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Dielectric properties of hydrated Nafion-(SO_3K) membranes: thermally stimulated depolarization currents

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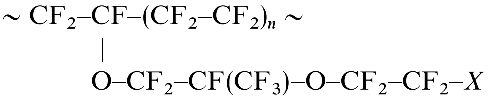
Dielectric studies have been carried out on hydrated perfluorosulfonate polymer membranes in potassium salt form, 1190 g equivalent^{-1} by means of thermally stimulated depolarization current (TSDC) techniques in the temperature range 77–300 K. Three dispersions I–III, are observed in a TSDC thermogram, and their positions depend upon the water content. We employ thermal sampling (TS) to analyse the three relaxation process experimentally, into approximately single responses and to determine the spectra of activation energy, $E(T)$, on a sample with a water content of 0.9 H_2O/SO_3K. Dispersion I is analogous to the γ-relaxation mechanism, which was observed in mechanical relaxation studies, with an activation energy between 0.55 and 0.68 eV. Measurements with different electrode configuration reveal different aspects of the dynamics of the relaxation mechanism and allow distinction between dipolar and interfacial polarization contributions of Dispersion II. Dispersion II is analogous to the β-relaxation mechanism that was observed in mechanical relaxation studies on hydrated membranes. Dispersion III may be due to a phase or structural change of the material in this temperature range. However, a contribution to this peak from electrochemical effects at the electrodes cannot be excluded.

1. Introduction

Perfluorosulfonate polymers are used very successfully in many industrial applications that require a conducting polymer membrane with good thermal and chemical stability. There are various uses of these cation conducting membranes in electrochemical processes and devices such as battery separators and fuel cells. Nafion is the trade name of perfluorosulfonated polymers and was first developed by Du Pont in the 1960s. Nafion in the sulfonate form has the polymeric structure



$$\begin{array}{l} \sim CF_2\text{–}CF\text{–}(CF_2\text{–}CF_2)_n \sim \\ \qquad\;\; | \\ \qquad\;\; O\text{–}CF_2\text{–}CF(CF_3)\text{–}O\text{–}CF_2\text{–}CF_2\text{–}X \end{array}$$

where $X = SO_2F$, SO_3H or SO_3K. The polymeric composition is expressed in terms of equivalent weights, EW, defined as the weight in grams of polymer containing 1 equivalent of acid or

$$EW = 100n + 482$$

for $X = SO_3K$, where n is the number of moles of tetrafluoroethylene (TFE) per mole of comonomer.

The acid and salt forms are hydrophylic. Small angle X-ray scattering (SAXS) reveals evidence for the existence of ionic rich domains or "clusters" and this somewhat ill-defined micro-phase separation is in the form of sulfonate-rich ion clusters (about 4 nm in diameter) embedded in a crystalline perfluorocarbon matrix [1, 2]. The back-bone TFE segment tends to crystallize the structure, while the side groups hinder crystallization. The degree of crystallinity decreases with decreasing EW due to increasing concentration of the side-chain material with decreasing EW.

The present work is a study of the relaxation mechanisms that contribute to the TSDC thermograms, on hydrated perfluorosulfonate membranes in potassium salt form.

2. Experimental procedure

Dielectric studies by means of TSDC, were carried out on hydrated perfluorosulfonate polymers in potassium salt form, 1190 g equivalent^{-1}. The principle of the TSDC method is based on the strong dependence of the dielectric relaxation time, τ, on temperature, T; which can be expressed in most cases by the Arrhenius equation

$$\tau = \tau_0 \exp\left(\frac{E}{kT}\right) \qquad (1)$$

where E is the activation energy for dipolar reorientation, k is the Boltzmann constant and τ_0 is the so-called pre-exponential factor. A brief description of the method is given below [3, 4]. The sample is inserted between the plates of a capacitor and polarized

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by the application of a constant electric field, E_p, at a temperature, T_p, for a time, t_p, large compared with the relaxation time at T_p of the dispersion under examination. With the electric field still applied, the sample is cooled down to a temperature, T_0, sufficiently low to prevent depolarization by thermal energy. The sample is then short-circuited and reheated at a constant rate, b. A discharge current is generated as a function of temperature, which is measured with a sensitive electrometer. In general, a TSDC thermogram consists of several peaks whose shapes and locations are characteristic of the relaxation mechanisms of the sample. In the case of a single relaxation process, the depolarization current density, $J(T)$, is given by

$$J(T) = \frac{P_o}{\tau_o} \exp\left(\frac{-E}{kT}\right) \exp\left[-\frac{1}{b\tau_o}\int_{T_o}^{T} \exp\left(\frac{-E}{kT'}\right) dT'\right] \tag{2}$$

where P_o is the initial polarization. The maximum depolarization current density occurs at

$$T_m = \left[\frac{bE\tau(T)}{k}\right]^{1/2} \tag{3}$$

at which the relaxation time, τ, becomes of the order 10–100 s, for heating rates of a few Kelvins per minute.

