Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Journal of Power Sources 172 (2007) 72–77
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Broadband dielectric spectroscopic characterization of Nafion® chemical degradation

David W. Rhoades, Mohammad K. Hassan[1], Shawn J. Osborn,
Robert B. Moore, Kenneth A. Mauritz*

The University of Southern Mississippi, School of Polymers and High Performance Materials, 118 College Drive, Hattiesburg, MS 39406-0076, United States

Received 30 October 2006; received in revised form 13 April 2007; accepted 16 April 2007
Available online 22 April 2007

Abstract

H^+-form Nafion 212 films were chemically degraded via Fenton's reagent and characteristic polymer chain motions were analyzed using broadband dielectric spectroscopy. The β-relaxation peak maximum frequency (f_{max}) shifts to higher temperatures upon degradation, reflecting slower chain motions. Perhaps this is due to an upward shift in average molecular weight caused by low molecular weight fragments being leached out of the membrane during the degradation experiment. Permittivity data for degraded and undegraded materials were fitted to the Havriliak–Negami equation. The quantities extracted from these fits were the relaxation time (τ) and parameters that reflect the breadth and asymmetry of the distribution of τ. These parameters were also used in the Vogel–Fulcher–Tammann–Hesse (VFTH) equation which was well-fitted to relaxation time versus temperature data. The increase in the Vogel temperature with degradation reflects more restricted chains. The distribution of relaxation time curve shifts to longer times, broadens, and is transformed from being bi- to tri-modal which reflects an increase in microstructural heterogeneity after degradation. It is concluded that dielectric spectroscopy can be a powerful tool in assessing the chemical degradation of Nafion membranes in the fuel cell environment.

Keywords: Broadband dielectric spectroscopy; Nafion; Chemical degradation; Distribution of relaxation times

1. Introduction

In the realm of fuel cell science and technology, Nafion perfluorosulfonic acid ionomers are considered the benchmark material for proton exchange membranes (PEM). To separate H_2 and O_2 gases in the anode and cathode regions a PEM must be mechanically, thermally and chemically stable. However, during operation, PEMs eventually fail often due to chemical degradation caused by OH radicals that result from the decomposition of generated H_2O_2 [1–4]. Although it is commonly accepted that these free radicals are the reason for failure, their specific mechanism of degrading the membrane is ill-understood. Recent research has focused on generating small molecule model compounds to simulate the complex polymer degradation process [5]. Peroxide radical attack on the polymer endgroups with residual H-containing terminal bonds is believed by DuPont researchers to be the principal degradation mechanism [6,7]. Schlick et al. utilized electron spin resonance to study oxygen radicals that were generated via UV-irradiation of aqueous H_2O_2 solutions in the presence of model compounds that were chemically similar to the ether side chain or the backbone and their view is that Nafion can degrade along the chain and in side chains as well as at the chain ends [8–10]. Schiraldi reports in a review of this topic that the primary problem is the generation of H_2O_2 that breaks down forming peroxide radicals [11,12]. These peroxide radicals then abstract hydrogens from the carboxyl acid groups that are located at the polymer chain ends according to the DuPont view. Reducing the carboxylic acid groups by fluorination drastically reduces the degradation process and improves the PEM lifetime.

Recently, Mauritz et al. demonstrated that a similar hydrolytic degradation process that takes place in polylactides can be characterized and tracked using dielectric relaxation spectroscopy (DRS) [13]. It was seen that there is a shift in the glass tran-

---

* Corresponding author. Tel.: +1 601 266 5595; fax: +1 601 266 5635.
E-mail address: kenneth.mauritz@usm.edu (K.A. Mauritz).

[1] Permanent address: Bani Suef University, Faculty of Science, Department of Chemistry, Bani Suef, Egypt.

0378-7753/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2007.04.032

sition, monitored in this way, due to increased chain mobility resulting from hydrolytic degradation. Motivated by the success in characterizing biodegradation in this way, DRS was chosen to track the chemical degradation process of Nafion.

1.1. Background

Modern broadband dielectric spectroscopy is, in a sense, the electrical counterpart to dynamic mechanical analysis (DMA). For a number of polymers, especially those having strong dipoles, DRS is superior to DMA in that it probes the molecular dynamics of polymers over a much broader frequency range, i.e., from the milli- to giga-Hertz region. This allows for the examination of motional processes which take place on vastly different time scales [14]. In the bulk entangled state, amorphous polymers are in fact heterogeneous and this heterogeneity gives rise to a distribution of relaxation times. The long and short range molecular motions in an array of amorphous entangled polymer chains can exist on very different time and length scales and the motional processes can depend on the morphology of the system. Thus, information on chemical structure, phase separation, molecular chain length and distribution, glass and sub-glass transitions, can be extracted using this sensitive probe [14].

