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Aqueous Phase in a Perfluorocarboxylate Membrane

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ABSTRACT: A perfluorocarboxylate membrane has been characterized by dynamic mechanical relaxation, NMR on ^1H and ^{19}F, and ^{57}Fe Mössbauer spectroscopy of the ferric salt. Results are similar to those reported for perfluorosulfonate membranes, indicating that the specific charged end group has little influence on the structure or behavior of the aqueous phase. Exchanged ions in the membranes at ambient humidity and above are not directly coordinated by sulfonate or carboxylate groups, but by water. Precipitation of ferric hydroxide in a ferric membrane reexchanged with KCl is inferred from the Mössbauer spectrum at 4.2 K and confirmed by NMR relaxation times.

Introduction

The properties of perfluorosulfonate ion-exchange membranes depend sensitively upon the cation present and on the amount of absorbed water.[1-3] The behavior of the aqueous phase, in particular the glasslike character at low temperatures, has been studied in a number of membranes, but especially in Nafion[4] using techniques[1-3] which include nuclear magnetic resonance (NMR)[5-8] and Mössbauer spectroscopy.[9-11] This paper focuses upon a relative newcomer to the field, a perfluorocarboxylate membrane in which the side group is terminated with COOH rather than SO_3H. It is of interest to ascertain, for example, the relative tendency of the ionic phase to cluster, to explore the stability of the membrane with increasing temperature, and, more generally, to determine the extent to which the macroscopic properties are altered by the presence of carboxylate. NMR, Mössbauer, and mechanical relaxation results are presented and compared with data for other perfluorinated membranes. This combination of experimental probes gives microscopic information on the motions of the polymer chains, and of the ions and water which constitute the aqueous phase, besides providing a macroscopic overview of the relaxation processes.

Experimental Methods

The sample under investigation was obtained from the Asahi Glass Co. in the form of a pressed sheet 250 μm thick. The water content at ambient humidity was determined, by heating under vacuum at 423 K, to be 6 wt %. Prompted by the findings of an earlier study on Nafion[6] (as received) in which impurity iron and potassium were detected in significant amounts, we carried out an X-ray fluorescence microprobe analysis of the carboxylate sample. The results, presented in Table I, reflect similar amounts of iron and potassium impurity and indicate further a sulfur content about 60% of that recorded for a comparable volume of the acid perfluorosulfonate membrane. Additionally, a microprobe line scan showed that the sulfur was concentrated toward the membrane surfaces. If the sulfur is a constituent of SO_3H (or SO_3K) end groups, this would imply that the membrane was only about 40–45% carboxylate exchanged.

^1H and ^{19}F T_1, T_2, and $T_{1\rho}$ NMR data were recorded over the temperature range 120–380 K using the experimental procedures and methods of data analysis described previously.[8] Mössbauer spectroscopy, also described previously,[9] was applied to the Fe^{3+}-exchanged carboxylate sample. Iron was initially incorporated by stirring the membrane in a 0.2 M aqueous solution of $FeCl_3$ for 12 h and subsequently precipitated by reexchange in a solution of 0.1 M KCl. In both cases a microprobe line scan was reasonably flat across the thickness of the membrane, implying a correspondingly uniform distribution of iron across the profile. Dynamic mechanical relaxation studies were carried out with a dynamic mechanical thermal analyzer (Polymer Laboratories), operating at 1 Hz over the temperature range 180–520 K.

Table I
Number of Iron Atoms/cm^3 and Ratio of Potassium to Sulfur Content for the COOH Membrane As Received and an Acid Nafion of Comparable Water Content

sample	no. of Fe^{3+}/cm^3	K/S
COOH membrane	3.7×10^{18}	0.33
Nafion (115)	7.2×10^{18}	0.41

Membranes were conditioned by boiling in water and drying under various conditions.

