DIELECTRIC RELAXATION SPECTROSCOPY STUDIES ON WATER-SATURATED NAFION 117 MEMBRANES

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Hydrated Nafion membranes (acid form) exhibit both dielectric relaxation and dc conductance. The dielectric response in an alternating electric field contains contributions from the polarization of bound charges and the motion of free charges. Because of the latter, the dielectric response is frequently masked by electrode space-charge effects, especially at low frequencies. By inserting a layer of a non-dispersive insulator between the metal electrode and the Nafion sample, it is possible, in principle, to eliminate electrode space-charge effects and to observe the intrinsic dielectric relaxation processes of the Nafion membranes. In this study, the blocking effects of Teflon layers were investigated and the dielectric relaxation spectra at low temperatures (in the absence of water loss) were analyzed.

Dielectric relaxation studies of water-saturated Nafion 117 membranes were carried out over the frequency range of 10^{-2} – 10^{7} Hz and at temperatures of –140°C to 20°C. Gold-coated copper electrodes were used in a standard two-terminal cell. Nafion samples were sandwiched between layers of polytetrafluoroethylene (Teflon™). The dielectric spectra obtained with bare metal electrodes showed unreasonably high dielectric constants and dielectric loss factors (Fig. 1). On the other hand, the results with the Teflon spacers showed a dielectric constant of 40 at 20°C, similar to the value obtained at microwave frequencies[1]. No relaxation was observed for a saturated sample within the experimental frequency range above 0°C. Below 0°C, two main relaxation mechanisms were observed (Fig.2). The low frequency relaxation mechanism is due to interfacial polarization, which takes place in the hydrated ionic regions and at the interface between the Teflon spacers and the Nafion membrane. Careful analysis of the interfacial relaxation data reveals two activation energies of 35.3 kJ/mol above –70°C, and 45.1 kJ/mol below –70°C (Fig. 3). The high frequency mechanism is attributed to water relaxation, which takes place above –110°C, probably reflecting the glass transition of the aqueous domains[2,3]. An activation energy of 80.3kJ/mol (Fig. 4) was calculated for the water relaxation in saturated Nafion 117 membrane.

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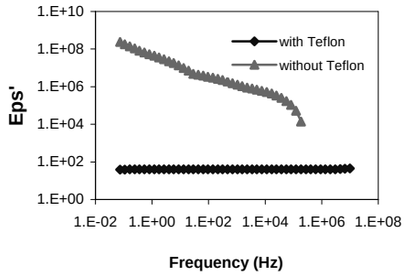

Fig.1 The real part of complex dielectric constant of a water-saturated Nafion 117 membrane vs frequency at 20°C. The spectra "with Teflon" are corrected for the inserted Teflon spacer.

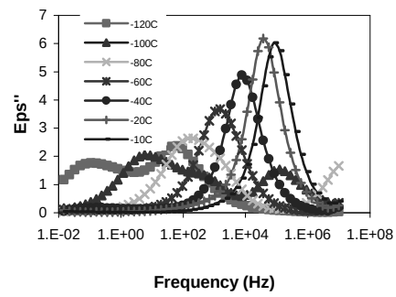

Fig. 2 The imaginary part of the dielectric constant versus frequency for a water-saturated Nafion membrane at low temperatures (< 0°C). The spectra are corrected for the inserted Teflon spacer.

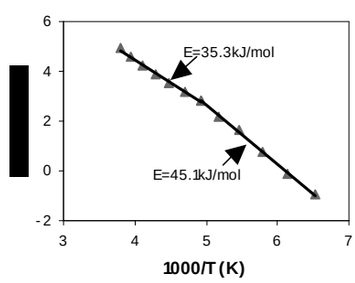

Fig. 3 Arrhenius plot of the maximum frequency of the imaginary part of complex dielectric constant for the low frequency relaxation.

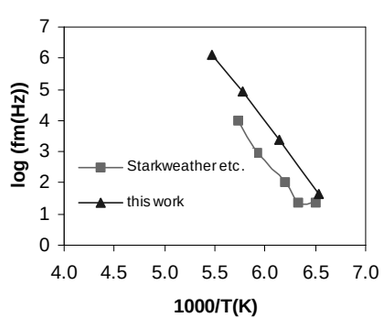

Fig. 4 Arrhenius plot of the maximum frequency of the imaginary part of complex dielectric constant for the high frequency relaxation. Also shown in the figure are the result of Starkweather and Chang[2].