

THERMAL CHARACTERIZATION OF FLEMION[®] MEMBRANES SUBSTITUTED BY ALKALI METAL CATIONS

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The thermal behavior of perfluorosulfonated membranes of three equivalent mass ($EW=910$, 1000 and 1100 g eq⁻¹) has been studied for membranes in acid form and in the alkali metal counteranions substituted samples. The water contents of the membranes decrease progressively with increasing EW and the counteranions charge density. The monovalent cations substitutions increase the membranes thermal stability. DSC curves show a single endothermic peak around 120°C that give low peak temperature for low EW and high peak temperature for large cations size. The membrane mechanical properties changed for different EW and temperatures of membranes. Stress-strain analysis showed that K^+ substituted membranes at both temperatures present a highest YM compared to the other alkali cation substitutions. The thermal properties of perfluorosulfonated membranes depend on the water contents, cation size, temperature and also on EW value.

Keywords: DMA, DSC, Flemion[®], perfluorosulfonated ionomer, TG

Introduction

Asahi Glass Flemion[®] belongs to the perfluorosulfonated ionomeric (PFSI) polymer class from which the most studied and known member is DuPont's Nafion[®]. Figure 1 shows Flemion's structure constituted by a polytetrafluoroethylene-like backbone with ionic fluorosulfonic acid pendant groups.

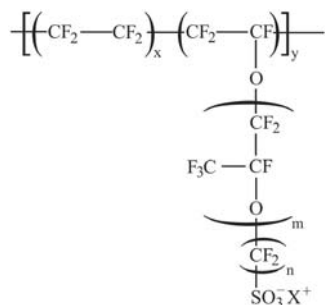


Fig. 1 Flemion[®] structure

According to Asahi Glass Co., Flemion[®] membranes have x values from 1.5 to 14, m values of 0 or 1, n values from 1 up to 5, and are produced in the form in which X^+ is a proton (acid form).

These membranes are attracting attention in recent years because of their extended applications in electrochemical devices such as ion selective transport membranes or, when modified by other chemical species, like ions or ionic complexes or even coupled with metal plates (IPMC – ionic polymer-metal compos-

ites), as electrolytes in fuel cells [1–4]. To accomplish great performances in such applications, some properties of the Flemion[®] membranes such as water content, ionic and water transport mechanisms and also the electrochemical data need to be understood, since all of these properties are related to the interaction between the incorporated chemical species (such as alkaline cations) and the polymer's sulfonated group. It is also important to study the membrane characteristics that are changed with these incorporations. The morphological features of Flemion[®]-like membranes are based on hydrophilic/hydrophobic phase separation in which the ionic groups converge to hydrophilic aggregates (clusters) that are linked, forming a network. However, this approach is considered on several morphological models that vary from the most basic cluster-network that treats the hydrophilic domains as linked inverted-micelle systems to more sophisticated ones such as lamellar systems [5–7]. This subject is still under discussion in literature [7].

Concerning the ionomeric membrane one major parameter to determine specific properties is the membrane equivalent mass (EW), defined as the number of grams of dry ionomer per equivalent of sulfonic groups (g eq⁻¹). This property is also related to the ion exchange capacity (IEC), defined as $\text{IEC}=1000/\text{EW}$. As the membranes' EW grow, the IEC become smaller.

Previous works have already performed studies concerning DuPont Nafion[®] membranes substituted by alkaline cations but a few dealing with Flemion[®].

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No works concerning the Flemion[®] membrane substituted by alkali metal cations and its thermal characteristics profiles have been published in literature. Okada *et al.* [1] have studied the electrochemical properties of some alkali metal cations-substituted Flemion[®], concluding that the substitution makes the ionic conductivity and water permeability to decrease because the cations have stronger interactions with the absorbed water molecules. Nasser and Wu [2] have determined general physical properties (density and stiffness) of Nafion[®] and Flemion[®] substituted by some alkali metal cations, showing differences that arise by the interactions of the cations with the ionic groups on both ionomers.

