

Proton exchange membranes based on the short-side-chain perfluorinated ionomer

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Abstract

Due to the renovated availability of the base monomer for the synthesis of the short-side-chain (SSC) perfluorinated ionomer, fuel cell membrane development is being pursued using this well known ionomer structure, which was originally developed by Dow in the 1980s. The new membranes under development have the trade name Hyflon Ion. After briefly reviewing the literature on the Dow ionomer, new characterization data are reported on extruded Hyflon Ion membranes. The data are compared to those available in the literature on the Dow SSC ionomer and membranes. Comparison is made also with data obtained in this work or available in the literature on the long-side-chain (LSC) perfluorinated ionomer (Nafion). Thermal, visco-elastic, water absorption and mechanical properties of Hyflon Ion are studied. While the general behavior is similar to that shown in the past by the Dow membranes, slight differences are evident in the hydration behavior at equivalent weight (EW) < 900, probably due to different EW distributions. Measurements on dry membranes confirm that Hyflon Ion has a higher glass transition temperature compared to Nafion, which makes it a more promising material for high temperature proton exchange membrane (PEM) fuel cell operation ($T > 100^\circ\text{C}$). Beginning of life fuel cell performance has also been confirmed to be higher than that given by a Nafion membrane of equal thickness.

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1. Introduction

1.1. Long- and short-side-chain perfluorinated ionomer membranes

Perfluoropolymer ionomers are known since the late 1960s, when the Nafion ionomers were developed by the Du Pont company and employed as polymer electrolyte in a GE fuel cell designed for NASA spacecraft missions. Since then, Nafion polymers have found wide application especially in the chlor-alkali industry as membrane materials, but also in other applications where very high chemical inertness (given by the perfluorinated structure) and low resistances to cation transport are required at the same time.

In more recent years, the growing interest related to cleaner energy production technologies has promoted the

consideration and study of ionomers as proton exchange membranes (PEMs) in fuel cells. Again, due to electrochemical stability requirements, perfluorinated materials have been preferred as the best candidates for satisfying the needs of the system. Innumerable papers investigating the properties of Nafion under virtually all possible aspects have been published. The data available include fuel cell performance, transport characteristics (of water, gases, protons), swelling and solubility properties, mechanical, visco-elastic and thermal behavior, morphology and structure, etc. Nafion is therefore by far the most extensively used and studied ionomer for fuel cell application.

In the mid 1980s, Ballard Power Systems showed significant improvements in fuel cell performance using ionomer membranes obtained from Dow Chemical [1]. This ionomer, commonly known as the Dow ionomer, is perfluorinated and similar in structure to Nafion, save for a shorter pendant side-chain which carries the functional ion-transporting group (see

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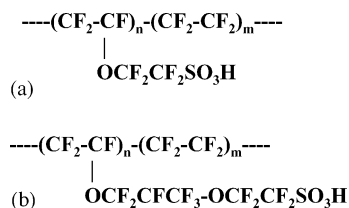


Fig. 1. (a) Hyflon Ion/Dow and (b) Nafion polymer structures.

Fig. 1), wherefrom this ionomer is known as the short-side-chain (SSC) ionomer. Correspondingly, Nafion is sometimes referred to as the long-side-chain (LSC) ionomer. Though demonstration of higher power-generating capability in fuel cell was demonstrated using the Dow ionomer, after the filing of a series of patents by the Dow company [2–10], the industrial development of this interesting ionomer structure was abandoned. No commercialization of these very promising experimental membranes followed. The complexity of the Dow process for the synthesis of the base functional monomer used for the production of the SSC ionomer [11], was possibly one of the reasons, which caused this interesting development to be abandoned.

Probably, due the lack of commercial availability of SSC ionomer samples, the scientific literature is not very rich of works describing the characteristics of this material. This is actually quite surprising when one thinks that the first works on the SSC ionomer already put in evidence the big property differences induced by the presence of a shorter side-chain, and that the Dow patents showed possible interesting applicative advantages deriving from these differences.

1.2. SSC Dow ionomers: state of the art

The works by Tant et al. [12,13] contain very significant data on SSC ionomers of different equivalent weights (EWs) and highlight important differences induced by the shorter length of the side chain compared to a LSC ionomer. In particular, crystallinity – measured by wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) – and dynamic–mechanical properties – investigated by dynamic mechanical spectroscopy (DMS) – are studied for all forms of existence of the ionomer during the synthesis process, i.e., the precursor (SO₂F), salt (SO₃Na) and acid (SO₃H) form. The most significant differences found are the much higher crystallinity at given equivalent weight of the SSC ionomer compared to the LSC one and the higher glass transition temperature (*T_g*) of the SSC ionomer. This is true for all ionomer forms examined. Extrapolation of both WAXS and DSC data on different EW precursor polymers show disappearance of crystallinity below 700 EW for the SSC ionomer, compared to 965 EW for Nafion. Conversion of the precursor form to the salt or acid form is shown to result in a reduction of the crystallinity level (by

WAXS): an 800 EW SSC ionomer shows 7% crystallinity in the SO₂F form and no crystallinity in the acid or salt form.

