SO_3^- M^+$ groups, where M^+ is an exchangeable cation, that in the present work is H^+. In fact, beyond an outstanding chemical, thermal and mechanical stability, Nafion membranes show high proton conductivity, thus providing crucial properties that can be suitably exploited in polymer electrolyte fuel cells [1, 2].

Moderate operating temperatures for fuel cell membranes are required because of the need for aqueous proton transport and because the polymers used have relatively low glass transition temperatures ($T_g \sim 100\,°C$), especially when hydrated. In current PFSA membranes, hydration must be quite high to produce sufficient conductivity [3] and to prevent membrane or catalyst layer dry out [4], thus restricting the operating temperatures of PEM fuel cells to about $80\,°C$. One current thrust of fuel cell research is to increase the operating temperature of PEM fuel cells to $120\,°C$ or above, where the electrode kinetics of the oxygen reduction reaction is much improved. PEMs that retain water and conductivity, and are more thermally and mechanically robust at high temperatures, can be operatively produced by including into the polymer matrix nanoparticles made of a properly chosen solid proton conductor, or 'nanofiller'. It was suggested that the presence of these hydrophilic additives decreases the chemical potential of the water inside the membrane, thus creating an additional pathway for the proton conduction. At the same time, these inorganic compounds provide new hydrogen-bonding sites to water so that the hydration of the membrane will be increased and the transport and evaporation of water will be reduced [5].

As the chemical behaviour of water absorbed in Nafion membranes is strongly affected by the insertion of a nanofiller, one may wonder if its dynamics is also modified, and how. This question may be crucial to the good understanding of the microscopic mechanisms that rule proton conduction, whose onset and amplitude is strictly correlated with the water dynamics, as is demonstrated by many experimental evidences [6–10]. To give new insights into the proton dynamics in the picosecond time window and in the angstrom spatial scale, a neutron scattering (NS) investigation of the water absorbed in a Nafion/zirconium phosphate (Nafion/ZP) composite membrane was performed, zirconium phosphate being one of the most used constituents of nanofiller particles [11].

Very recently, the dynamical behaviour of water absorbed in Nafion membranes was studied through NS spectroscopy as a function of the water content [10]. In such an investigation the motions of protons were schematized in terms of random jumping confined within a hard sphere. In the present work a similar approach to interpret the data is used and the dynamical behaviour of water in Nafion/ZP composite membranes is compared to that of water in simple Nafion, and of bulk water.

2. Materials and methods

2.1. Materials and preparation of samples

Nafion 115 membranes, with thickness of $\sim$127 μm and equivalent weight of 1100 g/(mol sulfonic group), were purchased from Aldrich. To remove impurities the membranes were boiled for 1 h in 3% H_2O_2, 1 h in 0.5 M H_2SO_4 and 1 h in deionized H_2O. In all treatments

the ratio (membrane mass, g)/(liquid volume, ml) was 1/100. After the first and the second treatment the membranes were rinsed in deionized water. The membranes were then wiped with a filter paper and cut so as to obtain (5 cm × 2 cm) rectangular strips.

Zirconium phosphate was incorporated into Nafion 115 by using a procedure similar to that described in [12]. The Nafion 115 strips, previously swollen in a methanol–water solution (1:1 (v/v)), were dipped overnight into a 0.76 M solution of zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, at 80 °C. After washing in cold water to remove zirconyl chloride from the surface, the strips were left to react with a solution of H_3PO_4 1 M at 80 °C for about 8 h. The strips were then treated with 1 M HCl (4 h at 80 °C and 20 h at room temperature) and finally dried at 80 °C for several hours to remove the HCl. The amount of incorporated zirconium phosphate, obtained by thermogravimetric analysis and ion exchange capacity determinations, turned out to be 9 wt%.

The composite strips were stored in H_2O or D_2O. To determine the liquid phase content, the strips were wiped with a filter paper, weighed, heated for 2 h under vacuum at 120 °C and weighed again. The ratio (moles of liquid phase)/(mole of sulfonic group), hereafter λ, was calculated on the basis of the observed weight loss and turned out to be 25 ± 1 for both H_2O and D_2O.

