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# Nafion beta-relaxation as a function of relative humidity probed by dielectric spectroscopy

B.R. Matos[1], M.A.Dresch[1], E.I.Santiago[1], M.Linardi[1], D.Z. de Florio[2] and F.C.Fonseca[1].

1 CCCH - Centro de Células a Combustível e Hidrogênio, 2242, Lineu Prestes Avenue, 05508000, S.Paulo, Brazil.

2 CECS – Universidade Federal do ABC, 166, Santa Adélia Street, 09219170,S.André, Brazil.

Yeo and Eisenberg have pointed out that Beta relaxation of Nafion depended strongly on the ionomer water content [1]. As the water content increased beta relaxation shifted to lower temperatures as a result of a plasticizing effect [2]. The assignments of the phenomena involved in the beta relaxation are under debate [3]. Moreover a detailed study showing the dielectric response as a function of relative humidity ranging from low RH values to full polymer saturation is still missing. The dielectric spectroscopy of commercial extruded (N115) and cast Nafion (Ncast) was measured using a specially designed apparatus capable of varying the temperature from ca. 30 to 180°C (RH = 100%) and the relative humidity from ca. 5 to 100% at the desired temperature. The electrodes are made of stainless steel; however the membranes were sandwiched with carbon cloth to facilitate water equilibration. Dielectric Spectroscopy measurements were performed using Solartron 1260 frequency response analyzer in the frequency range of 4mHz to 3MHz applying a dc voltage of <100 mV. Nafion in the acid and salt forms (Cs+ and Na+) was studied in order to evaluate the effect of the electrostatic interactions. Dielectric loss was measured as function of relative humidity at temperatures below (80°C) and above (130°C) the Nafion alfa relaxation temperature (ca. 110°C) to separate contributions arising from ionic phase and eventual crystallization [4]. Proton Exchange Membrane (PEM) Fuel Cells polarization curves was obtained as a function of temperature (from 80 to 130°C) and relative humidity (from 50 to 100%). Beta relaxation of extruded and cast Nafion displayed similar behavior, as the relative humidity increased up to ca. 60%, the beta relaxation shifted to higher frequencies indicating that as the water content increases the segmental chain mobility increased. On the other hand above ca. 60% of relative humidity the beta relaxation shifted to lower values in the frequency domain. The left-shift of the beta relaxation in the frequency domain can be attributed to decreased segmental mobility owing to electrostatic repulsions of bare anionic groups in these high swollen membranes. The dielectric loss as a function of relative humidity possessed a maximum at 85% and 60% for cast and extruded Nafion, respectively. It was recently reported that the change in relative humidity can activate ion motion in polyelectrolytes resembling the thermally activated processes [5]. It can be expected that as Nafion absorbs water, a dissociation of the counterion from the polyanionic matrix occurs, leading a change in the chain morphology thereby generating dielectric losses. In this manner, the maximum observed in the ε" vs. RH graph can be understood as a change in the polymer morphology, from a cluster network to a more rigid rodlike network [6]. This result is in accordance with reported Small Angle X-ray Scattering (SAXS) measurements which indicated that at high water content a crossover in the polymer morphology is expected at similar values of water content (50vol%) [7]. The Proton Exchange Membrane (PEM) fuel cell polarization curves as a function of relative humidity and temperature obtained was discussed in terms of the available data.

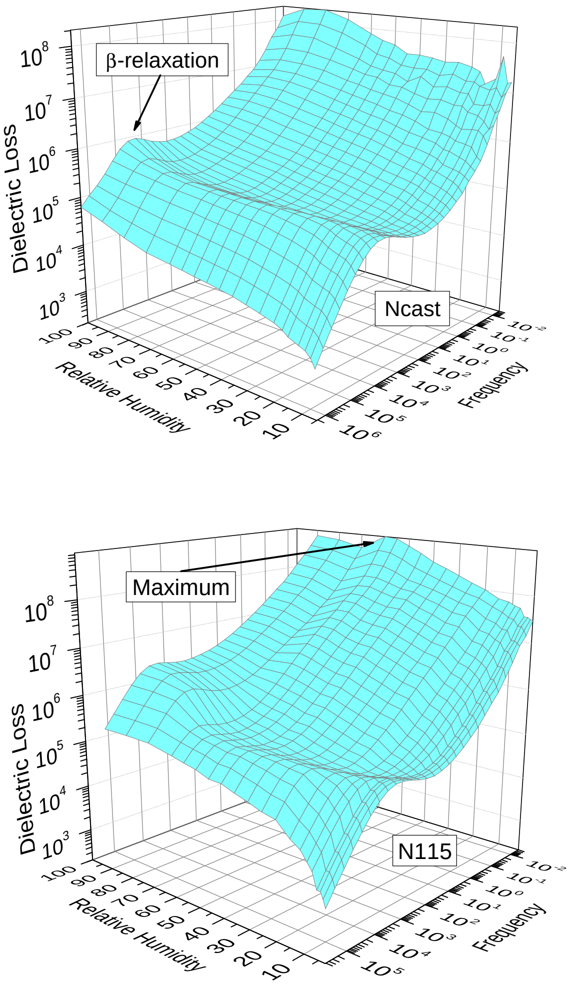

Figure 1 – 3D-plot showing the dielectric loss as a function of both frequency and relative humidity at 130 °C for extruded and cast Nafion.

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