The work by Moore and Martin [14] confirms the results obtained by Tant et al. [12] regarding higher crystallinity of SSC ionomers. In particular, a more intense crystalline diffraction peak is measured by WAXS on a 909 EW SSC ionomer compared to a Nafion 1100 EW in the sodium sulfonate form. No crystallinity can be detected on an 800 EW SSC in this form, in agreement with the data reported by Tant et al. [12]. DSC thermograms on the Na⁺ form of different EW SSC ionomers show thermal transitions, which are not easily put in relation to those observed by DMS in the work by Tant et al. [12]. Two endotherms are measured for all EW ionomers in the 150–180 °C interval and in the 270–300 °C interval, respectively, while a higher temperature endotherm (about 335 °C) is detected only for high EW ionomers. This high temperature endotherm can be put in relation to the one observed for higher EW weights around 323 °C by Tant et al. [12] on the SO₂F form, which would induce to think of a PTFE-like secondary crystalline structure which is not disrupted by conversion of the sulfonyl groups to sulfonate groups. The lower transitions do not have a step-like shape typical of a glass transition but are not related by Moore and Martin [14] to crystallinity due to their existence also for a 635 EW polymer. They are described as glass transitions of the matrix and ionic cluster phase, respectively. Lower liquid water absorption values are shown for the SSC versus LSC ionomer at given EW (Na⁺ form), and attributed to the higher crystallinity of the SSC ionomer; in fact, elimination of crystallinity by melting and quenching is shown to result in higher water absorption values also for a 909 EW SSC ionomer. Small-angle X-ray scattering (SAXS) was used to demonstrate an ion-cluster structure similar to that of Nafion, with cluster dimension decreasing with increasing EW. Finally, dissolution conditions for EW ≥ 800 SSC ionomer Na⁺ form membranes in water–alcohol mixtures are reported to be more severe than those required for Nafion membranes. This is again attributed to higher crystallinity.

The paper by Eisman [15] explores the properties of acid form SSC ionomer membranes under several aspects, some of which specifically interesting for fuel cell application. In particular, water sorption, HCl solution sorption, ionic conductivity, gas (H₂ and O₂) permeability, visco-elastic and tensile data are reported. Gas permeability of an 850 EW SSC ionomer is reported to be similar to that of Nafion. Ionic conductivity data are reported only in 5.5% HCl soaked membranes. These measurements have limited sense for fuel cells, since no other electrolyte than the membrane is present in this case. However, comparison to the LSC ionomer can be made in relative terms: the SSC ionomer shows lower conductivity at same EW. The same conductivity of a 1100 EW Nafion is obtained with a 900 EW Dow membrane. Conductivity is shown to sharply increase at decreasing EWs for the SSC ionomers. A higher *T_g* for the SSC ionomer is confirmed

by DMS as reported by Tant et al. [12]. More specifically, $T_g = 110^\circ\text{C}$ is reported for Nafion, while $T_g = 165^\circ\text{C}$ (with scarce dependence on EW) is measured for the SSC ionomer in the acid form. It is commented that this could allow for high temperature operation ($>100^\circ\text{C}$) in fuel cells.

Additional physical data on SSC ionomers are reported in [16–20].

Tsou et al. [16] study the hydrogen diffusion and solubility in SSC ionomer membranes (sulfonic and carboxylic) and their water uptake from Na_2SO_4 solutions. For the sulfonic form, it is found that hydrogen solubility decreases at increasing EW, and that it stays practically constant above 900 EW. On the other hand, the hydrogen diffusion coefficient shows an interesting behavior exhibiting its maximum value at about 950 EW.

The work by Ezzell et al. [17], though focused on chlor-alkali, reports useful data on membrane hydration versus LSC ionomers. It is shown that the lower hydration of the Dow membranes results in higher caustic current efficiency and lower cell energy consumption.

