



Short communication

## Measurement of the Young's modulus of Nafion membranes by Brillouin light scattering

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## ABSTRACT

Brillouin light scattering from acoustic phonons has been used to investigate the elastic properties of Nafion 115 membranes in the GHz range of frequencies. Measurements were carried out as a function of temperature from 0 to 60 °C on samples with different hydration. Detection of longitudinal bulk waves travelling either parallel to the free surface or at an angle with respect to the normal to the surface enabled us to evaluate the refractive index and the longitudinal modulus of the membranes. A marked decrease of the latter with increasing either the temperature or the hydration degree was found. Moreover, a comparison of the above results with those obtained from measurement of the Young's modulus ( $E$ ) in the quasi-static regime (stress–strain curves) shows that the high-frequencies values of  $E$  are an order of magnitude larger than in quasi-static conditions, reflecting the viscoelastic character of Nafion.

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### 1. Introduction

Nafion is currently one of the most interesting materials for the construction of proton exchange membranes to be exploited in fuel cells. Proton exchange membranes made of polyperfluorosulfonic acids are well known for their high chemical inertness, good thermal stability, reasonable mechanical strength and excellent proton conductivity when highly hydrated. Due to these outstanding characteristics perfluorinated membranes, and among them mostly Nafion membranes in hydrogen form, are currently used as solid polymeric electrolytes in fuel cells [1–5]. The mechanical properties of Nafion membranes have been widely studied during the last decade, mainly using tensile stress–strain measurements and dynamical mechanical analysis [6–8]. However, a study of the high-frequency response of such material in the GHz range is still lacking in the literature.

In this paper we report on the results of a study of the elastic properties of Nafion 115 membranes in the GHz range of frequency, as a function of temperature and for different water contents. The experimental investigation has been carried out using the Brillouin light scattering (BLS) technique which relies upon the inelastic scattering of photons by thermal phonons and has proved to be a powerful non-destructive tool for the elastic characterization of layered structures [9–12]. In contrast with conventional ultrasonics techniques, BLS does not require external generation of acoustic

waves and it probes acoustic phonons which are naturally present in the medium under investigation, with wavelengths in the sub-micron range and frequencies in the GHz range.

### 2. Experimental

#### 2.1. Preparation of membrane samples

Commercially available Nafion 115 membrane, supplied from DuPont, have been used in this study. The equivalent weight (EW) and the thickness of the membranes are 1100 g(mol of sulfonic group)<sup>-1</sup> and 125 μm, respectively. To remove impurities and to achieve comparable starting conditions, all the Nafion membranes were cleaned using a standard procedure as follows:

- (i) boiling in 3% hydrogen peroxide for 1 h to oxidize organic impurities;
- (ii) rinsing with boiling water for several hours;
- (iii) boiling in 1 M sulfuric acid for 1 h to remove any metallic/ionic impurities;
- (iv) rinsing again in boiling water to remove any excess acid.

After the pre-treatment, the membranes were stored for 24 h in the oven at 140 °C, then rinsed and dried at room temperature. Finally, the membranes were treated under different conditions of temperature and relative humidity (RH) in order to obtain samples with different levels of hydration. The sample equilibrated at 20% RH was stored, at room temperature, in a desiccator containing a solution of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O (0.5776:1), while the complete hydrated

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**Table 1**  
Values of relative humidity, of  $\lambda = N_{H_2O}/N_{SO_3^-}$  and of mass density for the samples studied in this work.

RH	$\lambda$	Mass density, $\rho$ (g cm <sup>-3</sup> )
Dry	0	2.00
20%	2.60	2.08
100%	15.10	1.78

membrane was obtained storing it in H<sub>2</sub>O. The dried sample was prepared by heating the membrane in an oven at 140 °C.

To determine the membrane water content, the membranes were weighed, heated under vacuum at 120 °C and weighed again. The ratio (number of moles of water)/(mole of sulfonic group), hereafter  $\lambda$ , was calculated on the basis of the observed weight loss.

Membrane mass densities were obtained on the basis of mass and volume determinations. In particular, a membrane sample (about 4 cm × 4 cm), after equilibration at controlled temperature and RH, was weighed and quickly clamped between two glass plates (5 cm × 5 cm) in order to avoid water loss or uptake. Membrane length and width were determined by a calliper, while membrane thickness was calculated by subtracting the thickness of the glass plates from the overall thickness of the membranes and the glass plates.