Thermal characterization of Nafion[®] membranes is widely presented in the literature. Several TG experiments concerning thermal stability and degradation products analysis [8, 9–16] were performed, the latter being evaluated with TG-IR [9, 11, 16] and also TG-MS [12] accessories. Surowiec and Bogoczek [9] showed for acid Nafion[®] that thermal degradation occurs mainly in 3 steps: water loss (up to ~180°C), sulfonic acid group splitting (~350°C) and polymer matrix decomposition (over 420°C). It is also shown [14–16] that this mechanism and the temperature at which these events occur depend on the counter-cation. A recent DMA work [17] shows that the Young modulus of Nafion[®] samples decreases with increasing water content and temperature.

The purpose of this work is to present thermal characterization of Flemion[®] membranes with different incorporated alkali metal cations (Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺), calling special attention to different behaviors from three different *EW* samples by means of thermogravimetry (TG), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) stress-strain analysis.

Experimental

All Flemion[®] membranes used in this work were kindly provided by Asahi Glass Co. Ltd. in the H⁺ form. All samples have thickness of 50 µm, with three different *EW* values as shown in Table 1, and were used without any pre-treatment. Cation substitutions with alkali metals were performed by immersing the samples in 0.1 M aqueous solution of LiOAc, NaOH, KOH, RbBr and CsI, respectively, at room temperature and under stirring for 24 h. Under these conditions, the substitution rate is believed to be 100%, except for the CsI. All samples were dried naturally for 24 h before any measurements were carried out.

Thermogravimetric (TG) experiments were carried out using a TA Instruments Hi-ResTM TGA 2950

Table 1 Flemion[®] samples available

Sample membrane	Ion exchange capacity/ meq g ⁻¹	<i>EW</i> / g eq ⁻¹
Flemion LSH50	0.91	1100
Flemion MSH50	1.0	1000
Flemion SH50	1.1	910

interfaced to the Thermal Analyst 2000 software. N₂ gas atmosphere was used in all analyses, performed at high-resolution mode from room temperature up to 700°C at starting heating rate of 20°C min⁻¹, resolution 3 and sensitivity 1 (default values). All samples had mass between 1.5 and 2.0 mg and were placed in a Pt made crucible.

DSC experiments were carried out in a TA Instruments Q-10 DSC coupled with a TA Refrigerated Cooling System (RSC) interfaced to the Thermal Analyst 2000 software. Analyses were performed in Al semi-hermetic crucibles from -10 up to 250°C with 20°C min⁻¹ heating rate.

DMA stress-strain experiments were carried out in a TA Instruments Q800 DMA analyzer coupled with a film tension clamp accessory interfaced to the Thermal Analyst 2000 software. Samples were all cut to a 15.5 mm² size. All stress-strain analyses were performed with 0.1 N preload force under a program of controlled force with rate of 0.5 N min⁻¹ at two fixed temperatures: 30 and 80°C.

Results and discussion

Figure 2 shows the TG/DTG curves of Flemion[®] membranes substituted by H⁺. As long as this profile is similar to every other cation substitution with few modifications, Table 2 below summarizes every onset temperatures and mass losses associated with the thermal decomposition steps of all TG/DTG analysis performed.

The observation of the TG/DTG results for the H⁺ form membranes shows that it has the same profile

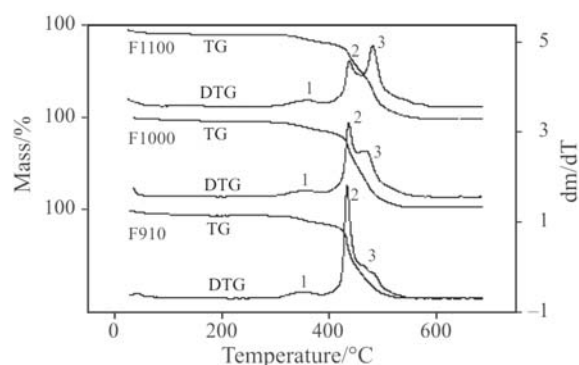


Fig. 2 TG/DTG traces of Flemion[®] H⁺ substituted samples

Table 2 TG/DTG onset temperatures and mass loss data for different cations and *EW*