Also the paper by Kohls et al. [18], though dedicated to the study of the separation of alkenes by using Ag^+ -neutralized perfluorosulfonic acid membranes, reports interesting data on SSC ionomers. Specifically, water uptake and dimensional variation upon hydration of an 800 EW SSC ionomer neutralized by different counter-ions (H^+ , Na^+ and Ag^+) are studied.

Boakye and Yeager [19] study the water sorption and ionic diffusion of both cations and anions in SSC ionomers of different EW in the Na^+ and Cs^+ forms.

Eisman [20], besides showing increased fuel cell performance of an 800 EW Dow membrane of $130\ \mu\text{m}$ thickness versus a Nafion N117 (1100 EW, $175\ \mu\text{m}$), uses the current interruption method to estimate membrane proton resistance. Value ranges for tensile strength, water uptake, water permeability and gas (H_2 and O_2) permeability are also reported for the Dow membranes.

Fuel cell performance of SSC versus LSC membranes is reported also by Prater [1]. This work shows the improvements obtained by Ballard Power Systems by substituting Nafion membranes with Dow membranes in fuel cell (single cell and stack). Considerable improvement is shown also with membranes of similar (but not identical) thickness as N117. However, the EW of the Dow membranes used is not disclosed.

Finally, more studies involving SSC ionomers under different aspects can be found in [21–28].

1.3. Hyflon Ion membranes

Recently, due to a different and more simple route for the synthesis of the base monomer for SSC ionomers [11], Solvay Solexis has restarted the development of polymer electrolyte membranes based on this perfluorinated ionomer type. The commercial name for this ionomer (and the membranes made therefrom) is Hyflon Ion. Main focus of this novel development is membranes for fuel cell application.

Preliminary data on Hyflon Ion membranes, including fuel cell performance, mechanical characteristics and hydration properties, were published in [11]. The present work studies further these new membranes which are becoming available, with specific comparisons to data on Dow membranes (old SSC membranes) and Nafion (LSC membranes). The Hyflon Ion membranes on which more data are reported are in the interval around 850 EW. This is because such an EW has been found as the most adequate in terms of balance of properties for fuel cell application.

2. Experimental

2.1. Differential scanning calorimetry

Differential scanning calorimetry experiments were performed using a Perkin-Elmer DSC7 calorimeter equipped with a refrigeration unit for controlled cooling to -20°C . Scans were made on samples weighing around 10 mg in the temperature range from 10 to 350°C at a heating rate of $10^\circ\text{C}\ \text{min}^{-1}$. Before measurement, all samples were pre-treated at 350°C for 15 min.

2.2. Dynamic mechanical spectroscopy

Measurements were carried out according to ASTM D4065 by means of a controlled strain mechanical spectrometer (Rheometrics ARES) equipped with a very sensitive transducer (low torque resolution: $0.02\ \text{g}\ \text{cm}$) that allows to perform measurements on very thin samples. The specimen has a rectangular shape (length $\sim 30\ \text{mm}$; width $\sim 10\ \text{mm}$) and is subjected to mechanical oscillations of constant amplitude and constant frequency (1 Hz). The mode of deformation is torsional. The damping and shear moduli are obtained from measurements of the torque that the sample generates in response to the applied deformation. The spectrometer is operated with a continuous flow of liquid nitrogen, which enables the samples to be scanned from -150 to 200°C at a heating rate of $2^\circ\text{C}\ \text{min}^{-1}$. Measurements are taken at 2°C intervals.

The measurements were started after drying the specimens in the rheometer under a flow of dry nitrogen at $+150^\circ\text{C}$ for 30 min.

2.3. Water uptake and dimensional variation

Water uptake from liquid water at 100°C was measured by weighing the samples dry and after soaking in boiling water for 30 min. Weighing after water soaking was performed by blotting the samples dry on the surface and rapidly weighing.

Water uptake from saturated water vapor was measured by weighing the samples dry and after exposure to boiling water vapor in a closed vessel.

Dry weight was determined on the samples kept for 1 h at 105°C under vacuum.

Dimensional variation was measured by means of a ruler with a precision of 1 mm on samples of 20 mm × 50 mm dimension.

2.4. Tear resistance

Tear resistance tests were carried out on samples pre-conditioned at 23 °C and 50% relative humidity. Initiation resistance was measured according to ASTM D1004, while propagation resistance was measured according to ASTM D1938 at a speed of 250 mm min⁻¹.