The data are summarized in Table 1, where the values of relative humidity RH are reported, with the corresponding values of  $\lambda$ .

## 2.2. BLS measurements

For the BLS measurements, each sample was put inside a home-made optical cryostat, with the Nafion membrane kept in between the optical glass window and an optically polished Silicon substrate. Spectra were taken, using about 250 mW light beam (single mode of the 532 nm line of a diode-pumped solid state laser). The incident light was focused within the specimen at an angle of incidence  $\theta$  and the back-scattered light collected by means of a lens with  $f$  number 2 and focal length 50 mm. The frequency analysis was performed using a Sandercock-type, 3+3 pass, tandem Fabry–Perot interferometer [13], with typical sampling time per spectrum of a few minutes. Taking advantage from the presence of the reflecting Silicon interface, two kinds of longitudinal waves can enter the scattering process satisfying the wavevector conservation, as illustrated in the upper panel of Fig. 1:

- waves travelling parallel to the free surface, with a wavevector:  $\mathbf{Q}_1 = 2\mathbf{k}_i \sin(\theta)$ , where  $\mathbf{k}_i$  is the light wavevector and  $\theta$  the angle of incidence. Their phase velocity can be extracted from the measured frequency  $f_1$  as:

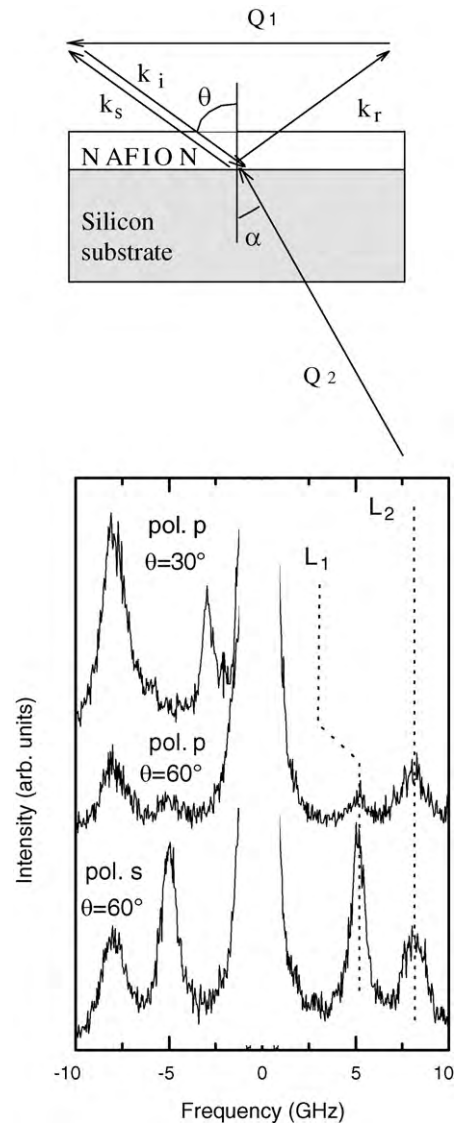
$$v_1 = \frac{2\pi f_1}{\mathbf{Q}_1} = \frac{\pi f_1}{\mathbf{k}_i \sin(\theta)} \quad (1)$$

- waves travelling at an angle  $\alpha = \arcsin(\sin \theta/n)$  with respect to the sample normal, whose wavevector is:  $\mathbf{Q}_2 = 2n\mathbf{k}_i$ , where  $n$  is the refractive index of the medium. Their phase velocity is:

$$v_2 = \frac{2\pi f_2}{\mathbf{Q}_2} = \frac{\pi f_2}{n\mathbf{k}_i} \quad (2)$$

## 2.3. Stress–strain measurements

The quasi-static mechanical properties of the membranes were investigated by stress–strain static mechanical tests with a Zwick Roell Z1.0 testing machine, and the data were elaborated by the TestXpert V11.0 Master software. The size of specimen was of 90 mm × 5 mm, and the test speed was 2 mm min<sup>-1</sup>. Each value of the obtained Young's modulus is the average of at least four tests.