Results and Discussion

NMR. It is recalled that the ^1H data reflect predominantly the response of absorbed water in the membrane while the ^{19}F resonance probes the onset of molecular motion in the fluorocarbon backbone matrix. The ^1H results of Figure 1 confirm that the behavior of the aqueous phase in the perfluorocarboxylate acid membrane is in most respects comparable with that observed in a perfluorosulfonate acid Nafion of similar water content for which a detailed interpretation of NMR data, including a treatment of the role of impurity iron, was presented in two earlier papers.[5,6] Briefly, (i) the onset of general motions in the aqueous phase, typical of a glass transformation process (T_g = 182 K), was evident in the sharp rise in T_2 near 170 K and in the formation of $T_{1\rho}$ and T_1 minima at ~180 and ~230 K, respectively; (ii) as temperature increased, chemical exchange between heterogeneous water sites was presumed to set in and to become fully activated near ambient temperature; (iii) comparison of the magnitudes of the NMR relaxation times as a function of iron content implied that the iron in the membrane as received was most probably in the aqueous phase and that $T_{1\rho}$ was much less sensitive than T_1 or T_2 to the presence of iron. Either $T_{1\rho}$ is dominated by mo-

Table II
Room-Temperature T_1, T_2, and $T_{1\rho}$ Data for the Fe^{3+}-Exchanged and Reexchanged Perfluorocarboxylate Membrane

	T_1		$T_{1\rho}$		T_2	
sample	^1H	^{19}F	^1H	^{19}F	^1H	^{19}F
as received	6 ms	200 ms	1 ms	4 ms	900 μs	30 μs
exchanged with $FeCl_3$	20 μs	4.3 ms 0.9 ms		1.5 ms	14 μs	28 μs
reexchanged with KCl	140 μs	22 ms	115 μs	4 ms	115 μs	30 μs

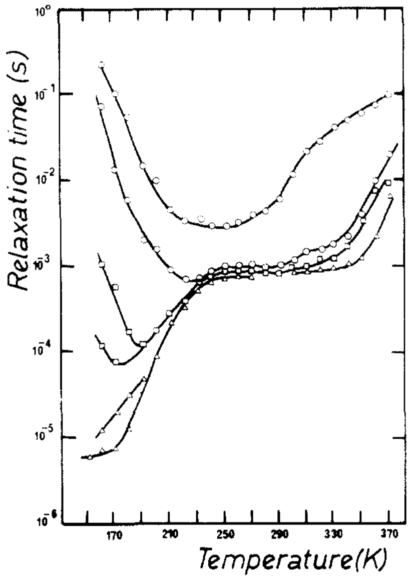

Figure 1. ^1H resonance data for the partially exchanged COOH membrane: T_1 (○), $T_{1\rho}$ (□), and T_2 (△).

lecular motion at low temperatures or the protons are, on average, further removed from the iron sinks than the albeit short diffusive path length corresponding to the $T_{1\rho}$ time scale of $\sim 10^{-4}$ s at low temperatures. Definitive resolution of this complex point must await further work.

When room-temperature data were remeasured after completion of the high-temperature cycle it was noted that $T_1(^1H)$ and $T_{1\rho}(^1H)$ increased by factors of about 10 and 5, respectively. This observation will be examined further in conjunction with parallel trends in the ^{19}F resonance data.

The ^{19}F results are shown in Figure 2. The filled experimental points represent the response of the sample, as received, over the temperature range 150–290 K. The temperature was then increased to 370 K (unfilled points) after which the low-temperature data were rerecorded to give the unfilled points as indicated. Nonexponential decays observed in the first low-temperature run were fitted with two $T_1(^{19}F)$ and $T_{1\rho}(^{19}F)$ components, indicating either that two regions were relaxing at different rates and only weakly coupled by spin diffusion or that some of the ^{19}F nuclei were more tightly coupled to impurity iron atoms than others, resulting in lower relaxation times. Note too that diffusion-limited relaxation to paramagnetic sinks (iron) leads to nonexponential T_1 relaxation.[12] The magnitudes of $T_1(^{19}F)$ and to a lesser degree $T_{1\rho}(^{19}F)$ confirm that the ^{19}F nuclei and the iron atoms are indeed communicating. On the second run, following cycling over the high-temperature range, both $T_1(^{19}F)$ and $T_{1\rho}(^{19}F)$ become exponential and the magnitude of $T_1(^{19}F)$ increases significantly in similar fashion to the ^1H data. A likely explanation for the annealing phenomenon is at least a partial reduction of the ferric ions in the aqueous phase in the high-temperature cycling. In support of this, $T_1(^1H)$ and $T_2(^1H)$ were found to be approximately 20 times longer in a ferrous solution than in a ferric solution of the same strength. Furthermore, reduction of some of the iron in an Fe^{3+}-exchanged membrane was observed directly by Mössbauer spectroscopy after heating to 375 K for 20 min.