2.5. Fuel cell performance

Fuel cell performance was measured on a Fuel Cell Technologies test station in a 10 cm² active area single cell. The fuel cell was operated at 75 °C and 2.5 bar absolute humidifying the gas streams in water bubblers at 80 °C. Commercial Elat (E-Tek) gas diffusion electrodes with 0.6 mg Pt cm⁻² catalyst loading (30% Pt/C) and 0.7 mg cm⁻² Nafion loading were used. The samples were assembled in the cell without previous hot pressing to the electrodes. Before taking the polarization curve measurement, the membrane–electrode assembly was conditioned in the cell at the temperature, pressure and relative humidity conditions of the measurement and at a fixed voltage (0.4 V) until the current was constant for at least 3 h.

3. Results and discussion

3.1. Thermal behavior

The thermal behavior of different EW precursor Hyflon Ion polymers was analyzed by DSC. Before the measurement, all samples were pre-treated at 350 °C for 15 min. The reported data represent therefore the second polymer fusion.

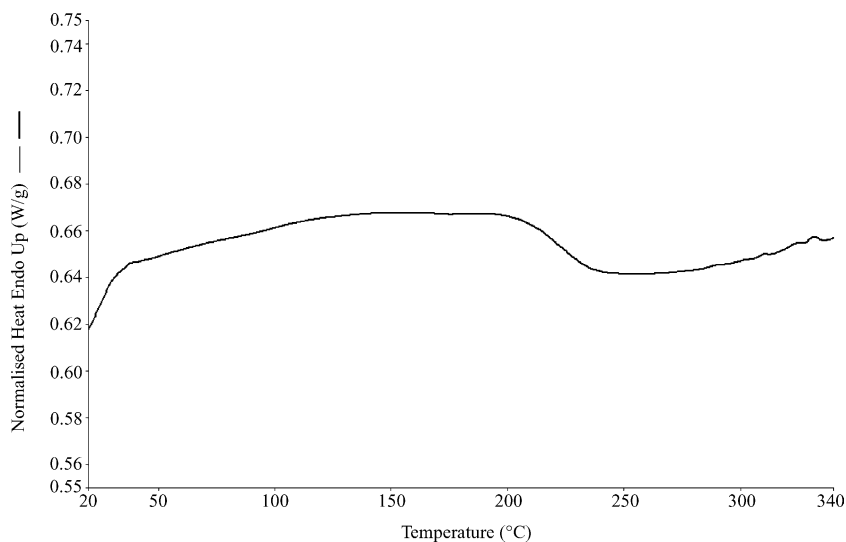


Fig. 2. DSC curve for an 850 EW Hyflon Ion precursor polymer.

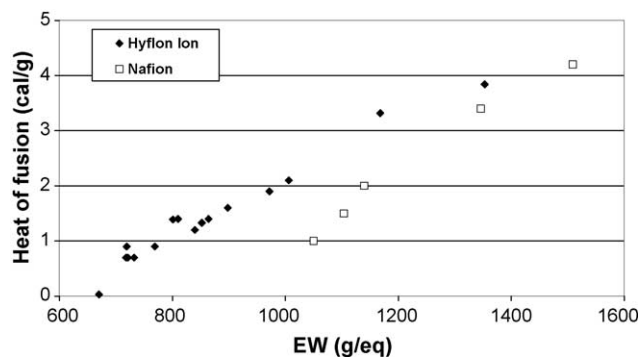


Fig. 3. Heats of second fusion of Hyflon Ion precursor polymers vs. Nafion as a function of EW.

An example of the curve shape which is typically obtained is reported in Fig. 2, where the spectrum of an 850 EW SO₂F form polymer is shown. It can be seen that while the temperature of complete melting (T_{cm}) is well identified, the initial melt temperature is not clearly defined. This is the case for all EWs examined, and is in line with what found by Tant et al. [12]. These authors investigated the melting behavior by variable temperature WAXS, and detect by this method a single initial melt temperature of 130 °C for different EW ionomer precursors. This temperature could therefore be used as a reference initial integration temperature for the calculation of the heat of fusion from the DSC curves. It is not clear, however, if this temperature value was used by Tant et al. [12] to calculate the heat of fusion which they report, nor how they selected a baseline for the integration of the spectra. Therefore, it is difficult to make any comparison to their data. Qualitatively, measurements carried out on Hyflon Ion ionomer precursors confirm the higher crystalline content of SSC ionomers compared to LSC ionomer, as shown by the heat of fusion data reported in Fig. 3. Note that these data must be considered only qualitative due to the uncertainties

in selecting the baselines for the DSC spectra integration. No exact extrapolation to zero crystallinity is attempted due to this uncertainty. However, it can be seen that zero crystallinity occurs approximately around 700 EW for Hyflon Ion and between 900 and 1000 EW for Nafion. Therefore, there is a wide region of EWs between 700 and 900 where Nafion is completely amorphous while Hyflon Ion still retains some crystallinity. In this EW range, Hyflon Ion ionomers can be obtained with high conductivity and good mechanical properties and resistance to solubilization (due to crystallinity). The combination of these properties would not be possible in this EW interval with a LSC ionomer.