The thermal sampling (TS) technique consists of "sampling" the relaxation process within a narrow temperature range by polarizing at a temperature, T_p, and depolarizing at, T_d, a few degrees lower than, T_p. We used a modification of the TS technique in which the sample was continuously cooled down at a rate of about 4 K min^{-1} and the electric field was applied at T_p and switched at T_d [5]. The temperature was scanned in steps of 5 K. During one polarization step, only a fraction of the dipoles were polarized and these dipoles were characterized by values of τ_o and E giving relaxation times that were of the order of the time-scale of the experiment for temperatures in the range, i.e. T_d–T_p. In the depolarization step, the current density, which is due to reorientation of these dipoles, described by Equation 2 and the temperature of the maximum current is given by Equation 3 (in the range T_d–T_p). From each depolarization step, we obtain a TSDC peak from which we can calculate the activation energy and the pre-exponential factor for this fraction of dipoles (each depolarization process is assumed to be a single relaxation process). There are several methods that evaluate the activation energy [6–8]; here we used the initial-rise method [6], which is based on the fact that for the initial-rise temperatures of the peak the second exponential term in Equation 2 is very close to one and thus Equation 2 becomes

$$\ln J(T) = \text{constant} - \frac{E}{kT} \tag{4}$$

The pre-exponential factor is given by the condition for the peak maximum

$$\tau_o = \frac{kT_m^2}{bE} \exp\left(\frac{-E}{kT_m}\right) \tag{5}$$

We used a common experimental apparatus for TSDC measurements in the temperature range 77–300 K. The samples were cut from sheets and were cylinders of 13 mm diameter and about 0.063 mm thickness. The standard electrodes of the measuring capacitor were made of brass. Typical experimental conditions were 4–12 kV cm^{-1} for the polarizing field, 295 K for the polarization temperature, 5 min for polarizing time, 7 K min^{-1} for the cooling rate and 3–4 K min^{-1} for the heating rate.

Samples, in perfluorosulfonate potassium salt form, were dried in vacuum (6.8 Pa) at 380 K for two days and determination of the dry weight was made after drying. The water content, defined as the ratio of the number of H_2O molecules to the number of SO_3K group (H_2O/SO_3K), was adjusted over saturated salt solutions in sealed jars at controlled relative humidities and determined by weighing. Samples reached equilibrium (sample weight changed by less than 10^{-4} g) in a few hours.

The uncertainties were ± 0.5 K in the peak temperature, T_m ± 0.01 eV in the activation energy and ± 0.2 H_2O/SO_3K in the water content.

3. Results and discussion

Fig. 1 shows a TSDC plot of a sample of 0.9 H_2O/SO_3K water content. The TSDC thermogram shows three dispersions, I, II and III, at temperatures of 163, 216 and 252 K, respectively.

The influence of water content on the position of the peaks of Dispersions I, II and III is shown in Fig. 2. The position of the peak of Dispersion II was, at first, 243 K for a water content of 0.4, and after shifted to lower temperature; its magnitude increased with increasing water content. At higher water content a second peak appeared in the region of Dispersion II, and Dispersion I was masked. The position of Dispersion III occurred at similar temperatures, i.e. at about 252 K, for samples with a water content of 0.4 and 0.9 H_2O/SO_3K, and shifted to lower temperature, about 225 K, for the sample with a water content of 2.4 H_2O/SO_3K.

The activation energies, E, of the TS responses for Dispersions I and II for the sample with a water content of 0.9 H_2O–SO_3K, were calculated using the

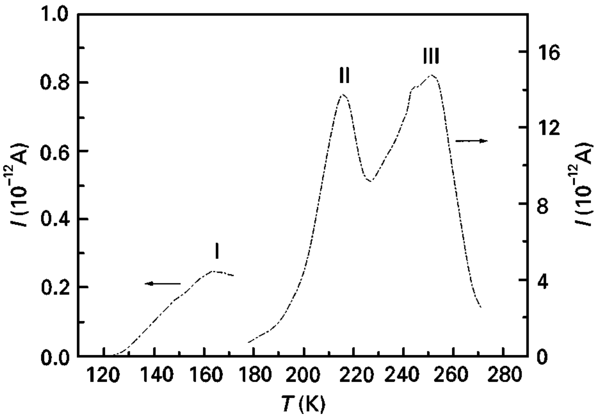

Figure 1 TSDC thermogram for a sample with a H_2O–SO_3K water content of 0.9.

