V.P.31 The Dielectric Response of Hydrated PFSA Membranes – Measurements with Single Post Dielectric Resonators

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Objectives

We are seeking to understand the connections between the hydrated morphology and the local dynamics of water in polymer electrolyte membranes (PEMs) of different equivalent weights (EWs) at various hydration levels through the measurement of their dielectric response. Dielectric relaxation behavior provides correlations between the polymer environment and the cooperative solvent dynamics, which can unveil important insights into water and proton transport in these membranes.[1,2] It is widely accepted that water confined in systems such as reverse micelles possesses different dynamics as compared to bulk/free water.

The choice to conduct measurements at microwave frequencies (1 to 20 GHz) is due to the observation that the principal absorption band, attributed to a Debye type relaxation of molecular origin, in pure bulk water occurs at about 18 GHz.[3-5]

Technical Barriers

All hydrated PEMs were removed from their equilibration chamber just prior to the dielectric measurement at room temperature in open atmosphere using single post dielectric resonators (SPDR). However, we observed that there is a rapid loss of water in them. As the dielectric properties are strongly dependent on the water content, it is critical to precisely control the RH of the test environment. Also, the SPDRs were unable to yield the dielectric constants for hydrated Nafion® 117 (thickness 185 microns) because the Q factor of the resonator with this sample under test is smaller than 100.

Abstract

EW is an important factor in determining the structure of the membrane and the dynamics of protons and water molecules within the membrane. The behavior of the acid form of the polymer is dramatically affected by the presence of water. The dielectric properties of PEM are dictated by the molecular structure of the system and the physical state of water in these materials. The dielectric spectra can provide insights into both the state of water and indirectly, the hydrated structure of polymer. Thus, knowledge of the state or nature of the water in the membrane is critical to understanding the mechanisms of proton transfer and transport in PEMs

When hydrated, these membranes exhibit a nanophase-separated morphology with the hydrophobic backbone of the polymer separated from a network of water and ions (both fixed SO_3^- groups and hydrated protons).[6] The rigidity of the backbone and the crystallinity of the polymer confine the water; and with the significant density and distribution of the pendant anionic groups give structural ordering to the water in the membrane.[7,8]

Project Report and Future Directions

The split-post dielectric resonator (SPDR) technique is a well established and accurate method for characterization of the dielectrics in the laminar forms up to 20 GHz.[9,10] Since no electrodes are involved this method, measurements are not affected by electrode/ferroelectric interfacial effects (i.e. dead layer). The split-post resonator consists of two low loss dielectric packs in a metal enclosure. The resonator uses $TE_{01}\delta$ mode of the electromagnetic field, which is insensitive to the presence of air gaps between the tested sample and the dielectric resonator. Our SPDRs were custom built to measure the dielectric response frequencies of: 1.9, 5, 10, 15, 18 and 20 GHz. The characterization of a PEM sample consists of two steps through measurement of the resonant frequency and quality factor of the (i) empty resonator, and (ii) resonator with the membrane. The first measurement provides the input for calculation of the dielectric permittivity. The real part of the complex permittivity is computed from the measured resonant frequencies with a SPDR both with and without the membrane sample from the following equation:

$$\varepsilon_r' = 1 + \frac{f_0 - f_s}{h f_0 K_\varepsilon \left(\varepsilon_r', h\right)}$$

where h is the thickness of the measured substrate, f_0 is the resonant frequency of the empty SPDR, f_s is the resonant frequency of the SPDR with the dielectric sample, and K_ε is a function of ε_r' and h. The latter is calculated for a number of ε_r' and h using the Rayleigh-Ritz technique. An iterative procedure is used to evaluate the values of K_ε and ε_r' from the above equation.

All the PFSA membranes (including Nafion® 117, Solvay E8705S, etc) were pretreated by cleaning in 1M HNO_3 at 80°C for 1 hr and in DI water at 80°C for 1 hour. They were then washed in DI water and stored in deionized water prior to placement in the SPDR for measurement under fully hydrated conditions. The films were weighed after removing any surface water to obtain the wet weight. They were then dried over P_2O_5 for determination of the dry weight.

