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THERMAL STABILITY AND DECOMPOSITION OF NAFION® MEMBRANES WITH DIFFERENT CATIONS
Using High-Resolution Thermogravimetry

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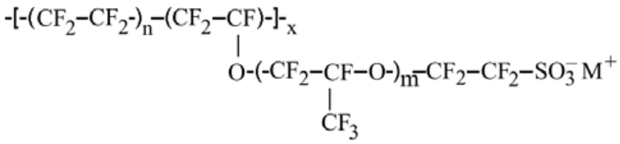
Abstract

The thermal decomposition of Nafion® has been studied by means of high-resolution and constant heating rate thermogravimetry (TG), under nitrogen and synthetic air atmospheres. Nafion membranes have been studied in acid and salt (alkali chlorides) forms. The TG curves of Nafion with alkali countercations show similar profiles, whichever the atmosphere employed. The kinetics of thermal decomposition of the Nafion-Cs^+ has also been studied. The method employed to calculate the kinetic parameters and to estimate the polymer lifetime from the data was based on Kissinger's method.

Keywords: high-resolution thermogravimetry, Nafion®, perfluorosulfonated ionomers

Introduction

Nafion® is a perfluorosulfonated ionomer that is used as an ion-exchange membrane that find applications in many processes (electrodialysis, diffusion dialysis, reverse osmosis, membrane electrolysis and membrane fuel cells) [1–3]. It possesses high chemical, mechanical and thermal stability. Nafion contains a polytetrafluoroethylene (PTFE) backbone with a side chain terminated in a sulfonated cation exchange site. The structure for Nafion 1100 equivalent mass is shown in Scheme 1.



$$-[-(CF_2-CF_2-)_n-(CF_2-\underset{\underset{\displaystyle O-(-CF_2-\underset{\underset{\displaystyle CF_3}{|}}{CF}-O-)_m-CF_2-CF_2-SO_3^-\,M^+}{|}}{CF})-]-_x$$

Scheme 1 Structure of Nafion 1100, where n=6.5, m=1, x=200–1000 and M^+ is an exchangeable cation

The thermal stability of Nafion membrane has been studied by several authors [4–12], especially the membrane in acid form, that has straight application in the fuel cell technology [3, 5, 10]. Surowiec and Bogoczek [4] used the simultaneous

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TG-DTA analysis to study the thermal stability of Nafion in air atmosphere and the products of decomposition steps were studied by infrared (IR) spectroscopy and ion-exchange capacity determinations. They found that the Nafion-H^+ decomposed in three stages, the first one being water loss (moisture only) from 50 to 180°C, the second one from 310 to 380°C, being the sulfonic groups loss, and the last one from 420 to 590°C, the oxidative destruction of the perfluorinated matrix. Chu *et al*. [5] have studied, by IR spectroscopy, the effect of heating platinum foils coated with Nafion films or with a similar perfluorinated sulfonic acid ionomer films at various temperatures in air atmosphere. The heating of the Pt-films up to 300°C lead to the observation of the loss of sulfonic groups, as showed by the IR spectra. Mauritz *et al*. [6–8] used the TG, DSC and TG-IR to investigate the thermal behavior of micro- and nanocomposites of Nafion and silicon compounds. It was shown that these compounds improved the thermal stability of Nafion. It was also observed the evolution of the products of thermal decomposition of filled and unfilled Nafion, analyzed via TG coupled to a FT-IR spectrometer [8]. For the Nafion-H^+, these products were mainly SO_2 (decomposition of sulfonate groups) and SiF_4 (HF reaction with TG quartz tube, by the decomposition of the fluorocarbonic side chains and/or matrix). The silicon composites has shown to be inhibitors of SO_2 evolution, possibly because the side chains could be immobilized within SiO_2 cages. The thermal decomposition of Nafion membrane was also monitored via TG-IR by Wilkie *et al*. [9], and via TG-MS by Samms *et al*. [10] and the mechanisms of decomposition were proposed. Wilkie *et al*. [9] have observed that the products of the first mass loss of Nafion-H^+, between 35–280°C, were H_2O, SO_2 and CO_2. The vacuum-dried films seem to have 2.7% of water. The second stage of decomposition, between 280–355°C, had the SO_2, CO_2, SiF_4, CO, H_2O and substituted carbonyl fluorides. The last step of mass loss involved the formation of HF, SiF_4 and substituted carbonyl fluorides. The overall mechanism of decomposition in [9], proposed the initial broken of the C–S bond, forming a fluorocarbon radical and a $\bullet SO_3H$ radical, that cleaves to produce SO_2 and an $\bullet OH$ radical. The fluorocarbon radical loses difluorocarbenes and produces an oxygen-based radical, that loses carbonyl fluoride and a substituted carbonyl fluoride. The remaining is PTFE, which degrades by a random scission process. It was also shown by Wilkie *et al*. [9] that K^+ exchanged Nafion did not show any SO_2 in its thermal decomposition, and it was suggested that the C–S bond in that system was much less susceptible to thermal cleavage. Samms *et al*. [10] has shown the products of decomposition of Nafion by TG-MS either with or without Pt in nitrogen and air atmospheres. In nitrogen atmosphere, the products of the first mass loss was mainly water (until 225°C), the second one SO_2, CO_2 and carbonyl fluoride, and in the last stage thionyl fluoride, carbonyl fluoride, C_xF_y, $C_mF_nO_z$, SO_2, HF and CO_2. In air atmosphere, the TG curves profile was similar to nitrogen, but a second peak of SO_2 evolution was also observed, which was not present in nitrogen atmosphere. There were two mechanisms proposed: a radicalar and an anionic one. As the first forming product was the same on both mechanisms, it could be possible to occur a branch into one and another pathway. The decomposition products of Nafion was also determined by DuPont [11], heating the sample in a stainless steel tube in air atmosphere, and quantifying them by IR, being the same as determined in [8–10], except for the SiF_4, which was not observed.

