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Factors enabling high mobility of protons and water in perfluorosulfonate membranes under low hydration conditions[1]

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ABSTRACT

This work describes new features describing the mechanism of proton and water transport in ion conducting membranes used in Proton Exchange Membrane Fuel Cells. A combination of NMR diffusion measurements and AC conductivity measurements as a function of water content reveal enhanced mobility of protons and water in low equivalent weight 3M perfluorosulfonic acid membranes at low water content. It is proposed that this is a result of the close proximity of adjacent acid-bearing sidechains in the lower equivalent weight ionomers. This proximity allows more facile exchange of species from group to group.

1. Introduction

The process of conduction of protons in aqueous environments is one of the most fundamental aspects of physical chemistry. It is well known that protons exhibit excess mobility relative to other ions in aqueous (or other hydrogen-bonded) systems [1,2]. A large body of work exists attempting to explain these phenomena. Our understanding has evolved from a cartoonish picture superposing 'vehicular' transport, in which protonated water carries the protonic charge, onto 'Grotthus' hopping of protons associated with rotationally mediated 'hand-off' of proton from water molecule to water molecule (or water cluster to water cluster) [3]. Theoretical and experimental studies over the past decade have replaced this appealing but demonstrably incorrect mental construct with a more nuanced picture. Rather than an almost pairwise serial interaction implied by this picture, extended hydrogen-bonded water clusters form. A series of small amplitude, low energy adjustments allow a proton to effectively translate through the network, with an excess proton rapidly transferred from water molecule to water molecule [4–6].

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Ion conduction processes in 'confined' regions are central to many processes. In particular, proton conduction plays important roles in ion conduction through pores and channels in biological systems [7] and in materials used in technological applications. Our understanding of these processes in the latter context has advanced substantially over the past 25 years, partly driven by the interest in proton exchange membranes (PEMs) used in PEM fuel cells (PEMFCs). In the principal materials used in PEMFCs, such as Nafion™, other perfluorosulfonic acid (PFSAs) membranes and sulfonated hydrocarbon membranes, the tendency toward clustering of sulfonic acid groups as well as phase segregation processes drive the formation of nanoporous morphologies [8]. The nanopores in turn are thought to facilitate proton transport in these membranes. (It should be noted that we use the term 'nanopore' in a generic sense; the detailed physical form(s) of these structures is still an issue of debate.) [9—12] Proton conduction is, in general, closely coupled to hydration of the material and critical processes of proton dissociation and hydration take place within the confined space of the nanopore. Extensive work has elucidated these processes. The basic observation has been that for normal ranges of water uptake, the proton conductivity and associated water mobility increase significantly with water content, with conductivity approaching or exceeding 0.1 S/cm for 'fully hydrated' materials exposed to pure liquid water or water at high relative humidity (RH) [13,14]. This is sufficient conductivity to render losses due to internal resistance in the fuel cell nearly insignificant [15].

Since the water uptake by the polymer membrane depends strongly on the RH and the temperature, a decrease in conductivity by more than an order of magnitude is observed in conventional membrane materials when the RH is lowered to ~25% or less or when the temperature approaches or exceeds 100 °C. Suggestions that fuel cells should operate in this range of RH and at elevated temperature have driven the push toward development of materials that show adequate conductivity with substantially less water. A great many pathways have been tried in attempts to meet this goal.

Here we present work along one such path that indicates important new features related to the mechanisms underlying ion and water mobility in proton-conducting membranes. In particular, we find that increasing the density of sulfonic acid groups along the polymer chain has substantial and surprising effects on the local and long-range mobility of protons and water at low water contents. The work employs
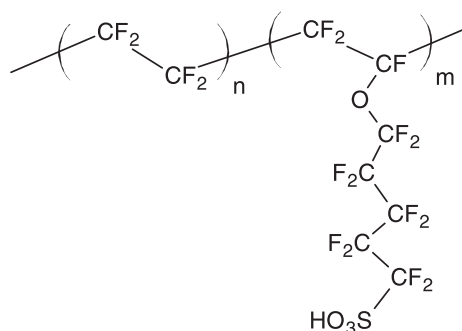
PFSA membranes based on the 3M Ionomer. The structure of the 3M Ionomer is shown in Fig. 1, where the ration of n:m varies from about 2 to 7 in this study. As illustrated, these ionomers [16] have a slightly shorter sidechain than the Nafion™ ionomer and are without the pendant −CF3 group in the sidechain. This provides the 3M PFSA membranes with a higher degree of crystallinity and higher modulus at a given equivalent weight (EW). They show excellent conductivity and improved mechanical properties and durability under hot and dry conditions [17].

