Identification of the Polymer and Electrode Polarizations of Nafion Dielectric Spectrum

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In order to understand the dynamic properties of amorphous ionic solids, which are related to ion motion as well as to network motion, it is important to study such materials over a wide range of frequencies [1]. The dielectric spectroscopy (DS) measurements cover the frequency range (~10^{-2}-10^{7} Hz range) that is not available by most traditional techniques and the behavior of the observed dielectric dispersions provides a method for directly probing the polarization of ions along the a broad range of length scales in amorphous materials [2]. The main aspects of the polymer relaxations at the fundamental level are needed for the advancement of the ionomer technology. In this context, ideally both the dynamics of electrode polarization, ion-hopping and polymer relaxations should be identified. However, the ion-hopping and polymer relaxations characteristic frequencies are commonly overlapped with electrode polarization, hindering the investigation of the dynamics of the dielectric dispersions observed in Nafion spectrum [2]. For around 40 years the origins of the α- and β-relaxations in Nafion have been in debate [3,4,5]. In this work, a comprehensive set of DS data of Nafion membranes and solutions in a broad range of temperature, relative humidity and frequency were analyzed in different spectral representations in order to pinpoint the frequency ranges of the dielectric relaxations, ion-hopping and the electrode polarization. In addition, the separation of the electrode from the polymer polarizations was obtained by testing different variables, namely: *i)* different membrane thickness; *ii)* distinct electrode materials and area; and *iii)* in-plane and through-plane DS configurations. Such characterizations were confronted with small angle-X-ray scattering (SAXS), dynamic mechanical analysis (DMA) and infrared spectroscopy (FTIR). Such techniques contributed for the determination of the nature of the each relaxation process of Nafion's dielectric spectra advancing the understanding the relationship between the ionic network and proton conductivity, which is crucial for tailoring new high-performance ionomers.

References

[1] A. Kusoglu, A. Z. Weber, Chem. Rev. 2017, 117, 987-1104.
[2] Schönhals, A.; Kremer, F. in *Broadband Dielectric Spectroscopy*. F. Kremer, A. Schönhals, Editors, p. 59, Springer Verlag, Berlin (2003).
[3] Osborn, S. J.; Hassan, M. K.; Divoux, G. M.; Rhoades, D. W.; Mauritz, K. A.; Moore, R. B. *Macromolecules*, **2007**, *40*, 3886.
[4] V. Di Noto, E. Negro, J-Y. Sanchez, C. Iojoiu, *J. Am. Chem. Soc.*, 132, 2183 (2010).
[5] Matos, B. R.; Goulart, C. A.; Santiago, E. I.; Muccillo, R.; Fonseca, F. C. *Appl. Phys. Lett.*, **2014**, *109*, 091904.