As observed by Wilkie *et al.* [9], Almeida and Kawano [2, 12] have also observed that the TG curve profile was affected by exchanged countercations. Feldheim *et al*. [13] have reported the dependence of the thermal stability of Nafion on the countercation (alkali metal and alkyl ammonium). The decomposition temperature of Nafion was inversely dependent on the effective size of the exchanged cation.

This work investigates the thermal stability and decomposition of Nafion membranes in acid and salt forms (alkali chlorides), and calculates the polymer lifetime from kinetic measurements, by means of thermogravimetric analysis (TG).

Experimental

Nafion-117 1100 equivalent mass, with thickness of 0.177 mm (E. I. DuPont de Nemours Co., purchased from Aldrich) was received in the acid form. The substitution of counterions was performed as follows: the membranes were stirred for 24 h with the alkali chloride (Li^+, Na^+, K^+, Cs^+ and Rb^+) aqueous solution of concentration 1 mol dm^{-3}, at ambient temperature, followed by washing with deionized water. The exchanged Nafion membranes were used without any further treatment or drying. These conditions are enough to exchange all the cations, as demonstrated by Shi and Anson [14], being the cations exchange rapid and quantitative. The PTFE film was the Teflon® spacer used in infrared solution cell.

TG experiments were performed under either nitrogen or synthetic air (79% of N_2 and 21% of O_2) atmospheres at 100 cm^3 min^{-1} on a TA Instruments Hi-Res™ TGA 2950 interfaced to the Thermal Analyst 2000 software. Sample mass was in the range of 2.0–3.5 mg, the crucible used was made of platinum, and the temperature range was from ambient to 700°C (Figs 1–5 show the 300–600°C range).

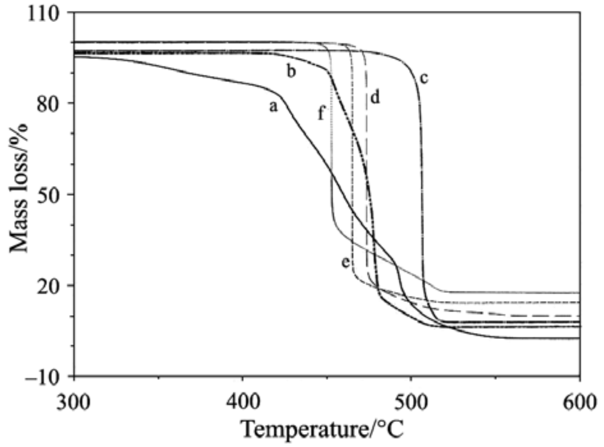

Fig. 1 TG curves of Nafion membranes: a – H^+, b – Li^+, c – Na^+, d – K^+, e – Rb^+, f – Cs^+ (20°C min^{-1}, resolution 3, nitrogen atmosphere)