2.2. Neutron scattering

In an NS experiment, the measured quantity is the dynamical structure factor $S(q, \omega)$, which corresponds to the probability for an incident neutron to be scattered by the sample with a momentum transfer $\hbar q$ and an energy transfer $\hbar\omega$, where $\hbar$ is the reduced Planck constant [13] and q is the wavevector transfer. Through the ω- and q-dependence of $S(q, \omega)$, it is possible to simultaneously obtain information respectively on the characteristic correlation times and on the spatial geometry of the revealed molecular motions. The dynamical structure factor can be regarded as the sum of a coherent and an incoherent contribution. They are respectively related to the inter-particle and self-particle density fluctuations of the target sample. Since hydrogen atoms have the biggest incoherent scattering cross-section, the signal we detected is mainly due to their contribution [13]. Actually, in the experiment it is the average dynamics of all the protons that is revealed, whether they belong to water molecules, as is the main case, or to ionic complexes that exist in the liquid phase.

To properly analyse the dynamical features of proton motions it is useful to introduce the so-called self-intermediate scattering function $F_S(q, t)$, which is the time Fourier transform of $S(q, \omega)$. The confined dynamics of water molecules in the Nafion/ZP composite membrane can be described as due to both rotational and translational diffusive motion. In terms of the $F_S(q, t)$, which accounts for the evolution of the density correlator, such a dynamics is represented through the equation [13]

$$F_S(q, t) = \langle \rho_q(0)\rho_{-q}(t)\rangle / N = \langle \exp[iq \cdot (r_T(t) + r_R(t))] \exp[-iq \cdot (r_T(0) + r_R(0))]\rangle \quad (1)$$

where r_T and r_R describe respectively the translational and rotational degrees of freedom of the scatterers. In equation (1) all the intramolecular and intermolecular vibrational and librational motions are neglected, as they are much faster than those considered in the present work, thus contributing in the energy range of the analysed spectra as a flat background only. As the samples can be considered isotropic, the dynamical structure factor depends only on the modulus q of the wavevector transfer. It should be noticed that, by supposing the translational and rotational motions decoupled, $F_S(q, t)$ is often written as the product of two decaying factors which represent the translational and rotational degrees of freedom. However, recent molecular dynamics simulations have shown that the two kinds of motion can be considered approximately decoupled only for relatively short times, i.e. 0.1–0.2 ps, but not in

the picosecond time range investigated here. Nevertheless, the authors explain how the effects on $F_S(q, t)$ due to the motional coupling and those due to the decay of rotational motions cancel each other [14–16], finally allowing one to neglect the rotational term in the dynamical structure factor. Thus, taking into account only translational motions and within the incoherent approximation, the $S(q, \omega)$ can be represented with the following expression [13]:

$$S(q, \omega) = e^{-\langle u^2 \rangle q^2} \{ p_f \delta(\omega) + (1 - p_f)[A_0(q)\delta(\omega) + (1 - A_0(q))L(q, \omega)] + B \} \otimes R(q, \omega).$$
(2)

The term $e^{-\langle u^2 \rangle q^2}$ is the so-called Debye–Waller factor, which describes the Gaussian q-decrease due to the purely vibrational atomic mean square displacements $\langle u^2 \rangle$. The first term within the curly brackets, $p_f \delta(\omega)$, takes into account the elastic contribution to the total spectrum, due to those scatterers whose diffusive motions are too slow to be detected, with p_f the fraction of such immobile appearing protons. In fact, also diffusive motions, when confined to a restricted geometry, contribute to the elastic response of the system. The term $A_0(q)\delta(\omega)$ represents this contribution, where the q-dependence is given by the elastic incoherent structure factor (EISF) $A_0(q)$, directly determined by the geometry of the motion of the confined protons. The third term, appearing in the spectra as a broadening of the elastic peak, accounts for the quasielastic signal originating from the translational confined motion of the hydrogen atoms. This term can be described through a properly normalized Lorentzian function $L(q, \omega)$. In this work, only the diffusive motions in the energy range between -1.5 and 1.5 meV, thus appearing in a restricted region around the elastic peak, were analysed. In such an energy range, the inelastic scattering contribution can be considered as a flat background, and it was therefore taken into account by the constant term B. Finally, due to the finite resolution of the spectrometer, equation (1) must be convoluted with the experimental resolution function $R(q, \omega)$. At the elastic peak this function is provided by a vanadium standard measurement.