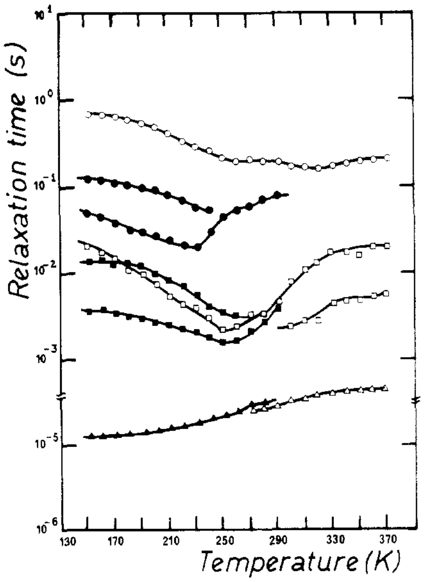

Figure 2. ^{19}F resonance data for the partially exchanged COOH membrane: T_1 (○, ●), T_1 (□, ■), and T_2 (△, ▲). The filled points denote the response before cycling to high temperatures.

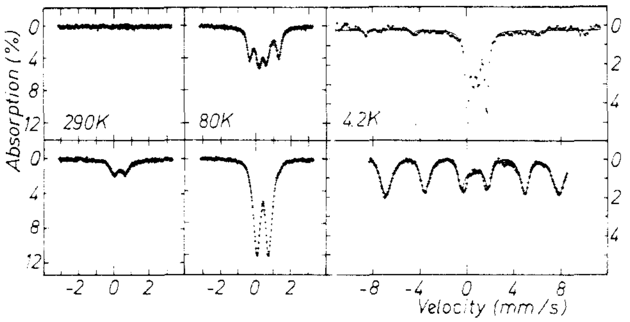

Figure 3. Mössbauer spectra of iron carboxylate membranes at 290 K (left), 80 K (center), and 4.2 K (right). The top spectra are for the membrane exchanged in $FeCl_3$, whereas the bottom spectra are those for the same sample reexchanged with KCl.

Mössbauer Spectroscopy. The role of iron was explored further by using the Mössbauer techniques applied to the Fe^{3+}-exchanged carboxylate membrane. Mössbauer spectra of the ferric membrane at three temperatures are presented in Figure 3. The absence of absorption at room temperature implies diffusion of the resonant iron over a fraction of an angstrom in 10^{-7} s. Absorption only appears below $T_0 = 260$ K, where the spectra are composed of two ferric doublets. The hyperfine parameters for the doublets A and B are listed in Table II, where they are seen to be identical with those of ferric Nafion prepared in the same way. There, the two doublets have been identified with two iron species, namely oxy-bridged dimeric iron, $(H_2O)_5$-Fe-O-Fe-$(H_2O)_5$ and hydrated Fe^{3+}.[9] Spectra at 4.2 K show that at least half of the latter are isolated ions at distances greater than 12 Å from each other, and as a consequence they must be more or less uniformly distributed in the aqueous phase. The only minor difference

Table III[a]
Parameters Derived from Mössbauer Spectra of Ferric Membranes

		δ, mm/s	Γ, mm/s	Δ, mm/s	I, %	Θ_D, K	T_0, K
perfluorocarboxylate exchanged with $FeCl_3$	*A*	0.47 (1)	0.42 (2)	0.44 (2)	59	157 (5)	260 (10)
	B	0.56 (1)	0.34 (2)	1.67 (2)	41		
reexchanged with KCl		0.46 (1)	0.44 (2)	0.69 (2)	100	218 (5)	310 (10)
perfluorosulfonate exchanged with $FeCl_3$	*A*	0.47 (1)	0.44 (2)	0.43 (2)	45	160 (10)	250 (10)
	B	0.56 (1)	0.32 (2)	1.67 (2)	55		
reexchanged with KCl		0.48 (1)	0.44 (2)	0.71 (2)	100	257 (10)	310 (10)

[a] δ, isomer shift relative to α-Fe measured at 80 K; Γ, full width at half-maximum measured at 80 K; Δ, quadrupole splitting measured at 80 K; I, relative intensity measured at 80 K; Θ_D, effective Debye temperature; T_0, temperature at which Mössbauer absorption vanishes.