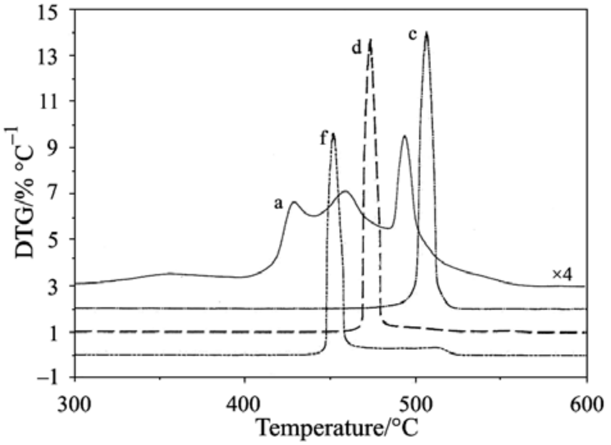

Fig. 2 DTG curves of some Nafion membranes in Fig. 1: a – H^+, c – Na^+, d – K^+, f – Cs^+

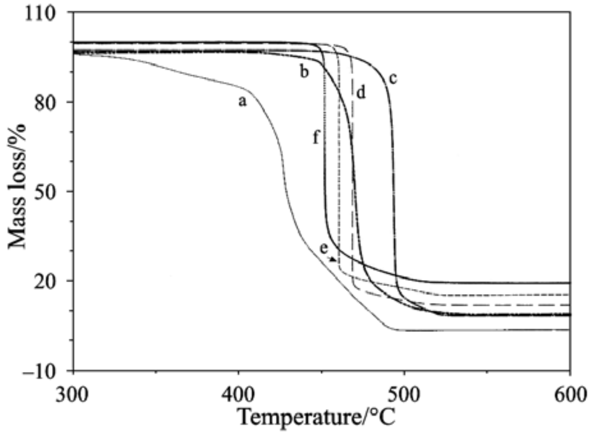

Fig. 3 TG curves of Nafion membranes: a – H^+, b – Li^+, c – Na^+, d – K^+, e – Rb^+, f – Cs^+ (20°C min^{-1}, resolution 3, synthetic air atmosphere)

TG was used in both conventional linear heating rate mode and high-resolution variable heating rate temperature program, while mass loss is measured. The high-resolution TG mode in the dynamic rate uses as an approach a mathematical function that relates the rate of change of sample mass to the sample heating rate [15, 16]. As the rate of change of sample mass increases, the heating rate is decreased, being the result a lowered heating rate through the decomposition step. Three experimental parameters need to be selected to perform a dynamic heating rate experiment: the initial (maximum) heating rate, the resolution index and the sensitivity. The increasing resolution implies in a lower heating rate and consequently an increasing separation of close events of mass loss, as well as the experiment time. For the experiments conducted here, the initial heating rate was 20°C min^{-1}, whereas the setting for resolution

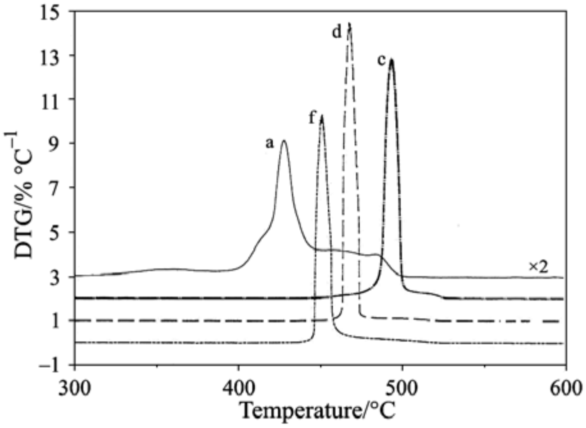

Fig. 4 DTG curves of some Nafion membranes in Fig. 3: a – H$^+$, c – Na$^+$, d – K$^+$, f – Cs$^+$