**Fig. 1.** Upper panel: schematic diagram of interaction between photons and phonons, in the backscattering geometry. Here  $\mathbf{k}_i$ ,  $\mathbf{k}_s$  and  $\mathbf{k}_r$  are the wavevectors of incident, scattered and reflected photons, respectively, while  $\mathbf{Q}_1$  and  $\mathbf{Q}_2$  are those of longitudinal waves travelling either parallel to the surface or at an angle  $\alpha$  with respect to the normal, respectively. Lower panel: Brillouin spectrum taken at different angles of incidence  $\theta$  and with different states of light polarization (s and p).

## 3. Results and discussion

Typical BLS spectra obtained from the Nafion membranes are shown in Fig. 1 (bottom panel). The measured lineshape appreciably depends on both the polarization state of the impinging light (either parallel (p) or perpendicular (s) to the plane of incidence) and on the chosen value of the incidence angle  $\theta$ . Two different peaks are present in the spectra. The peak at lower frequency ( $L_1$ ) depends on  $\theta$  according to Eq. (1), and corresponds to a longitudinal wave propagating parallel to the free surface. This is analogous to the so-called longitudinal guided mode observed in transparent films on opaque substrates [14,15]. The peak at larger frequency ( $L_2$ ), whose frequency  $f_2$  is independent of  $\theta$ , but depends on the refractive index  $n$  according to Eq. (2), corresponds to longitudinal bulk waves propagating at an angle  $\alpha = \arcsin(\sin \theta/n)$  from the surface normal, as stated in the previous paragraph. Note that in the case of p-polarized incoming light and large incidence angle (the condition usually exploited for studying surface phonons in opaque materials,

because it enhances the scattering from the rippling of the free surface [16]), the  $L_1$  peak intensity is much weaker than for s-polarized incoming light (see Fig. 1). This behavior was also observed in different classes of silicate glass films, especially those with low elastic constants and low mass density [17]. Unfortunately, in the present case we could not detect the peak corresponding to the Rayleigh surface wave (RW), usually observed in opaque materials. The missing of the RW peak can be ascribed to the scarce efficiency of the ripple-scattering mechanism in the present transparent material whose free surface is in contact with the optical window of the cryostat, together with the impossibility of using incidence angles larger than about  $60^\circ$ , because of the geometrical limitation imposed by the cryostat.

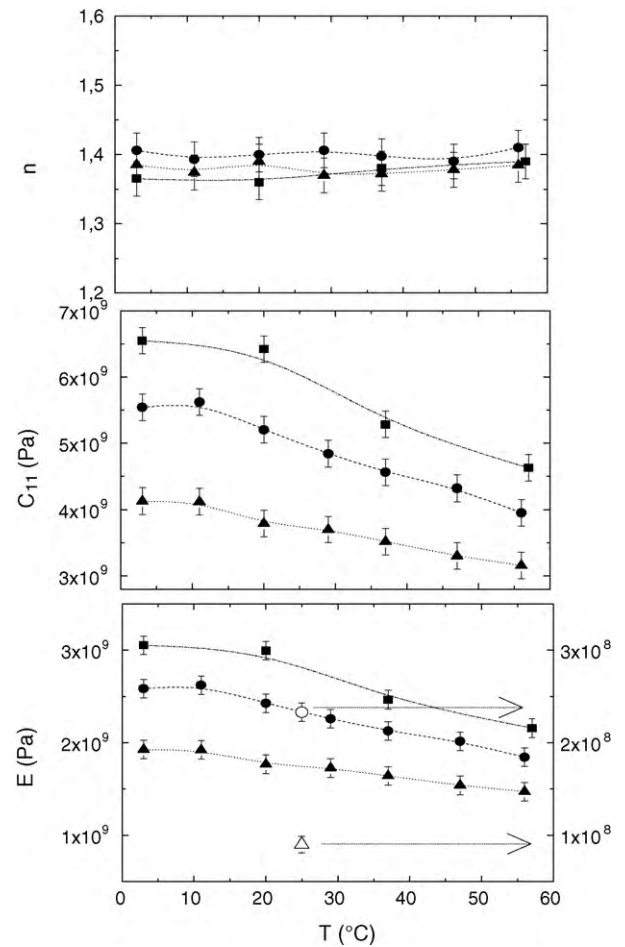
We measured the frequency of both  $L_1$  and  $L_2$  peaks at different temperatures in the range between 0 and  $60^\circ\text{C}$ . In this range of temperatures the measurements were reversible and we obtained the same values of the peak-frequencies, within the experimental error, for both increasing and decreasing the sample temperature [18]. Using the values of the mass density measured by a weight method (Table 1), we could thus determine the value of the phase velocity  $v_1$ . In addition, since the frequency of  $L_2$  did not exhibit any appreciable dependence on  $\theta$ , we assumed that the medium is elastically isotropic, so that the value of the refractive index was also estimated from measurement of  $f_2$ , under the condition  $v_1 = v_2$ . Now, it is well known that for an isotropic elastic medium, there are only two elastic constants: the longitudinal modulus  $c_{11} = \rho v_1^2$ , and the shear modulus  $c_{44}$ . The experimental values of  $n$  and  $c_{11}$  are plotted in Fig. 2. Before briefly discussing these results, in order to compare them with previous and present investigations of the mechanical properties of Nafion membranes based on the measurement of the Young's modulus  $E$  by stress-strain curves, we have estimated the values of  $E$  from our BLS data, using the well known expression:

$$E = \frac{(1 + \sigma)(1 - 2\sigma)}{(1 - \sigma)} c_{11}$$

where  $\sigma$  is the Poisson's ratio. This latter parameter can vary between 0.1 and 0.5 in the different materials and its value for Nafion membranes has been recently measured to be  $\sigma = 0.4$  [19]. Assuming such value for  $\sigma$ , the values of  $E$  derived from our data are shown in the bottom panel of Fig. 2.

From the data of Fig. 2 it turns out that the refractive index does not depend appreciably on either temperature or hydration. Different from this, both the longitudinal and the Young's moduli exhibit a marked decrease upon increasing water content or temperature, in agreement with previous investigations [6–8,20,21]. In fact, water acts as a plasticizer, while heating causes a weakening of chain-chain interactions: both mechanisms produce a softening of the material and a consequent decrease in the values of the elastic moduli.

As a final step of our investigation, let us now compare the values of the Young's modulus determined by our BLS measurements to those directly measured in static conditions at room temperature ( $25^\circ\text{C}$ ) by tensile stress/strain experiments. The latter results are shown as open symbols in the lower panel of Fig. 2. It appears that the values of  $E$  determined in static conditions are about an order of magnitude lower than those measured at high-frequency, i.e. in the GHz range. Unfortunately, to the best of our knowledge there are no previous data available in the literature concerning the high-frequency elastic properties of Nafion, to be compared with our results. The only available datum is a theoretical curve of  $\log(E)$  as a function of  $\log(\text{time})$  obtained on the basis of the time-temperature correspondence principle, valid for polymeric materials. This principle is based on experimental observations and states that the effects of time and temperature are equivalent [22] (i.e. a given viscoelastic property of a polymer measured for short times at a



**Fig. 2.** Experimental values of the refractive index  $n$  (upper panel), of the longitudinal modulus  $c_{11}$  (central panel) and of the Young's modulus  $E$  (lower panel) determined by BLS measurements at various temperatures  $T$  for the samples with 100%RH (filled triangles), 20%RH (filled circles) and dry (filled square). For comparison, the values of  $E$  determined by stress-strain curves for the 20% RH (open circle) and 100% RH (open triangle) samples are also reported in the lower panel. The values of the latter points refer to the right-side vertical axis.

given temperature corresponds to the same property measured for longer times at a lower temperature). Technically, frequency scans collected over a range of temperatures can be shifted horizontally along a  $\log(\text{time})$  axis. The result of this shifting is a master curve that represents the time-response of a material over a wide range of frequencies at a particular reference temperature. According to the master curve for Nafion (marked as Nafion H), constructed by Yeo and Eisenberg [23] from stress relaxation data taken for periods of time up to  $2 \times 10^4$  s, the value of the Young's modulus expected for  $10^{-9}$  s time range is between one and two orders of magnitude larger than those measured over the time range of seconds, in excellent agreement with our experimental results.

#### 4. Conclusions

The Brillouin light scattering (BLS) technique has been exploited to investigate the high frequency response of Nafion 115 membranes in the GHz range of frequencies. Humidity and temperature have negligible effect on the refractive index while, both the longitudinal and the Young's elastic moduli exhibit a marked decrease as hydration degree and temperature increase. The research has been completed by a quantitative comparison of these values with those obtained from measurements of  $E$  in static conditions. It turned out that the high-frequency values of  $E$  are an order of magnitude larger

than in quasi-static conditions. This result is in agreement with the theoretical expectation based on Nafion Master curve and it reflects the viscoelastic behavior of Nafion, due to its polytetrafluoroethylene backbone.