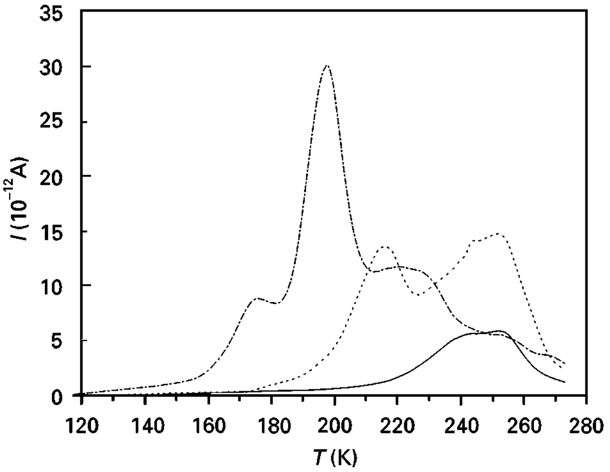

Figure 2 TSDC thermograms for a sample at H_2O–SO_3K water contents of 0.4 (—), 0.9 (- - -) and 2.4 (- · · -).

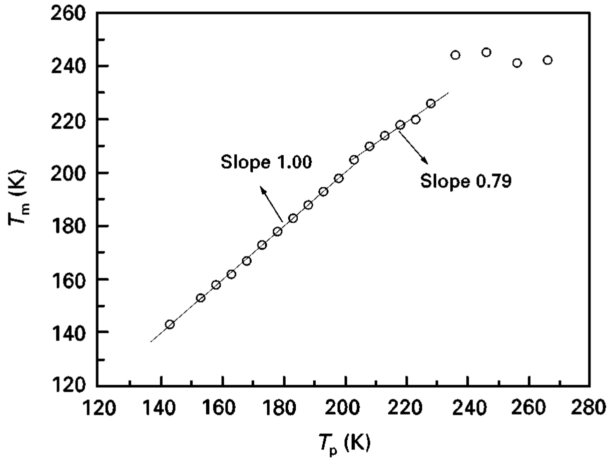

Figure 4 Peak temperature, T_m, versus polarizing temperature, T_p, of the TS responses of Fig. 1.

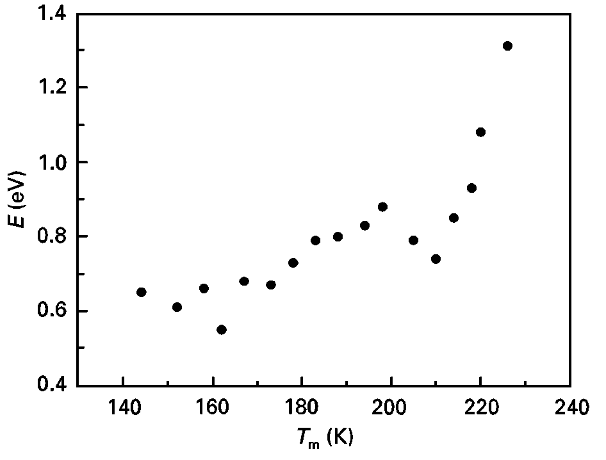

Figure 3 Activation energy, E, versus peak temperature, T_m, of the TS responses of Fig. 1.

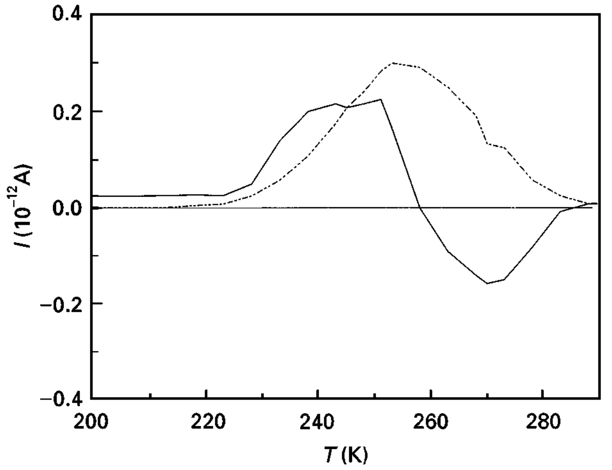

Figure 5 Thermogram without a polarizing field for a sample with a H_2O–SO_3K water content of 0.9: (—) heating, (- - -) cooling.