As DRS is a relatively uncommon means of characterization, a brief background of the theory will be given here. At a fixed temperature, a dielectric relaxation is identified by a peak on a loss permittivity (ε'') versus *f* curve which corresponds to a step decrease on the storage permittivity (ε') versus *f* curve. In addition to the primary, long ranged α-relaxation (glass transition) amorphous polymers usually exhibit at least a secondary, short ranged sub-T_g β-relaxation.

In order to extract the most information from spectra the data is commonly fitted to the phenomenological Havriliak–Negami (HN) equation [15–17]:

$$\varepsilon*(\omega) = \varepsilon' - \mathrm{i}\varepsilon'' = -\mathrm{i}\left(\frac{\sigma_0}{\varepsilon_0\omega}\right)^N + \sum_{k=1}^{3}\left[\frac{\Delta\varepsilon_k}{(1+(\mathrm{i}\omega\tau_{\mathrm{HN}})^{\alpha_k})^{\beta_k}} + \varepsilon_{\infty k}\right] \quad (1)$$

Eq. (1) has three relaxation terms in the summation and the term on the left accounts for dc conductivity, when present. ε_0 is the vacuum permittivity and $\omega = 2\pi f$. For each relaxation term, $\Delta\varepsilon_k = (\varepsilon_R - \varepsilon_\infty)_k$, which is the difference between ε' at very low and very high frequencies, respectively. For the dc conductivity term, σ_0 is the conductivity in S cm^{-1} and the exponent *N* ($0 < N \leq 1$) characterizes the conduction process in terms of the nature of charge hopping pathways and mobility constraints. The parameters α and β ($0 < \alpha < 1$, $\alpha\beta \leq 1$) characterize the breadth and symmetry, respectively, of ε'' versus ω peaks. τ_{HN} is the Havriliak–Negami relaxation time and is related to $\tau_{\max}$ by the following equation [Ref. 14, p. 64]:

$$\tau_{\max} = \tau_{\mathrm{HN}}\left[\frac{\sin((\pi\alpha\beta)/2(\beta+1))}{\sin((\pi\alpha)/2(\beta+1))}\right]^{1/\alpha} \quad (2)$$

$\tau_{\mathrm{HN}} = \tau_{\max}$ when $\beta = 1$ and $\alpha = 1$.

For most polymers, the glass transition is usually the most prominent relaxation. $\tau_{\max}$ versus 1/*T* plots for this relaxation often shows curvature that is non-Arrhenius in nature and is commonly modeled using the Vogel–Fulcher–Tammann–Hesse (VFTH) equation [18]:

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{k_B(T - T_V)}\right) \quad (3)$$

k_B is the Boltzmann constant and τ_0, E_a, and T_V are treated as parameters obtained by fitting Eq. (3) to experimental DRS data. τ_0 is a hypothetical relaxation time at infinite temperature. E_a, while having units of energy, is a ubiquitous quantity that it is not associated with an activated process in the usual sense. T_V, the Vogel temperature, is the temperature at which chain segments become frozen in a hypothetical situation in which a polymer is cooled at a quasi-static rate from the rubbery state. T_V is expected to be lower than T_g [19].

Recently, Moore et al. [20,21] identified the molecular and morphological origins of the α- and β-relaxations of Nafion®. The high temperature α-relaxation was attributed to the onset of long range mobility of the backbone as coupled to the side chains that are aggregated through electrostatic interactions in a way that these interactions are weakened and significant ion-hopping occurs. The α peak temperature was shown to be greater than 100 °C for H-form.

On the other hand, the low temperature β-relaxation was attributed to a glass transition involving the backbone within the framework of a static electrostatic network. Here, the glass transition for Nafion will be regarded as the β-relaxation.

In this work, we report the use of broadband dielectric spectroscopy to investigate the shifts in this relaxation caused by chemical degradation.

2. Experimental

2.1. Materials

Cast Nafion® 212 films (2 mil thick, 1100 equivalent weight) were obtained from the E.I. DuPont Company. To remove impurities these as-received (AR) membranes were cleaned by refluxing in 8 M HNO_3 for 2 h, rinsing them three times with deionized water, and then boiling them in deionized water for 1 h. Chemical degradation was conducted in the usual way using Fenton's reagent ($FeSO_4/H_2O_2$) at room temperature for prespecified times. The AR cleaned samples were dried at 70 °C for 12 h under vacuum and then kept in a vacuum oven at room temperature until tested.

Before being placed between the electrodes in the dielectric spectrometer, the films were preconditioned in a moisture chamber with controlled 6.4% relative humidity for 4 days. Upon removing the specimens from the chamber, the specimens were immediately loaded into the spectrometer. The loading process took less than 2 min. Quick sample transference is critical because it was determined that slight variations in atmospheric RH and loading times significantly altered the β (high temperature) relaxation of the AR sample. To enhance sample reproducibility, the moisture content of the AR sam-