2.   Materials and methods

PFSA polymers and casting dispersions were prepared as described in Reference [16]. Membranes were cast onto a Kapton™ liner, dried and annealed at 200 °C.

2.1.   Conductivity and water absorption experiments

Membranes used in conductivity and water absorption measurements (λ) were soaked in hot DI water (80—100 °C) for 30—60 min, and then dried at room temperature prior to the measurement.

Proton conductivity was measured at 80 °C using a standard, in-plane, 4-point probe conductivity apparatus with platinum electrodes. The cell was electrically connected to a potentiostat (Model 273, Princeton Applied Research) and an Impedance/Gain Phase Analyzer (SI 1260, Schlumberger). AC impedance measurements were performed using Zplot and Zview software (Scribner Associates). Temperature and relative humidity were controlled with a constant humidity oven (TestEquity Model 1000H). Water absorption measurements were also done at 80 °C. The samples (approximately 1 g) were suspended from a 5 g load cell (Transducer Techniques) mounted in a constant humidity oven (TestEquity Model 1000H). For both the conductivity and water absorption measurements, the samples were equilibrated for about 2 h at each RH, at which point the conductivity was relatively stable.

2.2.   NMR experiments

After releasing the membrane from the liner by soaking in DI water, membranes of EW > 600 were pretreated by boiling in 1M nitric acid (HNO$_3$ from Fisher Scientific) solution for two hours to remove any impurities, followed by boiling in deionized water for another two hours is to remove any residual acid. Membranes of lower equivalent weight (EW < 600) may dissolve while boiling so these were pretreated at room temperature.

After pretreatment, precut membrane samples were dried by suspending over phosphorus pentoxide (P$_2$O$_5$, used as received from Fisher Scientific) in sealed glass bottles at 25 °C—30 °C. The weight of each membrane is monitored daily until it reaches a steady value of dry weight after ~five days. The equilibration process then follows. The completely dried samples were suspended over aqueous lithium chloride (LiCl) solutions of different water activities in a sealed glass jar. Solutions of LiCl are prepared (98.5+% pure from Fisher Scientific) with different molalities to create the desired relative

Fig. 1 — Structure of 3M short sidechain PFSA.

humidity. The water uptake is monitored under isothermal conditions in which temperature is kept at 30 °C in a temperature bath. After five to seven days, a steady state is reached where the weight of wet membranes is constant. Water uptake at 80 °C was measured by attaching a 1—2 g membrane sample to a 5 g load cell mounted in a constant humidity oven (TestEquity Model 1000H).

NMR experiments were run using a Bruker Avance 400 MHz spectrometer to determine the ^{1}H diffusion coefficients and the ^{2}H spin-lattice relaxation times. A micro-imaging probe equipped with gradient coils and an appropriate RF insert to apply the pulsed field gradient stimulated echo NMR technique for the diffusion measurement. The inversion recovery sequence was used for the relaxation measurement.

Samples of 3M membranes of different EWs, equilibrated under different relative humidity (RH) conditions, were placed in a 10 mm diameter tube and sealed to minimize water loss. A coiled heater inserted into the center of the probe, a thermocouple connected to the top of the probe and a flow of dry air into the probe maintained a constant temperature for these measurements at 30 °C. The experiment time ranged from minutes to hours, depending on the number of scans required to achieve an adequate signal to noise ratio (SNR). Membranes with lower levels of hydration are problematic for these measurements due to their SNR and error ranges are accordingly larger for such samples. Measurements on samples were repeated at least twice in order to ensure reproducibility and reliability of results.