initial-rise method (Equation 4). The distribution of the activation energy versus the temperature of the maximum current, T_m, is given in Fig. 3. The values for the activation energies for the broad and weak Dispersion I, are between 0.55 and 0.68 eV, i.e. 12.7 and 15.7 kcal mol^{-1} respectively. The previous results combined with the fact that the maximum peak of Dispersion I is at about 163 K, suggest that this dispersion is the γ-relaxation mechanism, which is due to a rotational crankshaft motion along the Nafion back-bone similar to the motion in polytetrafluoroethylene (PTFE, 16 kcal mol^{-1}).

Yeo and Eisenberg [9] reported that the γ-relaxation mechanism in perfluorosulfonate polymers was observed mechanically at 1 Hz and 173 K. In their work, the position and the activation energy of this peak (13 kcal mol^{-1}) were the same in acid and salt form and the height of the peak was affected somewhat by the type of ion used, but this effect was not drastic. The γ-relaxation mechanism has been measured dielectrically on Nafion membranes by several researchers, e.g. Hodge and Eisenberg [10] on dried perfluorosulfonate membranes in –SO_2F form (about 173 K and 1 Hz, 11.3 kcal mol^{-1}), Fontanella *et al.* [11] on acid form dried Nafion 117 membranes (13.2 kcal mol^{-1}), Perusich *et al.* [12] on dried perfluorocarboxylate polymers (10–19 kcal mol^{-1}) and Zaluski and Xu [13] on solution cast perfluorosulfonated membranes. A γ-relaxation mechanism is found here that is dielectrically active with the presence of water (0.4 and 0.9 H_2O/SO_3K), and with higher water content it is masked by Dispersion II as shown in Fig. 2. The position and the magnitude of Dispersion I were similar for samples with water contents of 0.4 and 0.9.

In Fig. 4, we show the peak temperature, T_m, of the TS responses against polarization temperature, T_p, for the sample with a water content of 0.9 (the temperature window for Dispersion III was 10 K). The TS responses for Dispersion III show that T_m is almost independent of the polarization temperature, T_p. By increasing T_p the magnitude of the TS responses increases. The fact that the temperature peaks, T_m, are not in the range $[T_d–T_p]$ suggests that Dispersion III is not due to depolarization of the dipoles (see the description of TS in Section 2).

Measurements without a polarizing field reveal evidence for a phase or structural transition [14, 15]. Fig. 5 shows a thermogram without a polarizing field for a sample with a water content of 0.9. As we can see, during cooling there is a spontaneous current peak at 250 K and during heating there are two spontaneous current peaks with opposite signs at about 245 and 270 K. Differential scanning calorimetry (DSC) measurements do not show evidence for phase or structural transition at the temperature range of Dispersion III. Perhaps this is due to the weakness of the transition. The spontaneous current peaks may be due to the release of trapped charges during heating and cooling processes, occurring in regions undergoing phase or structural change. The thermogram of a sample with a higher water content, which had not been polarized, showed a shift of these peaks to lower temperatures in accordance with Fig. 2. Bearing in mind the relatively high temperature of Dispersion III and the low equivalent frequency of the TSDC measurements (relaxation times of the order of 10–100 s, see Section 2), it cannot be excluded from our results that electrochemical effects at the electrodes also contribute to this peak. Experiments with different electrode materials would help to investigate and clarify this point further.

As we can see, the plot in Fig. 4 is linear with a slope of one up to 200 K. The remaining Dispersion II TS responses lead to a slope of 0.79. This suggests that the part of the TSDC thermogram up to about 200 K, i.e. Fig. 1, is due to relaxation of dipoles (see the description of TS in Section 2). The deviation from the slope value of one at temperatures higher than 200 K for Dispersion II, suggests that "space charge polarization" contributes to this peak [16, 17]. As can be seen in Fig. 3, Dispersion II consists of two linear regions of activation energy versus T_m, the first between 173 and 198 K (0.67–0.88 eV) and the second between 210 and 226 K (0.74–1.31 eV).