More exact numbers (compared to the heat of fusion) can be reported for the temperature of complete melting (T_{cm}). These data are shown as a function of EW in Fig. 4. It can be seen that there is a good correlation between the EW and the T_{cm} , with T_{cm} increasing with EW. Due to the linear behavior of this dependency, a line has empirically been used to fit the data in Fig. 4. T_{cm} data obtained by Tant et al. [12] by WAXS on Dow polymers have also been reported for comparison and are in good agreement with the data found in this work.

3.2. Visco-elastic properties

The visco-elastic properties of an 850EW acid form SSC (Hyflon Ion) ionomer versus a 1100EW LSC (Nafion) ionomer were studied by DMS. The measurements were started after drying the specimens inside the spectrometer under a flow of dry nitrogen at 150 °C for 30 min. Preliminary tests showed that this was the procedure giving the most reproducible results.

Fig. 5 shows the dynamic mechanical spectrum of the Hyflon Ion ionomer, while the curve for the Nafion N117 (1100 EW) is shown in Fig. 6. Table 1 summarizes the three relaxation processes as found from the peaks of the damping = $\pi \tan(\delta)$ reported in Figs. 5 and 6 for the two ionomer types. These relaxations are: γ peak (occurring at the same temperature of poly-tetrafluoroethylene), β peak (probably due to water) and α peak, commonly considered as the glass transition of the ionic phase of the material.

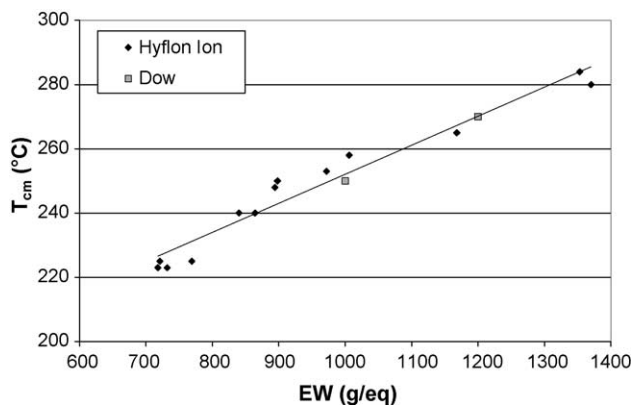


Fig. 4. Temperature of complete fusion of SSC precursor polymers as a function of EW.

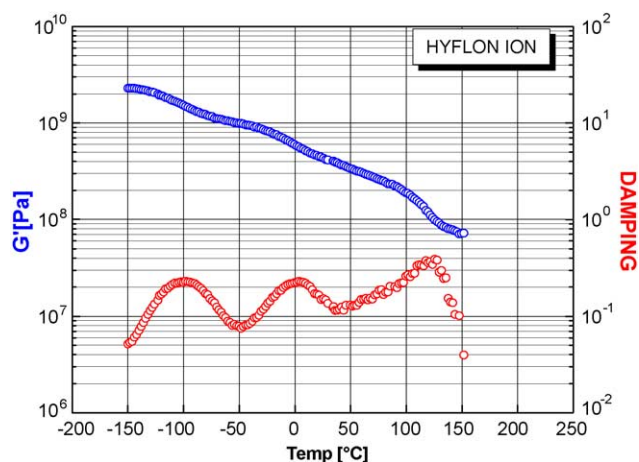


Fig. 5. Dynamic mechanical spectrum of an 850EW Hyflon Ion acid form membrane.

Table 1

Relaxation temperatures as detected by DMS for Hyflon Ion and Nafion acid form membranes

Sample	Relaxation processes		
	γ (°C)	β (°C)	α (°C)
Hyflon Ion 850EW	$\sim(-98)$	$\sim(+1)$	$\sim(+127)$
Nafion 117	$\sim(-102)$	~ 0	$\sim(+67)$

When comparing these data to those previously obtained in the literature [15], the great difference between the literature value of the α -transition temperature T_{α} and the value found in this work is immediately apparent. This is true for both ionomer types. More in detail, Eisman reports a T_{α} of 165 °C for the SSC and of 110 °C for the LSC ionomer, against 127 °C for the SSC and 67 °C for the LSC as found in this work (Table 1). This temperature difference is probably due to the different hydration state of the membranes between the two works. As a matter of fact, the measurements carried out by Eisman were performed on samples, which were water