3. Results and discussion

Proton conductivity and water mobility of 3M-PFSA membranes with different EW were determined as functions of temperature and relative humidity. The degree of humidification of the membranes, expressed as lambda (λ), or the number of water molecules per sulfonic acid group, was also measured. The effect of EW on the PFSA conductivity as a function of relative humidity (RH) and ionomer humidification is shown in Fig. 2. At every RH value, the low EW membranes have higher conductivity than the higher EW materials, with
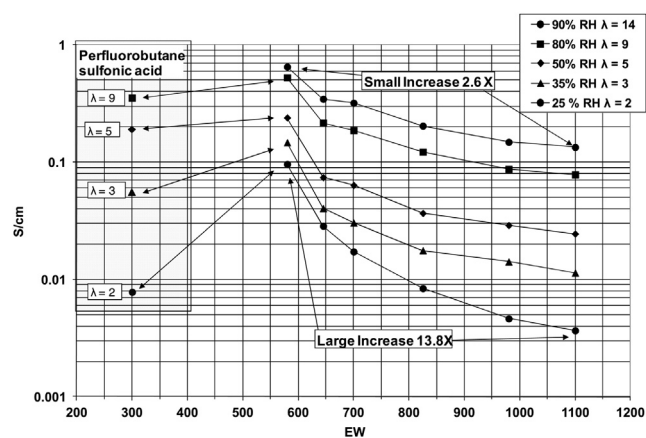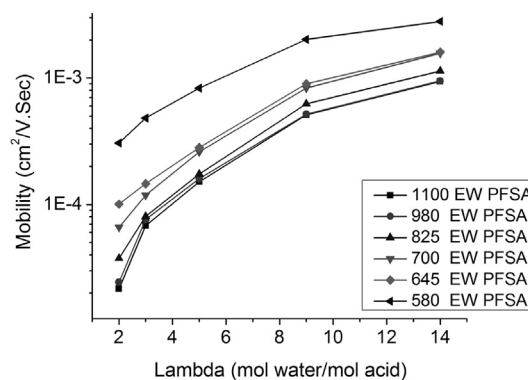

Fig. 3 — Proton mobility in 3M PFSA membranes as a function of water content for a series of polymers with different EW at 80 °C.

the difference increasing dramatically below 700 g/eq. The effect is most pronounced at low RH. For lower EW polymers, the decrease of conductivity with decreasing RH is substantially less than typically observed for commonly used PFSAs of EW ~1000 or greater. For 580 EW, conductivity approaches that (100 mS/cm) set as a target by automakers and the US DOE for operation of automotive fuel cells at 25% RH and elevated temperature.

At high water content, the conductivity increases 2.6-fold from the highest EW (1100 g/eq) to the lowest (580 g/eq). Under such relative humidity conditions, substantial water is imbibed into the polymer and protons are moving in a rather watery environment [18]. However, at low water content ($\lambda = 2$) we see that the increase in conductivity at low EW is very large. The conductivity of 580 EW is 13.8-fold higher than that of 1100 EW under these drier conditions. It is under these conditions that it becomes intriguing to understand the mechanism of proton conductivity and hence the factors controlling conductivity. Also shown is the conductivity of perfluorobutane sulfonic acid as a function of lambda. This model compound represents the lowest EW, shown here at 300, the MW of the acid. It is interesting to note that the conductivity is substantially lower that the low EW ionomers, emphasizing the role of the phase separated
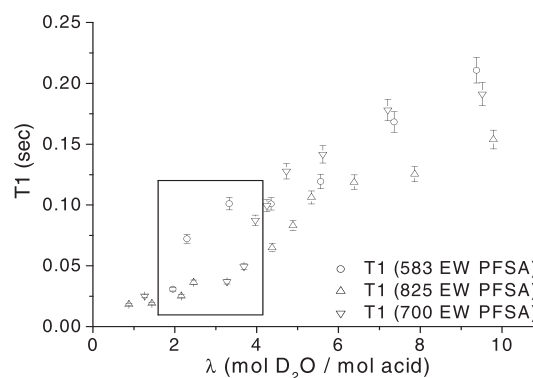

Fig. 2 — Conductivity of 3M PFSA membranes as a function of EW at different RH at 80 °C.

Fig. 4 — [2]H spin-lattice relaxation time of deuterated water in different EW 3M PFSA membranes as a function of water content (λ) at 30 °C.
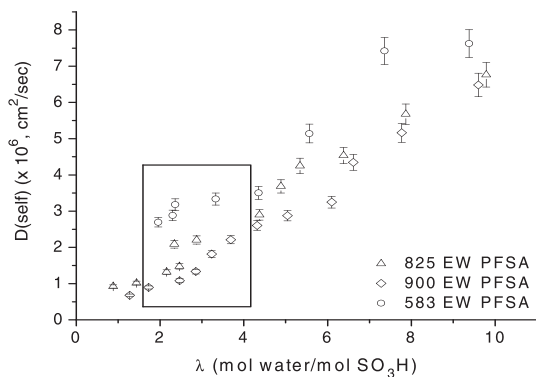
Fig. 5 — Comparison of self-diffusion coefficients of water in different EW 3M PFSA membranes as a function of membrane hydration (λ) at 30 °C.

ionomer morphology in providing a path for efficient proton transport.