Using thin insulating Teflon foils (diameter, $d = 0.05$ mm) between the sample and the metal electrodes, the mechanisms that are related to d.c. conductivity are eliminated [3, 4]. Fig. 6 shows the TSDC plot for the sample with a water content of 0.9 with metal (brass) electrodes (Metal-Sample-Metal [MSM] electrode configuration) and with blocking (Teflon) electrodes (Metal-Insulator-Sample-Insulator-Metal [MISIM] electrode configuration). The voltage applied in the MSM electrode configuration was 80 V and the voltage applied in the MISIM electrode configuration was 160 V. By making the approximation that in the MISIM electrode configuration we have three capacitors in series, the effective electric field, E_s, that polarizes the sample is $E_s = V_s/d_s$, where d_s is the thickness of the sample and

$$V_s = \frac{V}{1 + (2C_s/C_t)} \qquad (6)$$

where V is the total applied voltage and C_s and C_t are the capacitances of the sample and Teflon, respectively. Using the values of dielectric constant, 2.1 for Teflon and 7.5 (10 Hz, 295 K) for the sample, the effective voltage that is applied to the sample is found to be about 24 V. If Dispersion II is a clear dipolar mechanism, then in the MISIM electrode configuration the position of the peak will be at the same temperature as this of the MSM electrode configuration and the magnitude of the peak will be reduced by a factor of 3.3 (= 80/24), because for the dipolar mechanism the maximum current, I_m, is proportional to the polarizing field, E_p, [18]. The magnitude of the peak in the MISIM electrode configuration is reduced by a factor of about six as compared with what would be expected for a clear dipolar mechanism, and the position of the peak also shifts to a lower temperature, to 200 K. This significant reduction of the magnitude of Dispersion II indicates that the number of relaxing units contributing to this dispersion has been significantly reduced by use of the MISIM electrode configuration.

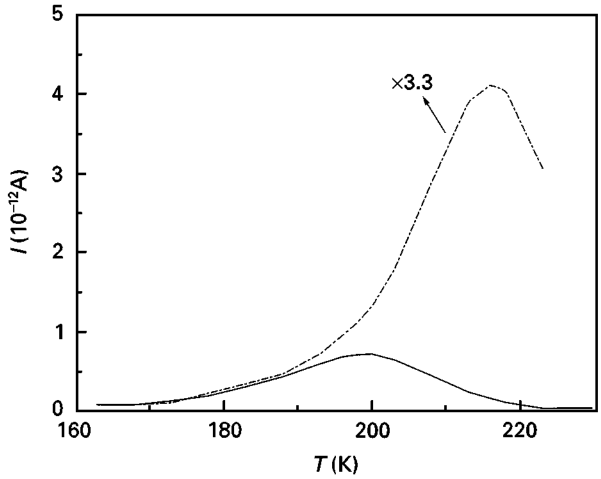

Figure 6 TSDC thermograms measured on a sample with a H_2O–SO_3K water content of 0.9 in MSM (- - -) and MISIM (—) electrode configuration.

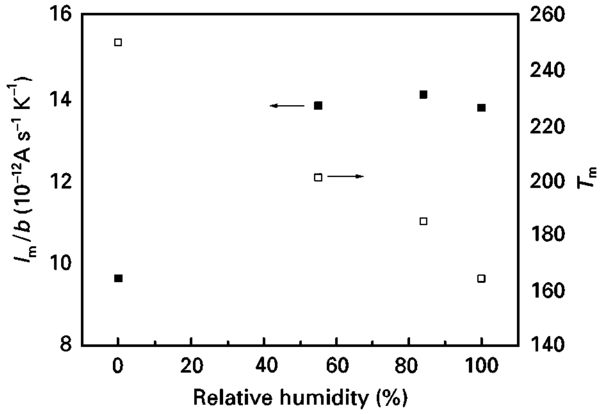

Figure 7 Peak temperature, T_m (□), and normalized current peak, I_m/b (■), versus relative humidity for Dispersion II measured in MISIM electrode configuration.

The normalized peak current, I_m/b, of Dispersion II in MISIM electrode configuration versus relative humidity (the sample was kept in a sealed jar at a controlled relative humidity for one night before it was measured, this time being sufficient for the sample to equilibrate) is shown in Fig. 7 (the total applied voltage was 320 V). As we can see, the normalized peak current, I_m/b (which is proportional to the polarization) is practically constant, independently of the water content, for relative humidities higher than 55% (for 55% relative humidity the water content is very close to 1 H_2O/SO_3K, i.e. room condition) and the water acts as a plasticizer for this dipolar mechanism.