The isopiestic equilibration scheme of Pushpa *et al*[11] was employed to control the membrane water content, enabling the study of the relative permittivity of the membranes over a range of water contents. Equilibration of the samples over the aqueous LiCl is critical in establishment of reliable and reproducible water contents in the membrane. The dried membranes were then equilibrated over aqueous LiCl solutions for at least 1 week. The concentrations of the LiCl solutions were selected to encompass the different regions' observed on the water adsorption isotherms for Nafion® 117 as shown in Table 1.

TABLE 1. Water adsorption isotherm data for Solvay films (EW 790 and 870)

LiCl(M)	Water Activity	Water Content, λ	
EW		789	870
Fully Hydrated	1	8.2	7.25
1	0.964	7	6.2
5	0.748	6.4	5.6

The water adsorption isotherm data for the Solvay films (Table 1) was obtained by measuring the weight of the films under fully hydrated conditions (100% RH), and following 1 week of equilibration in chambers at 96.4% RH and 75% RH. The dry weight of each of the films was also obtained by drying them over P_2O_5 for a week. The water uptake was calculated from the following:

$$\lambda = \left(\frac{W_{wet} - W_{dry}}{18.015}\right)\left(\frac{\mathrm{EW}}{W_{dry}}\right)$$

Presently, all dielectric measurements were conducted at room temperature in open atmospheric conditions using the SPDRs. They were removed from the equilibration chamber just prior to the measurement. However, we observed that there is a very quick water loss from these membranes in air. As the dielectric properties are strongly dependent on the water content, the dielectric constant depends on how long the sample has been out of the chamber as shown in Figure 2.

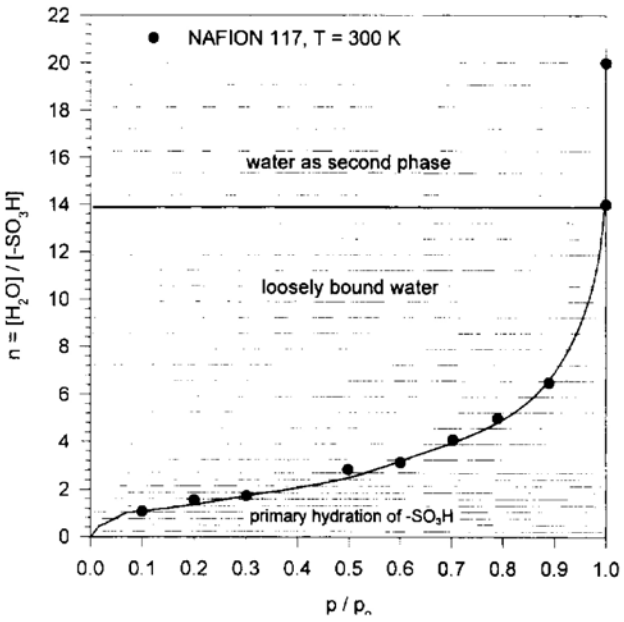

FIGURE 1. Water Adsorption Isotherm for Nafion® 117.

Hence, it is critical that the RH of the samples be controlled precisely during the actual measurements. We have designed a relative humidity controlled glove box for future experiments that will enable us to perform all our measurements under precisely controlled conditions of humidity and temperature. The equilibrated films, SPDRs, and weighing balance will all be placed in the glove box at a previously set RH to coincide with the activity of the LiCl solution and then equilibrated prior to making the dielectric measurements in-situ. The

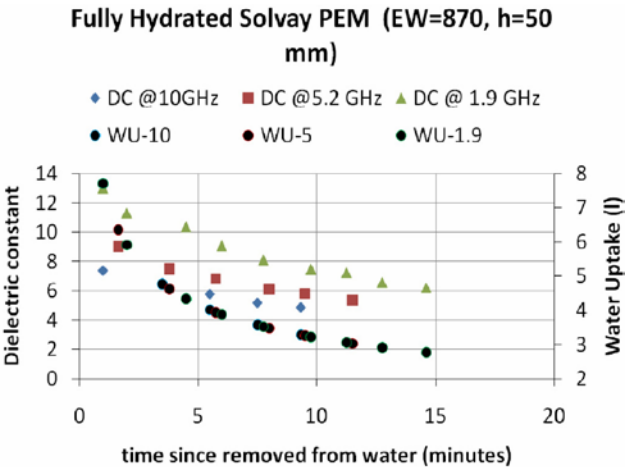

FIGURE 2. Water Loss and Dielectric properties of fully hydrated Solvay PEM (EW870).