The quasielastic component is characterized by the half-width at half-maximum Γ which is related to motions with characteristic time $\hbar/\Gamma$. Actually, due to the great structural complexity of Nafion membranes, the dynamics of water molecules is characterized by a remarkable heterogeneity, as they move in quite different local environments. Then, the Lorentzian function we used to fit the quasielastic contribution can be regarded as a broad, almost continuous, distribution of motions in the picosecond time-window. Indeed, this elementary description of the measured spectra, already used to describe the dynamics at room temperature of water absorbed in Nafion [10, 17, 18], gives an oversimplified sketch of the real system. At the same time, it allows one to obtain a phenomenological picture of the H dynamics through quantitative spatial and temporal parameters, which provide a description of the hydrogen atom motions. Some works on the dynamics of confined water make use of more complicated and rigorous fitting models, such as the stretched exponential model [19]. Anyway, it has been verified that these procedures neither provide a better fit to the present experimental data, nor do they add new relevant insights into the picture of the system dynamics.

The trend of the estimated linewidths as a function of q suggests that the most reasonable picture of the translational motion of protons in Nafion/ZP composite membranes is a random jumping confined within a spherical geometry. The same description was employed in a recent study of water absorbed in Nafion [10] at room temperature and in other porous matrices [20]. The model of continuous diffusion within a sphere of radius R would imply that at low q values the linewidth of the quasielastic component is constant, while at high q it would exhibit the Dq^2 trend coming from the well-known Fick's law of diffusion, where D is the diffusion coefficient. However, the linewidth estimated in the present work tends to a constant value at high q, which is the typical behaviour of random jump diffusion [13]. As previously said, the Lorentzian curve describes a distribution of motions, thus the approach of Hall and Ross [21] was used

to represent the quasielastic broadening at medium and high q. By assuming a Gaussian distribution of jump lengths, they modelled the spectral linewidth with the formula

$$\Gamma(q) = 1/\tau_{\text{jump}}[1 - \exp(-q^2\langle r^2 \rangle/6)] \tag{3}$$

where τ_{jump} is the residence time between two jumps and $\langle r^2 \rangle$ is the mean square jump length, related to the characteristic jump length r_0 through $r_0 = \sqrt{\langle r^2 \rangle/3}$.

The confined diffusion within a sphere of radius R provides the following EISF [21]:

$$A_0(q) = (3 j_1(qR)/qR)^2 \tag{4}$$

where j_1 is the first spherical Bessel function. This expression was fitted to the experimental EISF, which is the fraction of neutrons scattered elastically by the protons diffusing in confined geometry, relative to the total measured intensity: $\text{EISF} = I_{\text{el}}/(I_{\text{el}} + I_{\text{qel}})$, where I_{el} and I_{qel} are respectively the elastic and the quasielastic intensities [13].

The measurements were done at the high-flux time-of-flight spectrometer IN5, at ILL (Institut Laue-Langevin, Grenoble, France). An incident wavelength of 5 Å was employed, achieving a q-range from 0.2 to 2.3 Å^{-1}, an accessible energy transfer range from -1.5 meV to $2k_{\text{B}}T$ and an energy resolution with a full-width at half-maximum of $\sim$0.09 meV. With such range and resolution, motions with characteristic times faster than $\hbar/0.09$ meV$^{-1} \approx 15$ ps can be probed. The samples were held in a standard slab-shaped aluminium cell with a thickness of 0.5 mm, placed at an angle of 135° with respect to the neutron incident beam. The measurements were performed at 300 K. Before any data processing, the raw spectra were corrected for empty cell contribution, self-shielding and self-absorption, and normalized to a vanadium standard to take into account the non-uniform detector efficiency as a function of the scattering angle. The original 81 corrected spectra were then binned into 27 groups in order to improve the statistics and carry out a meaningful analysis of the quasielastic scattering as a function of the momentum transfer q. Due to the high value of the transmission coefficient ($t(90°) = 0.92$ and 0.98 for respectively the H_2O and D_2O hydrated sample) multiple scattering was neglected.