Events data		Water loss up to 375°C/%	Side groups decomposition		Backbone decomposition		Residual mass/%
			$T_{\text{onset}}/^{\circ}\text{C}$	mass loss/%	$T_{\text{onset}}/^{\circ}\text{C}$	mass loss/%	
H ⁺	F910	14.50	429	49.86	455	30.43	5.2
	F1000	12.26	430	40.02	456	42.67	5.0
	F1100	10.59	429	30.43	470	51.85	7.1
Li ⁺	F910	6.90	408	73.7	482	10.2	9.3
	F1000	5.06	430	69.0	493	13.8	6.05
	F1100	4.21	419	82.3	498	7.90	<1
Na ⁺	F910	0.26	494			87.5	12.7
	F1000	2.12	496			86.4	11.0
	F1100	0.18	497			88.2	11.9
K ⁺	F910	0.19	457			86.9	13.7
	F1000	0.36	461			88.1	12.2
	F1100	0.19	460			86.9	12.6
Rb ⁺	F910	0.72	447			81.6	17.6
	F1000	0.99	448			80.9	19.3
	F1100	<0.1	451			81.8	18.2
Cs ⁺	F910	2.49	491			86.0	11.8
	F1000	0.61	495			88.0	11.2
	F1100	0.93	500			89.4	9.1

as the Nafion membrane reported in earlier literature [9]: decomposition occurring mainly in 3 steps related to respectively a water loss (1), side chain groups decomposition (2) and backbone decomposition (3). Similar mechanism can be observed in Table 2 for TG/DTG traces of Li⁺ Flemion[®] membranes. For the membranes substituted by the other cations, one step decomposition curve is observed, i.e., an appreciable mass loss process starting above 450°C after only a small water loss below 200°C.

The water content of the membranes decreases progressively with increasing *EW* and the counter-cation charge density, indicating that membranes with counter-cations other than H⁺ and Li⁺ present water loss less than 1% mass due to their large ionic radii. This result is similar to those previously reported for Nafion[®] membranes, since large *EW* membrane is connected to smaller IEC, smaller and less organized hydrophilic aggregates and thus absorbs less water [6].

H⁺ from membranes present a relation between the mass loss% for the second and third decomposition steps and the membrane *EW*. As the *EW* grows, the second step mass loss% decreases by 10% while the third step's increases by almost the same amount, which agrees with the assumption that high *EW* means less side chain groups attached.

This *EW* effect is observed only for H⁺ samples, because cation substitutions make the sulfonate groups to be under strong ionic interaction and this increases the decomposition temperature of the second step as observed on Table 2. Hence, the second and third processes become merged into the onset decomposition temperatures higher than 450°C. For Li⁺ substituted membranes this effect is not observed, and it

may be attributable to the large water content within their aggregates, which minimize the strong ionic interaction between Li⁺ cation and sulfonate groups. Temperature near 450°C is near to the backbone decomposition onset temperature observed for H⁺ samples (step 3), so the monovalent cations substitutions would increase the membranes' thermal stability.

EW seems to be independent of this thermal stability, but by looking closer the counter-cation effect, an interesting behavior is observed (Table 2): Li⁺ samples start to decompose around 420°C in a behavior similar to H⁺ samples due to the relatively high water content inside the cluster, but for Na⁺, K⁺, Rb⁺ and Cs⁺ the stabilization is increased by around 30°C (K⁺ and Rb⁺ membranes) or around 80°C (Na⁺ and Cs⁺ membranes). This would give evidence that the polymer structures involved for the sulfonated side chain groups interacting with K⁺ and Rb⁺ are weaker than those for Na⁺ and Cs⁺.