This is in contrast to the results obtained with the MSM electrode configuration (Fig. 2), where a significant increase in magnitude with increasing water content is observed. In addition, Fig. 7 shows the position of the peak, T_m, in the MISIM electrode configuration as a function of relative humidity where the plasticizing effect of the water is clear. A relative humidity of 0% (P_2O_5 environment) does not mean that all of the water molecules left the sample.

The absorbed water in Nafion membranes exists in the hydrophilic ionic regions [19]. The fact that the magnitude of Dispersion II is practically independent of water content (for a water content higher than 1 H_2O/SO_3K), suggests that the increasing magnitude of this dispersion with water content, measured by metal electrodes, is due practically to the interfacial polarization contribution of the ionic regions, which is related to d.c. conductivity during the polarization process [16, 17]. These results reveal the influence of water on interfacial polarization and clearly associate the conduction mechanism with the water existing in the ionic regions of the Nafion membranes.

The mechanical β peak in the dry perfluorosulfonate polymer, in potassium salt form, occurs as a shoulder at the α-relaxation region, at about 423 K and 1 Hz, as Yeo and Eisenberg reported [9]. This peak moves to lower temperatures with increasing water content, as a small peak. These authors suggest that is possible that the β peak is due to a specific motion within the ionic region or to a polar group. Evidence of the plasticizing effect of water is also found in dielectric measurements of their work, in which two peaks are observed in the β-relaxation region. In a recent report, Perusich *et al.* [12], observed dielectrically the β-relaxation mechanism on dry perfluorocarboxylate polymers. They suggested that the β-relaxation mechanism was due to ester rotation at the end of the side chain. The activation energies of the dry salt forms were 13–16 $\mathrm{kcal\,mol^{-1}}$ and the position of the peak for the potassium salt form (1163 *EW*) was found to be at about 173 K and 1 Hz. In our material the $-SO_3K$ group at the end of the side chain has a larger inertia and a bigger size (a bigger size means stronger interaction with neighbouring $-SO_3K$ groups in ionic regions) in comparison with the $-CO_2K$ group, and thus $-SO_3K$ groups require greater thermal energy to relax than is required by $-CO_2K$ groups.

Considering all the above, we can claim that Dispersion II is analogous to the β-relaxation region, observed in mechanical relaxation measurements on hydrated perfluorosulfonate membranes in potassium salt form [11]. The peak measured with blocking electrodes is the dipolar contribution to this mechanism, which is attributed to the $-SO_3^-$ group–water complex at the end of the side chain. The water molecules solvate the cations (K^+) from the $-SO_3^-K^+$ groups and a water content of 1 H_2O/SO_3K is needed to form a stable dipolar unit at the end of the side chains (Fig. 7). In metal electrode measurements, the interfacial polarization mechanism of the ionic region dominates and masks the dipolar mechanism. The dipolar mechanism exists at a temperature 16 K lower than the interfacial polarization peak (Fig. 6) for samples with a water content of 0.9. At higher water contents (84.5 and 100% relative humidity) TSDC measurements with blocking electrodes show a small peak, like a shoulder, at a temperature about 30 K higher than the dipolar peak, which is due to depressed interfacial polarization. This is the reason for the separation of the two processes in Dispersion II at higher water content (Fig. 2). The fact that the dipolar mechanism is faster than the interfacial polarization mechanism can be explained as follows: the dipole rotations are local motions and after these local interactions are formed in a different way in the ionic regions by enabling the separated charges to migrate through the intracluster regions and by means of thermal energy by increasing the temperature.

4. Conclusions

Three dispersions are shown in the TSDC thermogram for a hydrated perfluorosulfonate polymer in potassium salt form. Dispersion I is the γ-relaxation mechanism. To the best of our knowledge this is the first time that the γ-relaxation was found to be active dielectrically in a hydrated perfluorosulfonate membrane in salt form. This is due to the high sensitivity and peak resolving power of the TSDC technique. Dispersion II is analogous to the β-relaxation, which is observed in mechanical relaxation measurements on hydrated membranes. The results of our measurements with (i) metal electrodes and (ii) blocking electrodes, suggest that Dispersion II consists of both dipolar and interfacial polarization in the former case, and of pure dipolar polarization in the latter case (with a small contribution from interfacial polarization at high water content, and 84.5 and 100% relative humidity). We believe that this dipolar mechanism is caused by rotation of $-SO_3^-$ groups–water complexes at the end of the side chains. Our measurements suggest that Dispersion III may be due to a phase or structural change of the material in this temperature range. However, a contribution to this peak from electrochemical effects at the electrodes cannot be excluded.

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