3. Data analysis

3.1. Contributions to the measured spectra

The signal of water absorbed in the Nafion/ZP composite membrane was derived by measuring samples hydrated with both H_2O and D_2O at the same hydration degree at room temperature. The signal from the two samples can be described as follows:

$$S_{\text{Nafion/ZP}+H_2O}(q,\omega) = S_{\text{Nafion/ZP}}(q,\omega) + S_{H_2O}(q,\omega) \tag{5a}$$

$$S_{\text{Nafion/ZP}+D_2O}(q,\omega) = S_{\text{Nafion/ZP}}(q,\omega) + S_{D_2O}(q,\omega). \tag{5b}$$

The first term on the right-hand side of the equations above, $S_{\text{Nafion/ZP}}(q,\omega)$, can be supposed to contribute mainly to the elastic part of the spectra, since the measurements were done well below the glass transition temperature of the Nafion membrane. On the other hand, the second term on the right-hand side of equations (5a) and (5b), $S_{H_2O}(q,\omega)$ and $S_{D_2O}(q,\omega)$, should contribute to both the elastic and the quasielastic signal, as a consequence of the dynamics of the water molecules confined within the membrane. A straightforward calculation of the total cross sections shows that in equation (5a) the incoherent contribution from $S_{H_2O}(q,\omega)$ ($\sigma_{\text{inc}} = 3996b$ and $\sigma_{\text{coh}} = 194b$) is larger than that from $S_{\text{Nafion/ZP}}(q,\omega)$, which is prevalently coherent ($\sigma_{\text{inc}} = 69b$ and $\sigma_{\text{coh}} = 309b$ per monomer). In equation (5b) the main contribution comes from the coherent signal of both the Nafion membrane and the heavy
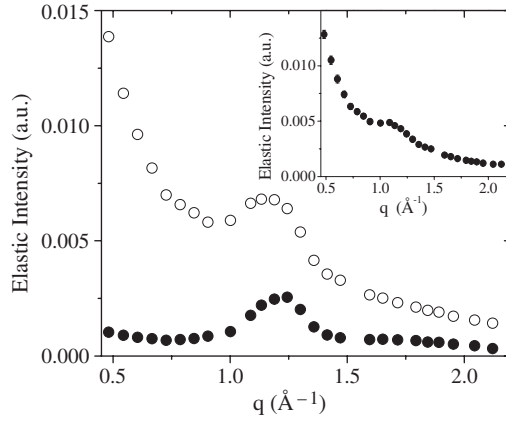
Figure 1. Measured elastic intensities of H_2O-hydrated (empty circles) and D_2O-hydrated (full circles) Nafion/ZP. Error bars are of the dimensions of the circles or smaller. Inset: elastic intensity difference.

water $S_{D_2O}(q, \omega)$ ($\sigma_{inc} = 102b$ and $\sigma_{coh} = 386b$). From these estimates it can be inferred that the elastic coherent contribution of the Nafion/ZP composite membrane can be approximately evaluated from the D_2O hydrated sample.