K⁺ and Rb⁺ have relatively similar z/r values – where z is the charge and r the proper ionic radius – (0.00658 and 0.00602 Å⁻¹, respectively) that are far from Na⁺ and Cs⁺ values (0.00862 and 0.00552 Å⁻¹, respectively) and the water content of membranes substituted by them does not change largely (Table 2). So it is possible to conclude that the former two alkali metal cations accommodated within the sulfonated aggregates in a different way than the latter ones. Also, their interaction with the polymer side groups seems to be somehow balanced by a morphological arrangement of the polymer network around these cations.

Table 2 shows also the residual mass after the TG analysis is performed, showing an expected re-

sults from H^+ up to Rb^+ samples, i.e., increasing residual mass along with increasing ionic mass, but an unexpected result is observed for Cs^+ samples that show a lower residual mass than expected. This may be partly due to incomplete substitution for Cs^+ ion due to its large ionic radius.

The different ionic interactions for alkali metal cation substituted Flemion[®] membranes can change the membrane structures and also their morphology. This can be observed in the samples' DSC trace profile (Figs 3–5, respectively, for 910, 1000 and 1100 EW samples).

The DSC traces show a single endothermic peak around 120°C, similar to that observed for Nafion[®] membrane [8] and is related to the water desorption from the sulfonated aggregates within the membrane, followed by morphology changes. The endothermic peak is largest for Li^+ membrane, and decreases in the order: $Li^+ > Na^+ > K^+ > Rb^+$, but for Cs^+ membrane increases again. This peak area should be related to the amount of water desorbed at this temperature. It is interesting to note that the amount of desorbed water is related to the amount of initially absorbed water in the equilibrated solution of various cation salts.

Figure 6 is a plot of the peak temperature determined from the DSC curves vs. the ratio z/r for the three EW membranes and the alkali metal cation substitutions.

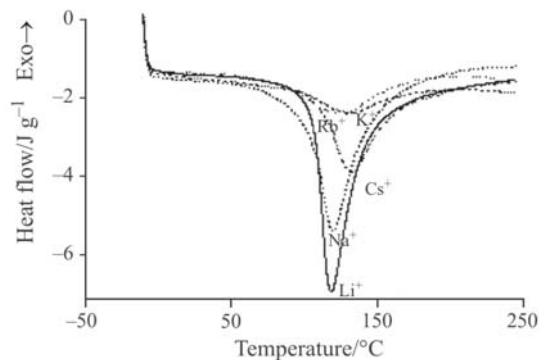


Fig. 3 DSC traces of Flemion[®]-910 samples

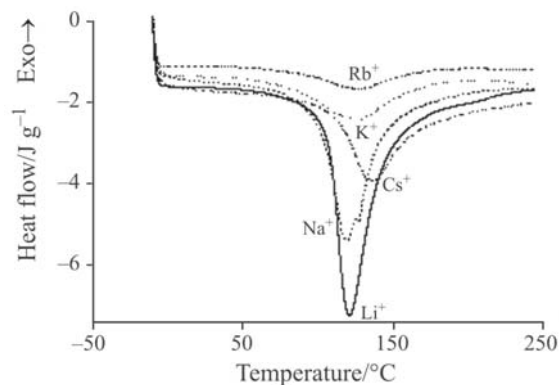


Fig. 4 DSC traces of Flemion[®]-1000 samples

K^+ , Rb^+ and Cs^+ substituted membranes show a higher peak temperature than the Na^+ and Li^+ substituted ones for all EW samples. For small size cations the peak temperature are almost the same, independent of membrane EW, but for large cations the peak temperature show a large dispersion for the different EW. This observation indicates that the interaction between sulfonated groups and counterions with intervening water molecules is stronger for the larger size cations than for the smaller size ones. So, the water contents in the clusters are dependent on the cations size and the membrane EW. Normally low EW gives a low peak temperature and large cations size result in high peak temperature. This behavior can be explained by considering the intensity of interactions between water molecules and the cations inside the aggregates and also of the cluster structure. The size and the cluster structure for the different EW membranes are not yet fully clarified, and this should be the subject of future study.