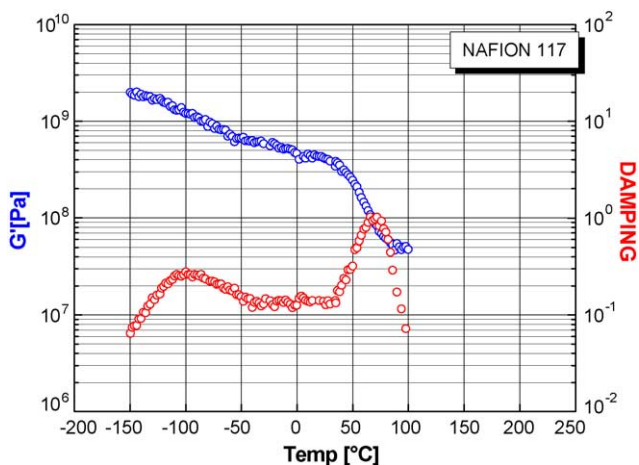


Fig. 6. Dynamic mechanical spectrum of a 1100EW Nafion acid form membrane (N117).

soaked and quickly cooled to the starting measurement temperature, i.e., highly hydrated samples. On the contrary, in the present work samples have been thoroughly dried in nitrogen before the measurement in order to optimize reproducibility. Lower T_{α} values for the dry samples is in line with decreasing T_{α} values observed on undried samples upon successive thermal cycling in the spectrometer. In spite of the difference found on T_{α} between this work and the literature, it must be noted that a difference of about 60 °C between Hyflon Ion and Nafion (in favor of Hyflon Ion) still remains, very near to the difference found by Eisman [15]. This difference suggests Hyflon Ion membranes to be more suitable than LSC membranes for high temperature fuel cell operation (>100 °C), as already indicated in the literature for the Dow membranes.

3.3. Water uptake

The water absorption behavior of acid form membranes from liquid water and saturated water vapor at 100 °C was analyzed. Different EW Hyflon Ion ionomers were studied and compared to Nafion.

Water uptake in liquid water at 100 °C as a function of EW is reported in Fig. 7 and compared to the absorption of Nafion membranes as reported in the literature [10] and measured by ourselves. The water absorption is notably lower for the SSC membranes at a given EW. Therefore, same water uptake is obtained with a lower EW SSC ionomer. A water uptake of 35%, typical of a 1100 EW Nafion membrane, is obtained with a 925 EW Hyflon Ion. Typical hydration at 100 °C for an 850 EW Hyflon Ion is 45%. From the curve shown for SSC ionomers in Fig. 7, it can be noted that at EW moving downwards to 850, the water uptake curve becomes progressively steeper. Therefore, proper compositional control in polymerization is necessary in this interval of EWs to obtain membranes, which have a reproducible water uptake behavior.

Water uptake in liquid water at 100 °C for Hyflon Ion membranes is reported in Fig. 8 compared to a collection of literature data on Dow ionomers [3,8–10]. It can be seen that the agreement between the two sets of data is good above

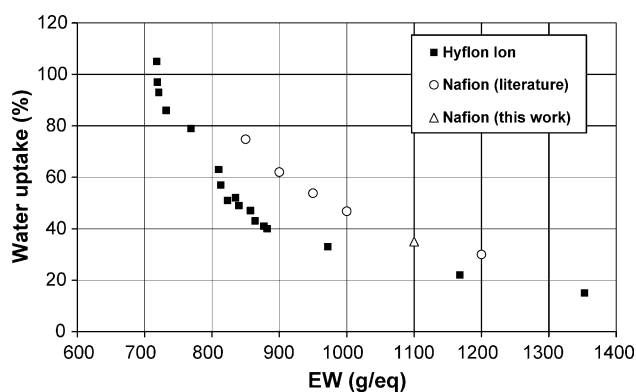


Fig. 7. Water uptake from liquid water at 100 °C for extruded Hyflon Ion and Nafion membranes as a function of equivalent weight.

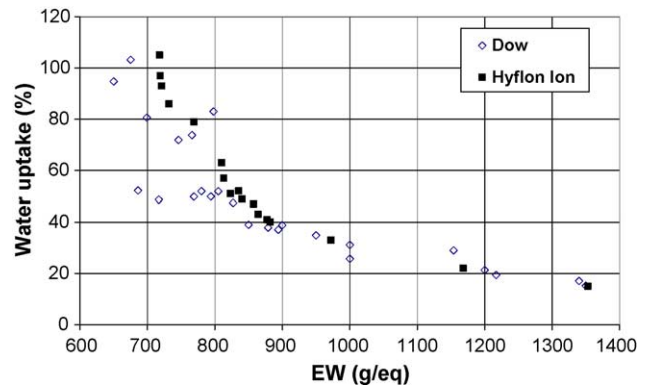


Fig. 8. Water uptake from liquid water at 100 °C for extruded Hyflon Ion and Dow membranes as a function of equivalent weight.