4. Results and discussion

The experiment performed was devoted to the study of the dynamical behaviour of water absorbed in Nafion membrane. The information was extracted from the comparative analysis of H_2O-hydrated and D_2O-hydrated Nafion/ZP spectra. The elastic intensities of both H_2O-hydrated and D_2O-hydrated Nafion/ZP samples are shown in figure 1. It can be observed that the membrane signal is a non-negligible part of the total intensity of H_2O-hydrated Nafion/ZP, about 8% at $q = 0.5$ Å^{-1}, almost 40% at $q = 1.3$ Å^{-1} and 25% at $q = 2$ Å^{-1}. The elastic intensities, that are markedly modulated as a function of q, display the largest coherent contribution in the region 0.9–1.5 Å^{-1} where a wide peak is easily visible. The inset of figure 1 shows the difference spectrum calculated through the equation

$$S_{H_2O}(q, \omega) \approx S_{Nafion/ZP+H_2O}(q, \omega) - S_{Nafion/ZP+D_2O}(q, \omega) \approx S_{H_2O}(q, \omega) - S_{D_2O}(q, \omega). \quad (6)$$

The I_{el} and I_{qel} of the difference spectra obtained via this procedure were used to evaluate the EISF. In this way, the coherent contribution of the polymer membrane to the elastic intensity is reliably subtracted out, even if a coherent bump is still visible. While equation (6) is important to properly evaluate the elastic intensity, it does not improve the estimate of the quasielastic contribution from water. In fact, in the quasielastic region, the main contribution to the spectra of H_2O-hydrated Nafion/ZP comes from water, while scattering from Nafion/ZP membrane can be neglected. Therefore to estimate the linewidth of the absorbed water, the spectra of H_2O hydrated Nafion/ZP were directly exploited.

In figure 2, where the spectra of H_2O-hydrated and D_2O-hydrated Nafion/ZP membrane are shown, it appears that $S_{Nafion/ZP+H_2O}(q, \omega)$ is much larger than $S_{Nafion/ZP+D_2O}(q, \omega)$, due to the high incoherent cross section of water hydrogen atoms. The difference spectrum is plotted in figure 3. As shown by the fit curve also reported in the figure, the adopted model represents excellently the experimental data with an elastic signal, a flat background and a clear Lorentzian component. The obtained difference spectrum was used to calculate the EISF,
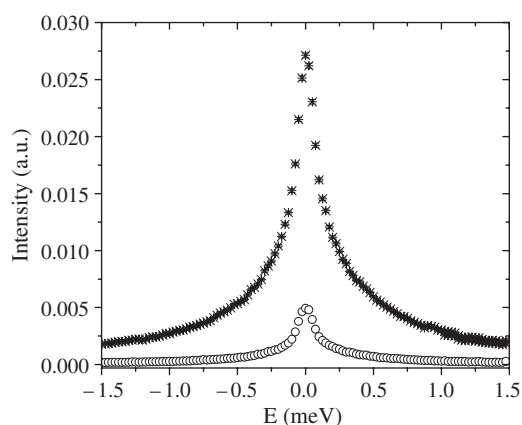
Figure 2. Comparison between the quasielastic spectra of H_2O- and D_2O-hydrated Nafion/ZP at $q = 2.12$ Å^{-1} (stars and empty circles, respectively).
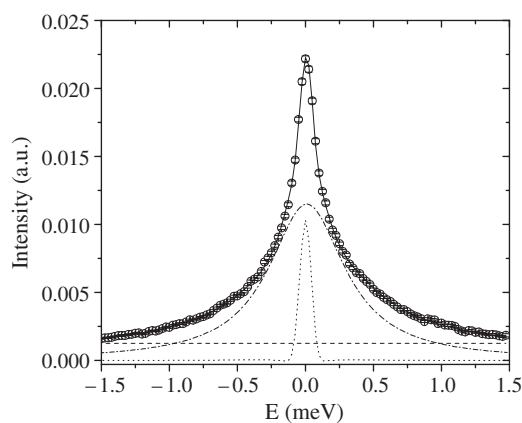

Figure 3. Difference spectrum from water absorbed in a Nafion/ZP membrane at $q = 2.12$ Å^{-1} together with the elastic delta function (dotted line), the quasielastic Lorentzian component (dash–dotted line) and the flat background (dashed line). The solid line is a fit to the expression given by equation (2).