For K^+ and Rb^+ substituted membranes, the cations are inserted within the aggregates in a different conformation than the other ones, with water molecules intervening between the cation and sulfonate groups. As water requires higher temperatures to leave the aggregates for these membranes (Fig. 6), the

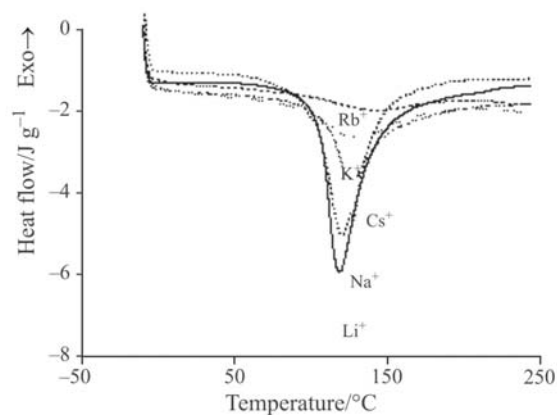


Fig. 5 DSC traces of Flemion[®]-1100 samples

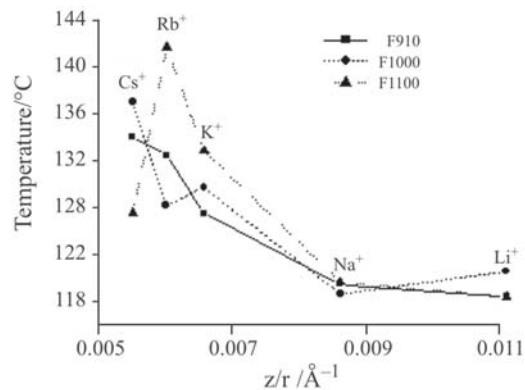


Fig. 6 DSC peak temperatures of Flemion[®] samples

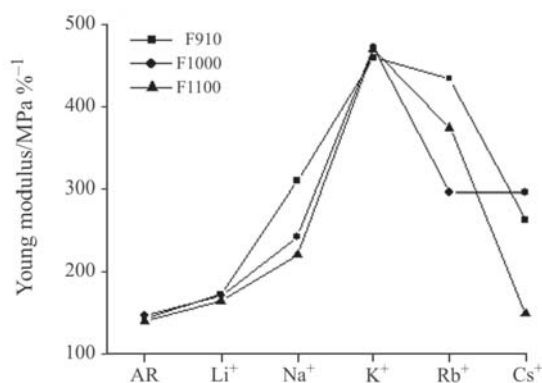


Fig. 7 DMA stress-strain Young modulus results for Flemion[®] membranes at 30°C

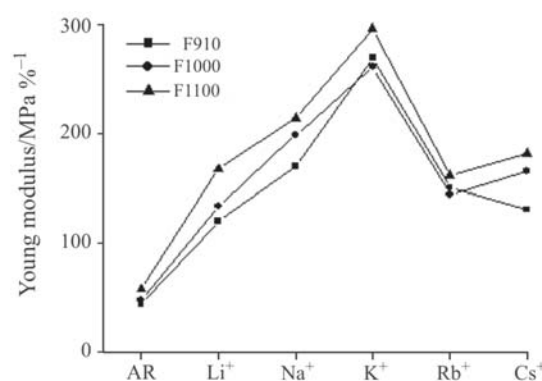


Fig. 8 DMA stress-strain Young modulus results for Flemion[®] membranes at 80°C

conformation assumed by them is such that water molecules inserted between cation and sulfonate groups balance the direct ionic interaction, which can explain the lower decomposition temperature observed for these membranes (Table 2). As the aggregate size decrease, this effect is more pronounced and as observed for high *EW* membranes, results in high DSC peak temperatures. For the Na⁺ membrane where this balance effect seems to be absent, the existence of water seems to shift the DSC peak temperature to lower directions (Fig. 6), indicating the involvement of less confined water molecules for these systems. Note that to these hydrophilic cations larger amount of water molecules are initially surrounding, and this may lead to higher freedom of motion for water molecules.