EW = 900, while the hydration of Hyflon Ion seems to be systematically higher below this EW value, with the exception of one point. The Dow data however have a very high scattering. Different hydration values could result from different EW distributions in the Hyflon Ion and Dow polymers.

The dimensional variation of two different EW Hyflon Ion membranes upon hydration at 100 °C in liquid water is reported in Table 2 and compared to the values measured on Nafion N112 (1100 EW, 2 mils nominal thickness). All membranes measured show anisotropic behavior, which is due to the fabrication process (extrusion). It can be seen that both of the Hyflon Ion membranes show higher dimensional variations in the plane compared to N112. This is consistent with higher water uptakes by weight. It is usually assumed in fuel cell application that the dimensional variation of a membrane should be minimal upon hydration, in order to minimize the buildup of stresses in the system during transitory hydration states, e.g., start-up and shut-down or variable electric power demand. From the data in Table 2, it can be inferred that 850 is a lower EW limit for a SSC ionomer extruded membrane in order not to have a dimensional variation greater than 20% in any direction of the plane. This can be assumed as a criterion of choice of the EW for the selection of Hyflon Ion ionomers for use in fuel cells.

Water uptake from liquid water has been compared to the uptake from saturated water vapor for both Hyflon Ion and Nafion membranes in the acid form. Measurements have been performed on different EW SSC ionomers. The results are reported in Table 3, where the ratio between the uptake from

Table 2
Water uptake and dimensional variation upon hydration in water at 100 °C for Hyflon Ion and Nafion membranes

Membrane	Water uptake (%)	Initial thickness (μm)	ΔI_1 (%)	ΔI_2 (%)
Hyflon Ion 770EW	79	62	24	35
Hyflon Ion 850EW	45	63	10	20
Nafion 112	35	48	5	14

Table 3

Water uptake from liquid water and saturated vapor at 100 °C for different EW Hyflon Ion membranes and Nafion (acid form)

Membrane	EW (g eq ⁻¹)	ΔW_{liq} (%)	ΔW_{vap} (%)	$\Delta W_{\text{liq}}/\Delta W_{\text{vap}}$
Hyflon Ion	670	123	49	2.5
	770	79	44	1.8
	825	49	27	1.8
	1170	22	22	1.0
	1350	15	14	1.1
Nafion 117	1100	35	20	1.8
Nafion 117 [29]	1100	36	23	1.6

the liquid (ΔW_{liq}) and the saturated vapor (ΔW_{vap}) is also reported. From the data it can be seen that the ‘Schroeder’s paradox’ is true also for SSC ionomers, i.e., lower weight absorptions are measured from saturated vapor compared to the liquid. Moreover, it can be seen that the paradox is increasingly important at decreasing EWs. For high EW Hyflon Ion membranes, the uptake from liquid and saturated vapor and virtually identical. In terms of fuel cell operation, this would mean that high EW membranes would behave similarly in the presence or absence of condensed water in the cell, while the behavior of low EW ionomers would be significantly different in the two cases, this difference increasing at decreasing EWs.

Finally, from Table 3, it can be noted that the data measured on Nafion N117 in this work are consistent with those found in the literature [29].

3.4. Mechanical properties

It has already been reported [11] that Hyflon Ion membranes of EW around 850 have similar mechanical properties compared to 1100 EW Nafion, both in the dry and hydrated state. This is notable considering the higher water uptake of an 850 EW membrane. It is believed that this coincidence in mechanical properties is related to equivalent levels of crystallinity.

Besides the tensile properties, another mechanical property which is believed to be crucial in fuel cell application is the tear resistance of the membrane. Actually, upon dimensional variation of the membrane during hydration/dehydration cycles, stresses can develop between the edge of the electrode and the gasket, causing catastrophic failure due to tearing of the membrane, with consequent fuel and oxidant mixing.