which is represented in figure 4. The EISF was then fitted with the model of confined diffusion within a sphere, described by equation (4). The bump at around $q = 1.3$ Å^{-1}, witnessing the residual contribution of coherent scattering, was excluded from the fitting range. The radius of the sphere where the diffusing protons are confined turned out to be $R = 4.03 \pm 0.05$ Å. This result is comparable with both the value of 3.66 ± 0.03 Å recently found for water absorbed in a Nafion membrane at a saturated water content ($\lambda = 16$) [11], and the value of about 4.25 Å estimated in the pioneering work of Volino *et al* [17, 18]. To reliably interpret the meaning of this radius we have to consider that the structural and dynamical properties of water depend on the interaction with the polymer and filler. However, the structure of the membrane itself is still a matter of discussion [22–24]. In the well-known model of Gierke *et al* [22], the ionomer polar heads (sulfonic groups) form nanometre-sized spherical aggregates, where water molecules would cluster in nano-pools, connected by small channels. Conversely, in a more recent model it was proposed that ionic domains are not spherical, but that they form
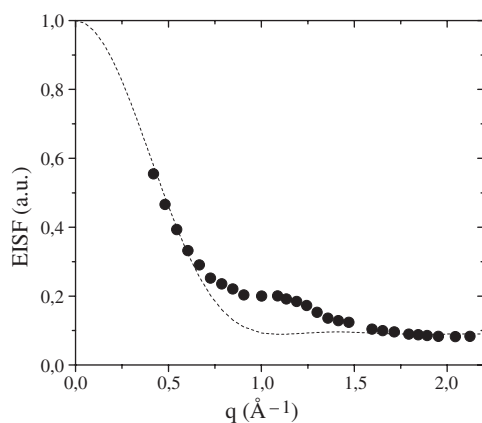
Figure 4. Elastic incoherent structure factor as a function of q relative to the difference spectrum. The dashed line is the best fit obtained by using the model of confined diffusion within a sphere.

a more or less connected cylindrical structure [23]. In this case, the transport properties are explained in terms of tortuosity (quantity of channels which are either connected or dead ends). This picture resembles the very recent elongated polymer particle model [24], where the Nafion matrix is supposed to be made of elongated (cylindrical or ribbon-like) polymeric aggregates, surrounded by ionic groups and collinearly packed in bundles, that are themselves randomly oriented in space at the sub-micron scale. In this model the polar solvent is not confined in clusters, but forms a continuous solvation phase around the polymeric aggregates. Whatever the model one takes into account, it may be argued that the radius found in the present work, which is significantly lower than both the characteristic size of the cages in the model of [22] and the distance between aggregates of [23, 24], describes an effective confinement arising from clustering of water molecules near the sulfonic acid sites.

The fraction $1 - p_f$ of mobile hydrogen atoms, that on the basis of the model is estimated to be approximately 0.91, is also in agreement with the value found for water in simple Nafion [10]. Additional insights on the dynamics of water protons within the Nafion/ZP membrane are given by the analysis of the linewidths of the H_2O-hydrated Nafion/ZP spectra, obtained through the already described fitting procedure. The behaviour of the linewidth as a function of q^2 is shown in figure 5. At very low q the experimental data seem to attain a constant value, which is the signature of a confined motion, in agreement with the mechanism of diffusion in a sphere already exploited above to interpret the calculated EISF. The low-q Γ values allow one to tentatively calculate a characteristic time of about $\tau_{sph} = \hbar / \Gamma = 10.2 \pm 0.6$ ps, corresponding to such a diffusive motion. Also in this case, τ_{sph} is very similar to the value of 9.8 ± 0.7 ps obtained for water absorbed in a simple Nafion membrane [10]. All these findings strongly suggest that the local dynamics of water molecules is quite similar to that of simple hydrated Nafion. Therefore, the insertion of a nanofiller component does not seem to alter the local rearrangement of water molecules.