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### References

- [1] S. Srinivasan, B.B. Dave, K.A. Murugesamoorthi, A. Parthasarathy, A.J. Appleby, in: L.J.M.J. Blomen, M.N. Mugerwa (Eds.), *Fuel Cell Systems*, Plenum Press, New York, 1993, pp. 37–72.
- [2] S.J. Cleghorn, X. Ren, T.E. Springer, M.S. Wilson, C. Zawodzinski, T.A. Zawodzinski, S. Gottesfeld, *J. Hydrogen Energy* 22 (1997) 1137–1144.
- [3] O. Savadogo, *J. Power Sources* 127 (2004) 135–161.
- [4] J. Rozière, D.J. Jones, *Annu. Rev. Mater. Res.* 33 (2003) 503–555.
- [5] K.A. Mauritz, R.B. Moore, *Chem. Rev.* 104 (2004) 4535–4585.
- [6] A quite complete and updated bibliography about the existing literature on the mechanical properties of NAFION membranes can be found in the recent Master thesis of N Silberstein: “Mechanics of proton exchange membranes: time, temperature, and hydration dependence of the stress–strain behavior of persulfonated polytetrafluoroethylene”, Massachusetts Institute of Technology, Dept. of Mechanical Engineering, 2008. Available from: <http://hdl.handle.net/1721.1/43125>.
- [7] F. Bauer, S. Denebler, M. Willert-Porada, *J. Polym. Sci. B* 43 (2005) 786–795.
- [8] S. Kundu, L.C. Simon, M. Fowler, et al., *Polymer* 46 (2005) 11707–11715.
- [9] G. Carlotti, D. Fioretto, L. Giovannini, G. Socino, V. Pelosin, B. Rodmacq, *Solid State Commun.* 81 (1992) 487–489.
- [10] G. Carlotti, D. Fioretto, G. Socino, E. Verona, *J. Phys. Condens. Matter* 7 (1995) 9147–9153.
- [11] D. Fioretto, G. Carlotti, L. Palmieri, G. Socino, L. Verdini, *Phys. Rev. B* 47 (1993) 15286.
- [12] G. Carlotti, L. Doucet, *J. Vac. Sci. Technol.* 14 (1996) 3460–3464.
- [13] G. Carlotti, D. Fioretto, L. Palmieri, G. Socino, L. Verdini, E. Verona, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* 38 (1991) 56.
- [14] G. Carlotti, G. Socino, L. Doucet, *Appl. Phys. Lett.* 66 (1995) 2682–2684.
- [15] B. Hillebrands, S. Lee, G.I. Stegeman, H. Cheng, J.E. Potts, F. Nizzoli, *Phys. Rev. Lett.* 60 (1988) 832.
- [16] P. Mutti, C.E. Bottani, G. Ghislotti, M. Beghi, G.A.D. Briggs, J.R. Sandercock, in: A. Briggs (Ed.), *Advances in Acoustic Microscopy*, I, Plenum Press, NY, 1995, p. 261.
- [17] G. Carlotti, N. Chérault, N. Casanova, C. Goldberg, G. Socino, *Thin Solid Films* 493 (2005) 175.
- [18] We verified that the reversibility of the measured frequencies as a function of temperature was lost if the annealing was performed up to temperatures larger than 80–90 °C, because of the non-perfect sealing of our optical cryostat. For such a reason we limited our investigation to temperatures not exceeding 60 °C.
- [19] R. Solasi, Y. Zou, X. Huang, K. Reifsnider, D. Condit, *J. Power Sources* 167 (2007) 366–377; R. Solasi, Y. Zou, X. Huang, K. Reifsnider, *Mech. Time Depend. Mater.* 12 (2008) 15–30.
- [20] J.T. Uan-Zo-Li, The effects of structure, humidity and aging on the mechanical properties of polymeric ionomers for fuel cell application, MSc thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA, 2001.
- [21] Y. Tang, A.M. Karlsson, M.H. Santare, M. Gilbert, S. Cleghorn, W.B. Johnson, *Mater. Sci. Eng. A* 425 (2006) 297–304.
- [22] A.V. Tobolsky, *Properties and Structures of Polymers*, Wiley, New York, 1960.
- [23] S.C. Yeo, A. Eisenberg, *J. Appl. Polym. Sci.* 21 (1977) 875–898.