



Investigation of ionomer structure through its dependence on ion exchange capacity (IEC)

E. Moukheiber, G. De Moor, L. Flandin, C. Bas*

LEPMI, UMR 5279, CNRS – Grenoble INP – Université de Savoie – Université J. Fourier – LMOPS – Bât. IUT – Campus de Savoie Technolac, F-73376 Le Bourget du Lac Cédex, France

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ABSTRACT

The ion exchange capacity (IEC) of conventional ion-exchange perfluorinated membranes based on the so-called Long-Side-Chain (LSC) polymers and their Short-Side-Chain (SSC) Aquivion® derivatives was determined using a series of experimental techniques. Newly developed and already used experimental analyses were compared in terms of sensitivity to the determination of the ion exchange capacity. The use of complementary techniques allows better determination of IEC with an uncertainty of about 3%. This IEC determination method was then applied to membranes with large chemical differences such as copolymers and reinforced membranes. In addition, based on these analyses, relationship between DMA, WAXS, TGA and conductivity parameters and either IEC or the molar number of tetrafluoroethylene (TFE) per comonomer unit are underlined, leading to a more comprehensive approach of architecture in perfluorosulfonic acid (PFSA) polymer membranes.

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1. Introduction

Perfluorosulfonic acid (PFSA) based membranes have been used in portable, stationary, and automotive commercial applications of PEM technology. In addition to providing an attractive combination of performance and reliability, these polymers demonstrated high durability. Much of the early literature describes the properties of conventional ion exchange ionomers based on the so-called Long-Side-Chain (LSC) monomer such as Nafion® (DuPont) [1], Flemion® (Asahi glass) and Aciplex® (Asahi Kasei) [2]. More recently, reliable information about the Aquivion® polymer (Solvay Speciality Polymers) [3] based on the Short-Side-Chain (SSC) monomer and previously known as Hyflon® has become available. This polymer is based on the same monomer as the experimental Dow polymer [4], which has been discontinued. Lately, Minnesota Mining and Manufacturing (3M) claimed the synthesis of another sulfonic monomer containing only a single ether linkage [5].

Perfluorinated ionomers are typically obtained by copolymerization of tetrafluoroethylene and a perfluorovinylether containing a sulfonyl halide such as the perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride (PFSVE) and it can be melt-extruded or tape-cast into membranes [6]. Membranes are commonly characterized

by their thickness, ion exchange capacity (IEC, mmol SO₃H/g polymer) or equivalent weight (EW (g/mol) = 1000/IEC).

One of the most important properties of a PEM is its ability to provide an ionic path for protons to travel from the anode to the cathode. In the case of Nafion® and other PEMs, water channels are believed to form due to phase separation between hydrophilic (ionic groups) and hydrophobic regions (polymer backbone). Proton conduction is thought to occur through these channels [1,7], mediated by the sulfonic acid groups and water. If the level of proton transport is insufficient, a resistive (Ohmic-like) loss is observed with a drastic impact on the performance of the fuel cell [8]. Factors such as polymers structure, morphology, water content and sulfonic content IEC alter proton conduction.

Acid–base titration seems to be the most direct and appealing method for the determination of IEC as well as for the calibration of other analytical methods. The major limitation of acid–base titration is the difficulty of drying the polymer to a known water content value. The drying procedures, mentioned in the literature [9], consist mainly in drying the polymer in the acid form or in the salt form under vacuum at higher temperature (70–140 °C) for at least 12 h, the salt form ionomer being more readily dried than the acid form. However, a large dispersion of ion exchange capacity values for commercially available membranes was reported compared to that provided by the supplier. For instance, for a Nafion 117 (EW = 1100, IEC = 0.91), the value of IEC was found within 0.83–1.02 mequiv./g [10,11]. Besides the technique uncertainty,

* Corresponding author. Tel.: +33 4 79 75 86 24, fax: +33 4 79 75 86 14.
E-mail address: corine.bas@univ-savoie.fr (C. Bas).

Table 1
Property of commercially available membranes.

Commercial reference	Supplier	EW (g/equiv.) ^a	Type	Acronyms
Aquivion® E79	Solvay Speciality Polymers	790 ± 20	SSC	SSC-79
Aquivion® E83		815 ± 20	SSC	SSC-81
Aquivion® E87		895 ± 20	SSC	SSC-89
Aquivion® E91		910 ± 20	SSC	SSC-91
Aquivion® E110		1100 ± 20	SSC	SSC-110
Nafion® Nr211	Ion Power	1020 ± 30 [17]	LSC	LSC-102
Nafion® 111		1100 ± 30	LSC	LSC-110
Nafion® XL100	FuMA-Tech	Unknown	Unknown	XL-110
F-930		900 ± 20	LSC	F-930
F-1030		1000 ± 20	LSC	F-1030
F-1440		1400 ± 20	VDF-HFP-PFSVE ^b	F-1440

^a From datasheet.

^b Determined from our NMR and FTIR analyses as described in Section 3.4.

Chen et al. [12] mentioned inaccessible sites that do not contribute to ion exchange (13% for recast Nafion® and 25% for melt extruded), in a way to explain the difference between titration results and reported value for an EW 1100 commercially available membrane.