dielectric response of completely dry samples of Solvay PEM (EW870) was measured at 1.9 GHz, 5.2 GHz and 10 GHz as shown in Figure 3. The values varied from 3.8 to 3 as frequency changed from 1.9 GHz to 10 GHz.

Our SPDRs were unable to measure the dielectric constants for fully hydrated Nafion® 117 with a thickness of 185 μm. From the graph in Figure 4, it is clear that the resonant frequency shifts can be substantial in thick high permittivity samples. The SPDR cannot measure the permittivity of the sample if the Q factor of the resonator with sample under test is smaller than 100. It is recommended to keep resonant frequency with sample within 10% of the resonant frequency of the resonator. If the Q factor < 100 or the resonant frequency shift > 10%, spurious modes, whose frequencies are changing faster with permittivity than for the TE mode, may overlap with the proper mode disturbing measurements. For all our future measurements we will use Nafion® 112 as our standard material. It has the same EW as Nafion® 117 but with a thickness of 51 microns.

We also plan to cast our own films on glass substrates using ionomer solutions of different EWs to achieve the desired thickness.

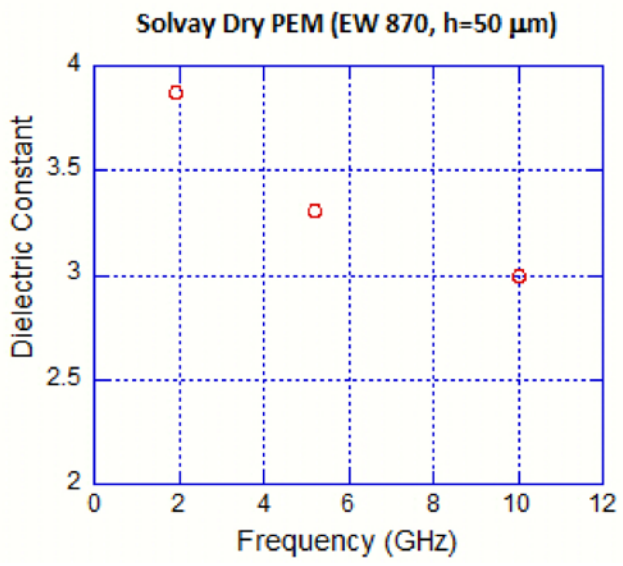

FIGURE 3. Dielectric Property of Dry Solvay PEM (EW 870) after 1 week over P_2O_5.

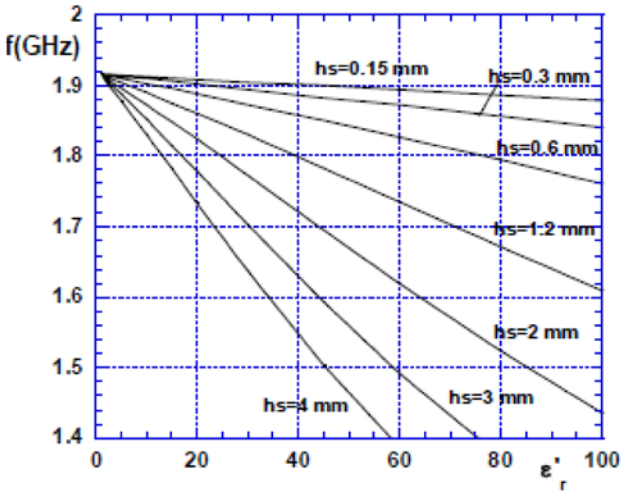

FIGURE 4. Frequency vs Permittivity for 1.9 GHz(SPDRManual)

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