In general, the conductivity of the polymer electrolyte will be a function of both concentration and mobility of H$^+$:

$$\sigma_{H^+} \propto \mu_{H^+} C_{H^+}$$

The concentration of protons is determined by the EW of the polymer, its density and by the extent of dissociation of the acid group in the polymer. The extent of dissociation should be similar for this series of polymers. It is most likely controlled by the water content and the type of acid group. The perfluorinated sulfonic acid is likely to be dissociated even down to the lowest RH values used here, as is the case for the monohydrate of the triflic acid, an analogue of the terminal acid moiety. It has long been known that the triflic acid forms a completely dissociated monohydrate, the triflate anion–hydronium cation ion pair, for which crystal structures have been obtained [19]. As shown in Fig. 3, correction for EW and density (i.e. concentration) does not substantially alter the trend observed before. Indeed, the calculated mobility of the proton is seen to increase for the lowest few EWs while remaining almost constant for the higher EWs.

The behavior of protons is closely coupled to that of water in the polymer. Combining the conductivity data with NMR diffusion measurements (a long-range probe of water motion) and NMR relaxation data (a molecular scale probe) sheds additional light on the behavior of water and protons in this environment. NMR diffusion coefficients and relaxation times as a function of water content at 30 °C for different EW polymer are shown in Figs. 4 and 5. At low water content $-2 \leq \lambda \leq 4$ — we see that at the lowest EW (585), the water diffuses faster over both long and short range. The relaxation data for various EW polymers, which reflect the limiting molecular scale motions and thus interactions of water in a given local environment, show that T_1 values are similar over much of the range of water content except for the crucial low water content region $2 \leq \lambda \leq 4$. For the 585 EW material, the relaxation rates are significantly slower, indicating faster water motion. Since in this range of water content, the water is primarily in the solvation sphere of a sulfonate/proton complex, this result reflects lower 'friction' between water and sulfonates to hinder motions. This effect is also reflected in the long-range diffusion coefficient at low water content.

To develop a hypothesis explaining these results, we consider factors controlling conductivity in fixed-site proton conductors. Based on the argument related to Fig. 3, we focus on factors that could influence the mobility of the proton. The most important factor is the water content of the polymer, We eliminate this as a factor since all comparisons are made at similar water contents, expressed as lambda (λ), water molecules per sulfonate.

This implies that some other factor(s) must play a role in the excess proton mobility observed. Two remaining possibilities are (i) changes in morphology as a function of EW, resulting in a more open proton conduction pathway and (ii) changes in the proton transport mechanism such that water molecules more readily 'hop' from one cluster of 2 or 3 water molecules plus a sulfonate anion (plus a proton) when the separation of the sulfonate groups is smaller (i.e. for the low EW case).

First, the morphology of the polymer most likely does change somewhat [20]. The morphology effect is likely best developed at high water content and therefore most purely reflected in the longer-range diffusion and conductivity patterns seen for high water content. In that case, factors of ~2.5 increase of conductivity and ~1.5 increase in diffusion coefficient are observed with decreasing EW [21]. Note also that the diffusion coefficients measured here and for other PFSAs are within a factor of 2—3 of those for water in liquid water, the 'morphology-free' extreme. These considerations suggest that
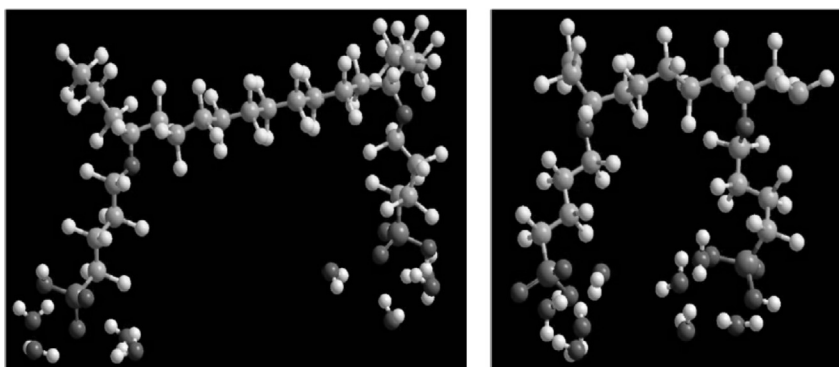

Fig. 6 — View of structure of 3M PFSA for EW = 585 and EW = 825 at lambda = 4.

morphology effects only account for a fraction of the observed increase at low water content.