The use of samples with various EWs may help create a calibration curve such as peak height ratio 2710/2360 related to SO₂F and overtone CF₂, respectively versus EW for the fast infrared analysis of the precursor resin [9]. Recently, Perusich [13] used the ratio of the absorbance at 982 cm⁻¹ over that at 555 cm⁻¹ in precursor ionomers to compute equivalent weight of thin films while the ratio of SO₂F band, located at 2704 cm⁻¹ over that at 2555 cm⁻¹ was used for the thick film EW measurement. The same author measured the EWs of precursor form ionomers using fluorine-19 NMR at melt temperature between 250 °C and 340 °C. Nevertheless, The FTIR and ¹⁹F NMR methods are not mentioned in literature for the determination of IEC on acid form ionomers. Moreover, ion exchange capacity was also determined from elemental analysis on the basis of the percentage of sulfur content, considering that all sulfur is present as sulfonic groups SO₃H. Nevertheless, the deviation from titration methods was found to be within 5–8% [14].

Other properties of PEMs are directly correlated to ion exchange capacity. A linear relationship is often observed for proton conductivity σ_{H^+} as a function of acid content [15]. The trend generally observed for PEMs is an increase in proton conductivity with increasing IEC. This is assumed to be a result of increasing concentration of acid groups and water content, water being necessary to ensure proton mobility. The water uptake of Aquivion® and Nafion® was also studied as a function of ion exchange capacity [3]. The water uptake increases with increasing the IEC, i.e. the concentration of ionic groups. The structure of the polymer, however, is also important. For a given EW, the shorter branch polymer exhibits lower water absorption. This was explained by considering that the longer branch of the Nafion ionomer increases water uptake by reducing crystallinity [16].

In this paper, the ion exchange capacity of commercially available PFSA membranes is determined using already used techniques with newly developed experimental methods. The aim of the study is to have a global vision about the sensitivity for each technique on the determination of IEC, and to determine a unique method that could be applied on different type of PFSA membrane (LSC or SSC). Finally, the study was extended to a direct determination of IEC on copolymer or reinforced membranes used in PEMFC or DMFC (Direct Methanol Fuel Cell).

2. Experimental

2.1. Commercially available materials

Membranes used in this study (Table 1) were provided by Solvay Speciality Polymers, Ion power Inc. and FuMA-Tech GmbH. The

Equivalent Weight (EW) was measured by the manufacturers using different methods of characterization, namely the analysis of the batch-EW in its precursor form using infrared spectroscopy or the analysis of batch-EW in its acid form using titration. However, these measurements will statistically scatter with some standard deviation [17]. For EW, this is in the order of 2–3% depending on the supplier. All samples were pretreated in an aqueous 10 wt.% in HNO₃ solution for at least 3 h at 80 °C followed by a treatment for 1 h in UHQ water at 80 °C. Four types of PFSA membranes can be distinguished: (i) homogeneous LSC membrane, (ii) homogeneous SSC membrane, (iii) poly(vinylidene fluoride-ter-hexafluoropropene-ter-perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonic acid) (VDF-ter-HFP-ter-PFSVE) terpolymer and (iv) reinforced PFSA membrane. The chemical structure of these polymers is shown in Fig. 1.

For SSC and LSC perfluorosulfonic acid membranes, the chemical structure can be described through the IEC parameter or the number of moles of tetrafluoroethylene (TFE) per mole of comonomer unit, n , related to the EW through Eq. (1).

$$IEC = \frac{1000}{EW} \quad \text{and} \quad n = \frac{EW - M}{100} \quad (1)$$

with M is the molecular weight of the vinyl ether monomers reported in Table 2.

2.2. Membrane characterizations

2.2.1. Chemical characterizations

2.2.1.1. *Titrimetry protocol.* The ion exchange capacity (IEC_T) was determined using acid–base titration method. The samples were soaked overnight in 10⁻³ M NaOH solution to exchange sodium

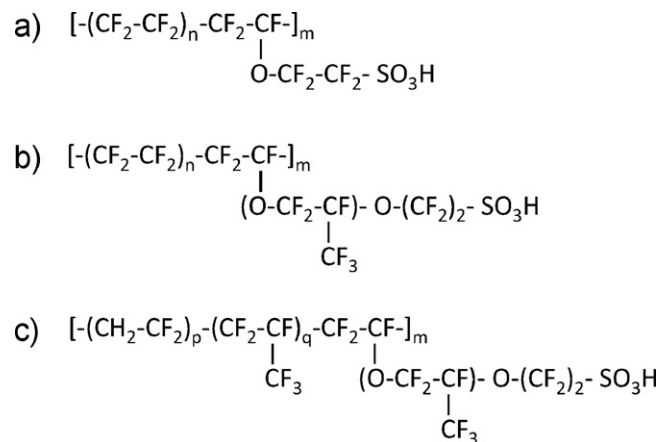


Fig. 1. Chemical structures of PFSA membrane – (a) Short-Side-Chain (SSC) type membrane, (b) Long-Side-Chain (LSC) type membrane, and (c) terpolymer VDF-HFP-PFSVE.

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