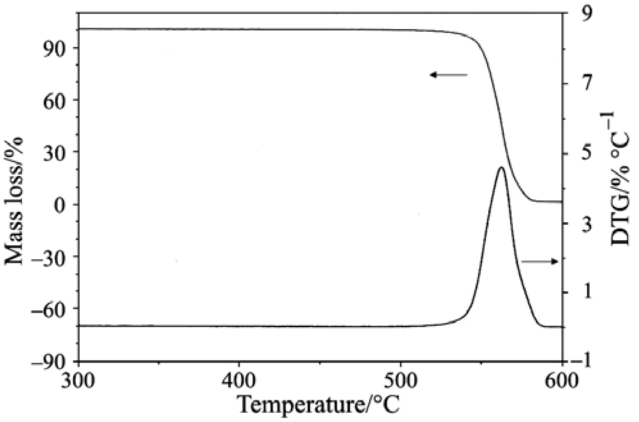

Fig. 5 TG and DTG curves of PTFE film (20°C min^{-1}, resolution 3, synthetic air atmosphere)

was from 1 to 5 and the sensitivity was 1 (default value). These parameters were selected to obtain well-resolved mass loss steps as well as to avoid long analysis time.

Experiments using constant heating rate were also performed in order to compare the results and to calculate the polymer lifetime, using the Kissinger [17] and Dobkowski and Rudnick [18] methods.

Results and discussion

Thermal stability of alkali chlorides-exchanged Nafion

TG/DTG curves for the acid and alkali metal-exchanged Nafion films under nitrogen and air atmosphere are shown in Figs 1–4. In Figs 1 and 3 the TG curves in nitrogen and air are presented, respectively, for all the countercations and their differences in thermal stability can be seen. Figures 2 and 4 are the DTG curves for Nafion-H$^+$, Na$^+$,

K^+ and Cs^+ in the range of 300 to 600°C; in these figures the DTG curves were all shifted one unit along the ordinate axis to improve the curves profile view. It is observed from Figs 2 and 4 that Nafion-Na^+, K^+ and Cs^+ decompose in one step, although there is a shoulder in the region of high temperature in those curves; Nafion-H^+ decomposes in 3 or 4 steps, for nitrogen and air atmospheres, respectively. Figure 5 shows the TG/DTG curves of PTFE film in synthetic air atmosphere, for the sake of comparison with the curves of Nafion membranes. ln Tables 1 and 2 the data of thermal behavior in nitrogen and air atmospheres of Nafion membranes and PTFE film are presented.

Table 1 Mass loss (m), initial (T_i), onset (T_o), inflection point (T_{ip}) and final (T_e) decomposition temperatures, and residue content of Nafion membranes and PTFE in nitrogen atmosphere (data obtained at 20°C min^{-1} and resolution 3)

Sample	m/%	T_i/°C	T_o/°C	T_{ip}/°C	T_e/°C	Residue* at 700°C/%
Nafion-H^+	4.9					
	8.3	291	329	356	395	
	19.8		421	427	439	
	31.8		451	460	484	
	31.3		492	493	565	3.1
Nafion-Li^+	3.3					
	19.2	410	447	454	462	
	70.1		475	477	526	7.5
Nafion-Na^+	2.9					
	88.7	465	505	507	529	8.8
Nafion-K^+	0.7					
	88.8	455	473	474	563	10.7
Nafion-Rb^+	0.4					
	84.8	450	465	465	524	15.0
Nafion-Cs^+	0.0					
	82.8	435	452	453	528	17.6
PTFE	96.1	512	553	563	608	3.9

*calculated considering the dry membrane, i.e., subtracting the first mass loss due to moisture, except for PTFE

The main difference between the initial and onset decomposition temperatures is in the way of their determination. The latter is strongly dependent on the shape of the TG curve, as it is obtained by extrapolation via software, while the former is determined by the initial variation in the DTG trace. The criterion of thermal stability adopted here is the initial decomposition temperature after the removal of water, as the mass loss that occurs between 290–470°C is the most critical because the membrane loses its ion exchange functionality [8].