Table 4

Resistance to tear initiation for Hyflon Ion and Nafion N112 membranes

Membrane	Direction	Average thickness (μm)	Initiation load (N)	Initiation load/thickness (N mm ⁻¹)
Hyflon Ion 815 EW	MD	60.7 (1)	3.4 (0.1)	55 (3)
	TD	59.7 (1)	4 (0.4)	66 (6)
Nafion N112	MD	51.7 (2)	2.8 (0.5)	54 (8)
	TD	53.7 (3)	3 (0.7)	56 (12)
Nafion N112 (DuPont product information)	MD–TD	51	3	58.8 (6000 g mm ⁻¹)

Standard deviations between brackets.

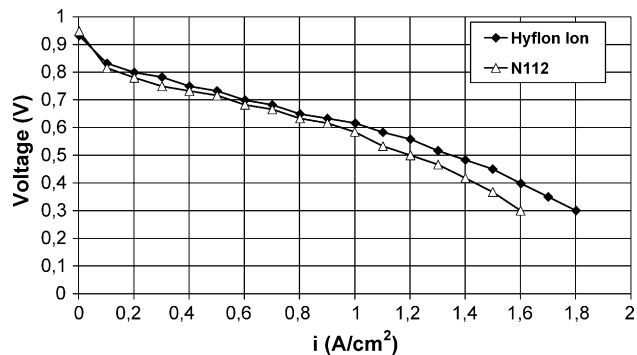


Fig. 9. Polarization curves for an 850 EW Hyflon Ion 50 μm membrane and Nafion N112.

Tear resistance of an 815 EW Hyflon Ion acid form membrane was investigated and compared to that of a Nafion N112 membrane. The samples were conditioned at 23 °C and 50% relative humidity before the test.

Table 4 shows the tear initiation resistance data obtained. The data have been normalized to the thickness since the samples had different thicknesses. Therefore, as stated by the norm, a comparison can be made only on a qualitative basis, since the difference in thickness is by far more than 10%. It is however clear that the two membranes show similar values for the resistance to tear initiation. Moreover, the data obtained in this work are in line with those reported on the N112 Product Information sheet (DuPont).

Resistance to tear propagation is shown in Table 5. Again, the data have been normalized to the thickness and can be compared only qualitatively. Tear propagation resistance is low for all membranes and it is not possible to prove substantial differences between the two membrane types.

3.5. Fuel cell performance

The fuel cell performance (beginning-of-life polarization curve) of an 850 EW Hyflon Ion membrane of thickness 50 μm is reported in Fig. 9 and compared to that of a N112 Nafion membrane. The choice of comparing an 850 EW SSC ionomer with a 1100 EW LSC ionomer has been taken based on same crystallinity level and same mechanical properties, as reported above. The fuel cell was operated at 75 °C and 2.5 bar absolute and the gas streams were humidified at 80 °C. Commercial Elat (E-Tek) gas diffusion electrodes with

Table 5
Resistance to tear propagation for Hyflon Ion and Nafion N112 membranes

Membrane	Direction	Average thickness (μm)	Intiation load (N)	Propagation load/thickness (N mm^{-1})
Hyflon Ion 815 EW	MD	59 (4)	7.4×10^{-2}	1.3
	TD	61 (3)	8.7×10^{-2}	1.4
Nafion N112	MD	47 (1)	7×10^{-2}	1.5
	TD	50 (3)	5.3×10^{-2}	1.1

Standard deviations between brackets.

0.6 mg Pt cm^{-2} catalyst loading (30% Pt/C) and 0.7 mg cm^{-2} Nafion loading were used. It must be noted that, contrary to what was reported previously in the literature, the same membrane thickness was chosen (50 μm). This allows for a fair comparison. It is confirmed that also at same thickness a SSC ionomer membrane gives a higher performance compared to a Nafion membrane. This is due to higher ionic content and higher water uptake, both features resulting in higher membrane conductivity.

4. Conclusions

Thermal, visco-elastic, water absorption and mechanical behavior of Hyflon Ion SSC perfluorinated ionomer membranes has been studied and compared to that of Dow and Nafion perfluorinated ionomer membranes. While the general behavior is similar to that already known for the Dow membranes, slight differences arise in the hydration behavior at $\text{EW} < 900$, probably due to different EW distributions. Measurements on dry membranes confirm that Hyflon Ion has a higher glass transition temperature compared to Nafion, which makes it more suitable for high temperature PEM fuel cell operation ($T > 100^\circ\text{C}$). Beginning of life fuel cell performance of Hyflon Ion has been confirmed to be higher than that of Nafion by comparing polarization curves obtained with membranes of same thickness. Hyflon Ion extruded membranes of EW comprised between 850 and 900 give the best balance of properties for fuel cell application in terms of dimensional stability, mechanical strength and beginning of life fuel cell performance.

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