As cation substitutions change Flemion[®]'s thermal behavior, it should also change its mechanical resistance. DMA stress-strain curves of all analyzed membranes were performed at 30 and 80°C in order to evaluate the mechanical behavior. Figures 7 and 8 show the Young modulus (YM) data obtained.

The mechanical resistance of the membranes changed with *EW*, in a way that YM being higher for lower *EW*, at 30°C. It can be understood that the

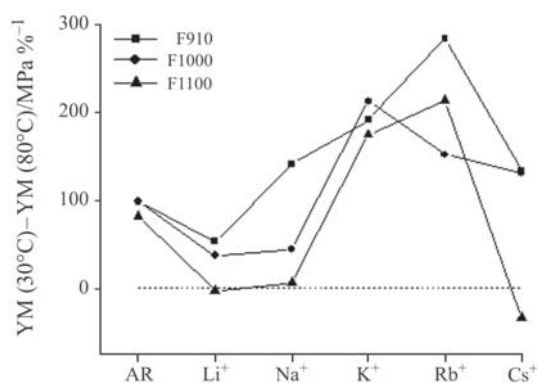


Fig. 9 Difference between Young modulus values at 30 and 80°C for Flemion[®] samples

larger and more organized are the aggregates for low *EW* membranes, the more stable the structures around the counteranions become and, as a result, it can resist more to stress effects. At 80°C, the *EW* effect is larger and reversed, due probably to the direct ionic contact interaction being stronger.

Figure 6 shows that H⁺ membranes (AR) have low YM than any other cation substituted membranes, and almost the same value for all *EW* membranes. Also YM values for Li⁺ substituted membrane at 30°C behave like H⁺ membranes. At 80°C (Fig. 8) the H⁺ membranes (AR) have lower YM values compared to the same membrane at 30°C. For other cation substituted membranes, increasing the temperature resulted in YM decrease.

Stress-strain analysis show also that Flemion[®] K⁺ membranes, in both temperatures, present the highest YM compared to membranes substituted by other alkaline cations. This results can indicate that the cluster arrangement and water content around K⁺ cation are those that fit the best ionic interaction. So, the ionic interaction strength depends on the cation size, water contents, temperature and the membrane *EW*.

Figure 9 shows the difference between the YM at 30°C and that at 80°C for all samples considered.

Flemion[®] 1100 samples change less with increasing temperature, this effect being more pronounced as the *EW* value decrease. It is reasonable to assume that as the cluster size becomes smaller, it absorbs less water and, with increasing temperature it changes to less aggregate arrangement and the ionic interactions, so that the change of the mechanical properties is small.

Conclusions

TG/DTG thermal data indicated that alkali cation substituted Flemion[®] membranes change the amount of cluster absorbed water and the decomposition temperature. It is confirmed that low *EW* membranes gener-

ate larger ionic clusters absorbing more water. Alkaline cations also improve the material's thermal resistance by almost 80°C (for Na⁺ and Cs⁺) and 30°C for K⁺ and Rb⁺, allowing the conclusion that for these cations the ionic interactions are balanced inside the membrane's ionic cluster domain due to a favorable arrangement of sulfonated side groups around the cations. This effect increases mechanical tension resistance of K⁺ and Rb⁺ samples. Cs⁺ samples showed a low mass residue that can indicate an incomplete substitution under the same conditions as other cations, due to its large ionic radius.

The water contents in the cluster depend on the cation size and the membrane *EW*. The single endothermic peak on DSC curves are approximately the same for all *EW* membranes for small size cations, but have a high dispersion for large size cations. The amounts of water, the sulfonate groups arrangements and the cations size define a conformation that are responsible for a good ionic interactions resulting in a high DSC peak temperature.

DMA stress-strain data show that alkali metal cations improve the membranes' mechanical resistance. High temperature caused a decrease in the YM. The water content and the interacting mode with cations are important parameter for mechanical properties of perfluorosulfonated membranes.

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