The initial and onset temperature of decomposition of the acid Nafion and the alkali metal-exchanged Nafion membranes follow the trend:

$$H^+<Li^+<Cs^+<Rb^+<K^+<Na^+$$

Table 2 Mass loss (m), initial (T_i), onset (T_o), inflection point (T_{ip}) and final (T_e) decomposition temperatures, and residue content of Nafion membranes and PTFE in air atmosphere (data obtained at 20°C min^{-1} and resolution 3)

Sample	m/%	T_i/°C	T_o/°C	T_{ip}/°C	T_e/°C	Residue* at 700°C/%
Nafion-H$^+$	4.0					
	10.1	296	333	360	390	
	58.7		422	427	447	
	22.8		459	462	503	5.0
Nafion-Li$^+$	3.3					
	86.7	417	464	470	546	10
Nafion-Na$^+$	2.7					
	88.5	457	492	493	531	9.2
Nafion-K$^+$	0.8					
	87.0	449	468	468	519	13
Nafion-Rb$^+$	0.6					
	83.4	445	460	460	524	17
Nafion-Cs$^+$	0.3					
	80.7	436	451	451	515	19
PTFE	98.5	499	552	563	593	2.1

*calculated considering the dry membrane, i.e., subtracting the first mass loss due to moisture, except for PTFE

Feldheim *et al*. [13] uses the onset temperature of decomposition to establish the thermal stability trend and this order is almost the same as observed here, except for the onset temperatures of Nafion-Li$^+$ and -Cs$^+$, that were approximately the same in [13]. The onset decomposition temperatures reported here are also higher than in [13], probably due to different experimental conditions, such as the high-resolution TG mode. One can also note that the temperature of decomposition is inversely dependent on the size of the countercation, excepting for -Li$^+$, as the Nafion membranes show improved thermal stability as the size of the countercation decreases. This can be related to the charge density of the cations and the interactions of them with the sulfonate groups. As the cation ionic radius increases, its charge density, as well as its hydration shell and the interaction with the sulfonate groups decrease. The exceptions for the Nafion-H$^+$ and –Li$^+$ can be explained by their large hydration energies, which lower the charge densities due to the greater extent of water association [13, 14], being the water present even at elevated temperatures [19].

From Table 1, it can also be observed that the residue content of Nafion-H$^+$ is almost the same as the PTFE residue, reinforcing those mechanisms proposed in [9, 10]. The residue of the exchanged Nafion increases as the atomic number of the cation increases.

The TG curves of Nafion membranes in air atmosphere have nearly the same profile as those in nitrogen, although the temperatures and the residue content are slightly different. These can be ascribed to a different decomposition mechanism, as observed in [10].

As reported in [9, 13], the mechanism of decomposition of exchanged Nafion could be different from the acid Nafion. The distinct decomposition profiles (Figs 1–4) and temperatures (Tables 1 and 2) confirm this observation. Wilkie *et al*. [9] has not observed the evolution of SO_2, probably because the sulfonate groups should be more protected from C–S bond scission by the countercations. The decomposition temperatures of PTFE matrix in Nafion are lower than that of PTFE homopolymer (Tables 1 and 2), possibly due to a formation of radicals and/or anionic species during the loss of sulfonate groups, which will further react with the PTFE backbone, resulting in chain scission.

The decomposition temperatures are in agreement with literature data [4–13]; however, the number of decomposition stages detected varies. The performance of the high-resolution mode on the TG curves profile is clearly seen in acid Nafion membrane decomposition. At least 3 steps of decomposition was observed in air and 4 in nitrogen (Figs 2 and 4). The better resolution produced is due to a remarkable reduction of the heating rate when the balance detects loss of sample mass.

Samms *et al*. [10] have considered that the temperature of complete loss of sulfonic groups for acid Nafion was 280°C, based on [4, 5]. Chu *et al*. [5] has observed the vibrational bands of sulfonic groups up to 300°C, and Surowiec and Bogoczek [4] has assigned the complete loss of sulfonic groups as sulfur dioxide up to 380°C.