Table IV
Temperatures (°C) Where Mechanical Relaxations Are Observed at 1 Hz in the Perfluorocarboxylate Membrane

		γ	β'	β	α	conditioned sample
Na salt	dry	-80	-30	130	245	dried at 160 °C for 24 h under vacuum
Na salt	room humidity	-80	-30	60	245	kept in atm for 24 h
Na salt	swollen	-80		-60	230	swollen in boiling water for 1 h
acid	dry	-80		40	120	dried at 110 °C for 4 h under vacuum
acid	room humidity	-80		-40	120	as received
acid	swollen	-100[a]		-65	125	swollen in boiling water for 1 h
acid	dry	-60		60	120	dried at 110 °C for 24 h under vacuum

[a] These peaks might be caused by decomposition of COOH due to too prolonged heat treatment.

between these Mössbauer results and those from the perfluorosulfonate Nafion rests in the somewhat lower proportion of dimers (41% of total iron) in the carboxylate membrane compared with the sulfonate one (55%).

Previous experience with the Nafion membranes has shown that iron in solution in the aqueous phase can be precipitated in situ either by reexchange with a wide variety of cations or by treatments that remove water from the membrane.[9-11,13] We therefore examined the membrane after reexchange in KCl, and the corresponding data are also shown in Figures 3 and 4. A single quadrupole doublet appears below T_0, which is now somewhat above room temperature, and this gives way to a magnetically split hyperfine pattern with H_{hf} = 445 kOe at 4.2 K. Again, the spectra are very similar to those of Nafion treated in the same way, for which $H_{hf}(4.2)$ = 463 kOe. In Nafion, the reexchange precipitates amorphous particles of hydrated ferric oxide which have a magnetic blocking temperature near 20 K.[10,11] There the ferric hydroxide tended to be concentrated toward the outer surfaces of the membrane, whereas in the present material the profile is essentially uniform. Iron in the carboxylate membrane exhibits a substantial increase in recoilless fraction after the reexchange, evident from Figure 4, where the temperature dependence of the absorption area, A, is plotted. This may be parameterized in terms of the Debye temperature Θ_D derived from the slope of the ln $A(T)$ curves in the linear range 80–160 K. Values of Θ_D are included in Table III. Precipitation of iron in the reexchanged membrane is confirmed in NMR room-temperature data also presented in Table III. As is evident from the foregoing discussion, segregation of iron within the ionic phase produces a significant increase in T_1, $T_{1\rho}$, and T_2.

Mechanical Relaxation. The mechanical relaxation results for the acid and sodium salt forms of the membrane under various conditions are collected in Table IV and depicted in Figures 5 and 6. In general, they confirm the conclusion from the Mössbauer and NMR studies of the similarity of the carboxylated membrane to the previously studied Nafion membranes. In view of the fact that the membrane contains a considerable quantity of sulfur, it may be that this is partially responsible for the result. However, in a number of ionomers studied it appears that the influence of both the cation and anion on the structure is of secondary importance. If the salt groups are attached to a flexible backbone of low dielectric constant and if they are more or less randomly spaced along the chain, the bulk

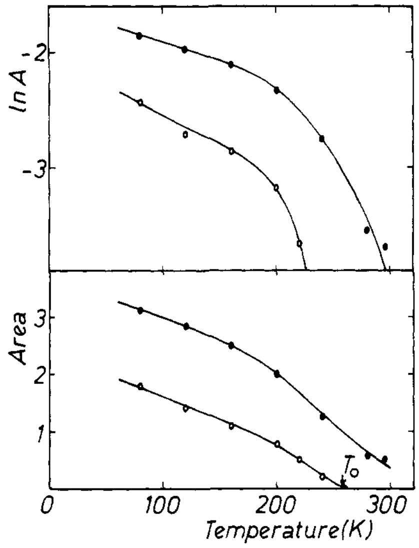

Figure 4. Temperature dependence of the Mössbauer absorbtion on a linear scale (bottom) and on a logarithmic scale (top): (○) Fe membrane; (●), reexchanged membrane.

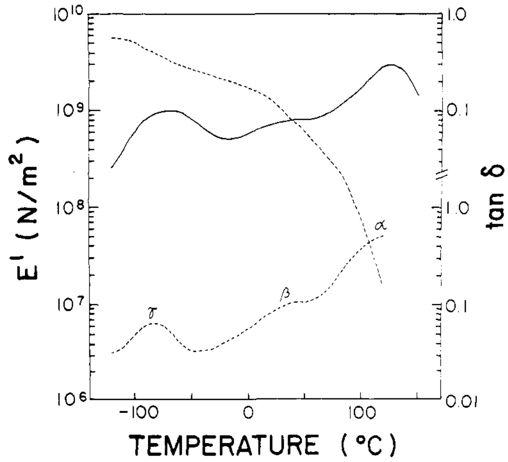

Figure 5. Temperature dependence of E' and tan δ at 1 Hz for the acid membrane in the dry state (---) and after boiling in water for 1 h (—).