For higher q values the behaviour of the linewidth shown in figure 5 can be satisfactorily described by the unbounded jump diffusion model of equation (3). The characteristic time for jump diffusion $\tau_{jump} = 1.9$ ps and the jump length $r_0 = 1.0 \pm 0.1$ Å can then be evaluated. These values are intermediate between those estimated for water in Nafion ($r_0 = 1.25 \pm 0.05$ Å, $\tau_{jump} = 3.6$ ps) [10] and those of bulk water ($r_0 = 0.75 \pm 0.05$ Å, $\tau_{jump} = 1.25$ ps) [25][8]. The

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[8] We remark that we estimated r_0 directly from the value of the parameter L reported in this reference.
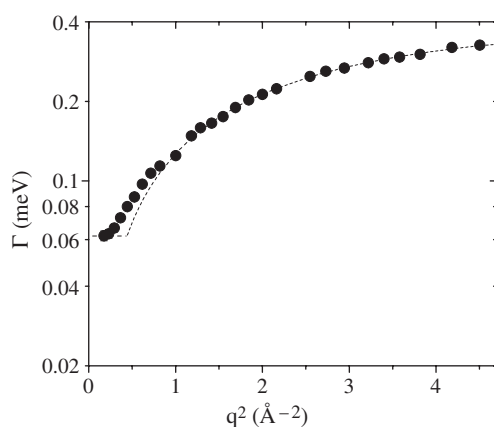
Figure 5. Half-width at half-maximum versus q^2 of the H_2O-hydrated Nafion/ZP spectrum. The dashed line corresponds to fitting with equation (3).

specific differences between these parameters in Nafion/ZP and Nafion membranes suggest that the jumping dynamics of protons in the former is more similar to that of bulk water. This is probably due to the fact that in the Nafion/ZP sample the higher water content ($\lambda = 25$) implies the presence of a much larger amount of bulk-like water molecules than in the case of the simple Nafion sample ($\lambda = 16$) [11]. From the knowledge of τ_{jump} and r_0, the diffusion coefficient $D_{jump} = r_0^2/(2\tau_{jump})$ can be straightforwardly calculated. Quite similar values of such a diffusion coefficient for water in Nafion/ZP ($D_{jump} = 2.7 \times 10^{-5}$ cm^2 s^{-1}), water in Nafion ($D_{jump} = 2.2 \times 10^{-5}$ cm^2 s^{-1}), and bulk water ($D_{jump} = 2.3 \times 10^{-5}$ cm^2 s^{-1}) are found. Therefore, the effective proton jumping dynamics appears to be rather similar in all the three cases. This result is consistent with the indication that zirconium phosphate plays little role in the actual conduction of protons through the membrane [12].

5. Conclusion

NS spectroscopy is an invaluable technique to study the dynamics of water confined in Nafion/ZP composite membranes, due to the large incoherent cross section of hydrogen atoms. In fact, in the present NS experiment it is mainly the average dynamics of protons belonging to water molecules that is revealed, even if there still remains a small, not easily estimable, contribution from protons that are part of complex ionic species always present in the liquid phase. Such an average dynamics of protons in Nafion/ZP membranes is well modelled as a random jump diffusion taking place in a confining spherical region, which corresponds to the effective confinement arising from clustering of water molecules near the sulfonic acid sites of the membrane and the charged phosphate groups of the zirconium phosphate nanoparticle.

The main features of this confined random-jump diffusive motion are nearly unaffected by the presence of the nanofiller component, as indicated by the comparison between the results found for Nafion/ZP and simple Nafion membranes hydrated at the saturation value. The zirconium phosphate forms internal rigid scaffolding in the composite membrane, but leaves unaltered the dynamical properties of protons at a molecular level. As these properties are related to proton conduction, this view is consistent with the evidence that the conductivity also depends only slightly on the presence of zirconium phosphate nanoparticles. It may be speculated that the similar behaviour of water in Nafion/ZP and Nafion membranes is also due

to the fact that the dynamical features of highly hydrated systems are comparable. Indeed, their proton jumping dynamics is also reminiscent of bulk water.

Acknowledgments

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