Kinetic study of Nafion-Cs$^+$

Nafion-Cs$^+$ membrane was chosen to perform the kinetic study of thermal decomposition by TG. Table 3 shows the results of this membrane in nitrogen atmosphere. As stated before, in the case of Nafion-Cs$^+$ it is observed that the high-resolution allows the observation of another step of decomposition, and the calculations were performed including these two steps. The calculations of activation energy (E_a), reaction order (n), and pre-exponential factor (A) were made by using Kissinger's method [17]. The advantage of this method is the use of the temperature at the maximum rate of mass loss (inflection point decomposition temperature T_{ip}), which determination is more precise than the initial or final temperature of decomposition. Figure 6 shows the graph of $\ln(q/T_{ip}^2)$ *vs*. $1/T_{ip}$, where q is the heating rate at the inflection point. The slope of this graph is $-E_a/R$, where R is the gas constant, and the intercept is a combination of parameters including A.

Table 3 Kinetic parameters calculated from TG/DTG curves, with high-resolution (HR, at 20°C min^{-1} and resolutions from 1 to 5) and constant heating rate mode (C, at 1, 2, 5 and 10°C min^{-1}) in nitrogen atmosphere

Step	E_a/kJ mol^{-1}	n	lg$A$
1 (HR)	307	0.5	21.4
1 (C)	196	0.8	13.7
2 (HR)	192	0.8	12.1
2 (C)	186	0.8	11.9

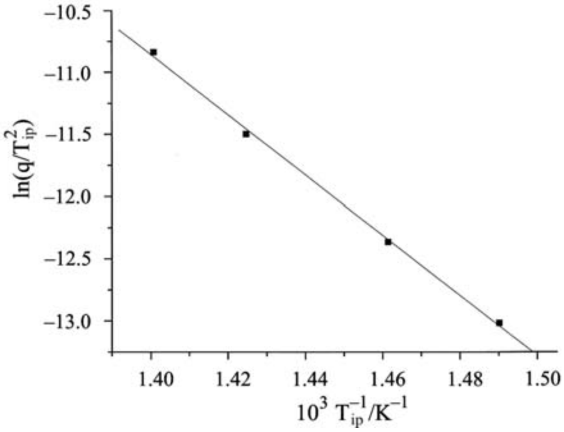

Fig. 6 Graph of $\ln(q/T_{ip}^2)$ *vs.* $1/T_{ip}$ (data obtained at constant heating rate, 1st step of decomposition of Nafion-Cs^+)

According to Denq *et al.* [20], when the reaction order is ~1 in polymers, this can be interpreted as a random scission of the bonds in the main chain. The reason between the differences in the values of activation energy in the first step of mass loss is not clear.

With a modification of Kissinger's method [17], made by Dobkowski and Rudnick [18], it is possible to estimate the lifetime of the polymer, in a specified temperature, as illustrated in Table 4. In this modification, only the conditions in the initial decomposition, such as T_i are considered, and it is assumed that in this case the reaction order is $n=1$.

Table 4 Nafion-Cs^+ lifetimes in different temperatures (experimental conditions on Table 3; E_{ai}=197 kJ mol^{-1}, m=2.4 to 4.0 mg; $\lg A_i$=14.0; *a*=year, *d*=day, *h*=hour)

T/°C	t
25	$8.9\cdot10^{12}$ a
50	$1.9\cdot10^{10}$ a
100	$1.1\cdot10^{6}$ a
150	$5.9\cdot10^{2}$ a
200	1.6 a
250	4.9 d
300	2.3 h

The activation energy in the initial conditions of decomposition is the same as the calculated one from Kissinger's method in both steps of degradation (Table 3). The lifetime of polymer decreases exponentially with temperature.

Conclusions

Acid and cation exchanged Nafion membranes have different thermal decomposition profiles. The decomposition profile is not affected by the purge atmosphere (nitrogen or air), only the temperatures are slightly different. Cations exchanged Nafion are more thermally stable than acid Nafion, with the thermal stability following the trend: $H^+<Li^+<Cs^+<Rb^+<K^+<Na^+$. The charge densities of the countercations can affect the interaction with sulfonate groups, which is responsible for the thermal stability of Nafion. It was observed that the residue content increases as the ionic radius of cations increases. The decomposition temperature of Nafion membranes are lower than that of PTFE homopolymer. The decomposition of acid Nafion is more complex than that of alkali exchanged Nafion, due to the high water content in the former. Lifetime of Nafion-Cs^+ membranes decreases drastically with increasing temperature.

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