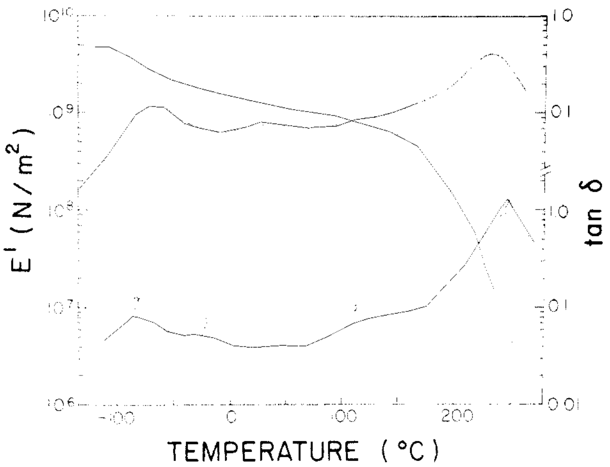

Figure 6. Temperature dependence of E' and tan δ at 1 Hz for the Na salt form of the membrane in the dry state (- - -) and after boiling in water for 1 h (—).

morphology tends to be independent of their chemical nature.[2]

The γ relaxation occurs at the same temperature in both acid and salt forms and in the wet and dry states. It also occurs very close to the temperature of the γ relaxation in perfluorosulfonate Nafion membranes as described by Eisenberg.[3] It therefore appears that the γ relaxation originates from local motions of the CF_2 groups and has nothing to do with the polar side groups.

The β' relaxation occurs only in the salt form of the perfluorocarboxylate membrane. It has also been observed in the salt form of perfluorosulfonate Nafion membranes. Its temperature is affected by water. For the sample boiled in water for 1 h, the β' peak temperature has been lowered so that it has become indistinguishable from the γ peak. Although the water sensitivity of the β' peak and its presence only in the salt form indicate that it is associated with the ionic groups, its exact origin is not clear at this time.

The β relaxation peak occurs at rather different temperatures in the dry acid and salt but water saturation decreases its temperature substantially in both cases. Once again, a similar relaxation occurs in Nafion and it has been assigned to the glass transition (T_g) of the fluorocarbon matrix. This assignment has been made despite the water sensitivity of the β relaxation and has been justified by Eisenberg.[3,14] On this basis, it seems reasonable to assign the β peak in the carboxylate membrane to motions accompanying the glass transition of the matrix.

The α relaxation is present in both the acid and salt forms, although it occurs about 100 K higher for the salt than for the acid. It appears to be insensitive to water but this may be an artifact since most of the water has evaporated by the time temperatures in the vicinity of the α relaxation are achieved. Kyu and Eisenberg have since demonstrated that α relaxation in Nafions is indeed sensitive to water.[15] In the case of Nafion, the α relaxation was assigned to motions within the ionic clusters.[14] If this assignment is also correct for the carboxylate membrane, it would imply that the free acid carboxyl groups also form clusters in the dry state. Further work is necessary to test this hypothesis.

The NMR results for the carboxylate membrane are largely consistent with the mechanical relaxation data although not unequivocally so in respect of the molecular interpretation of the α and β relaxations. The fact that the log ν_c vs. T^{-1} locus for the high-temperature α transition in Nafion and in the carboxylate membrane coincides with the transition assigned to $-CF_2-$ backbone motions in FEP may indicate that the α rather than the β relaxation finds its origins in matrix rather than ionic side-group motions. However, it would be difficult to visualize either the matrix or ionic side groups undergoing large-scale *independent* motions as expected for a glass transition, particularly at high temperatures where the preferential plasticizing effect of the water is much reduced or absent altogether.

Conclusions

The close similarity between NMR, Mössbauer, and mechanical relaxation for the present membrane and for Nafion indicates that the specific negatively charged end group has little influence on the structure or behavior of the aqueous phase. Exchanged ions are not directly coordinated by the sulfonate or carboxylate ions, but by water. Differences do appear however in the NMR data below room temperature following thermal treatment. Despite the fact that the temperature did not exceed 370 K in the NMR experiments, there is a clear indication of a reduction in the effectiveness of iron as a relaxation sink on heating, which may be associated with water loss but more particularly a reduction of the ferric species.

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