This leaves changes in the transport mechanism resulting from the new structures as a primary cause of higher mobility. The conduction process can be broken down into a series of mechanistic steps. These are (i) dissociation, (ii) formation of a solvent-separated ion pair, (iii) transport into a water network and (iv) long-range transport. The latter is strongly affected by morphology while the first three steps can be seen as successively increasing escapes of water and protons from the influence of the sulfonate anion. At low water contents, it is ordinarily expected that the first two steps are critical. Step (i) occurs at $\lambda = 1$ or 2, step (ii) occurs at $\lambda = 5$ or 6 and step (iii) is associated with transport at λ higher than ~ 6. Indeed, Modeling studies performed by Paddison indicate that the proton in a well-hydrated proton-conducting polymer occurs with the proton moving through the center of the channel [22]. Since we can expect a similar (or worse!) degree of dissociation for the low EW polymer, steps (ii) and (iii) seem to be central to explaining the observed results.

In the present case, we suggest that a different kind of connected water network forms because of the close proximity of the sulfonate groups in PFSAs with very low EW. Fig. 6 shows this schematically. Since even two to four water molecules can effectively bridge between sulfonates for EW = 585, we suggest that there will be significant connectivity along the pore wall of the membrane. The polymer equivalent weight is such that only ~ 2.5 additional TFE units are present between sidechains. Furthermore, since the homopolymer cannot be made, it is likely that random long 'runs' of closer sidechain spacing are not present [23]. As a visual reference, Fig. 6 provides a picture of the spacing between acid groups for EW_585 (right) and 825 (left), with $\lambda = 4$, in one configuration, that which will provide the nearest approach of the sidechains without their flexing toward each other. Clearly, it is plausible that water can bridge the space between sulfonates for EW = 585 but not for EW = 825.

Given these data and our hypothesis of a continuous water network along the pore wall, in which water molecules effectively bridge between closely spaced sulfonate groups, we propose a picture of the system formed at low water content that is consistent with our data and our reasoning above. We infer that transport of the water and protons is controlled by this network. On average, for $2 \leq \lambda \leq 4$, a water molecule will spend 25%–50% of its time in such a bridging environment given the tendency of water to remain within close proximity of the sulfonate and assuming one bridging water molecule per sulfonate. We suggest that this bridging leads to a more loosely bound water network than is normally seen at higher EWs. The interaction between a given water molecule and a given sulfonate anion is weakened by the presence of another sulfonate exerting force on the water molecule. The relatively high mobility of water in the water content range $2 \leq \lambda \leq 4$ for 585 EW ionomer is a consequence of this loose binding. The availability of this connected, mobile water network promotes more facile proton transport.

We note that there is no requirement that the sidechain move in this model to accommodate water and proton transport. In fact, substantial sidechain motion to facilitate water or proton transport is likely to be significantly slower than water motion and may even hinder water mobility [24]. Also, such motion only facilitates interactions between pairs of sidechains rather than forming a network. A sidechain flexing toward the next sidechain moves away from its other neighbor. Nonetheless, it is important that the sulfonate-bearing entity have some flexibility in forming the basic framework.

Our network hypothesis presents a rather different mechanism for transport in synthetic polymers. It suggests that high rates of transport can be achieved with tight packing of sulfonates with an appropriate lateral geometry to allow water bridging.

4.   Conclusions

In summary, results of experiments reflecting the mobility of protons and water in 3M PFSA membranes show that significantly increased mobility at low water contents is present in polymers with closely spaced sulfonate-terminated sidechains. We argue that this implies the development of a connected pathway for transport along the pore wall of these materials. We further suggest that higher local water mobility arises from interactions of water molecules with more than one sulfonate and that this mobility plays a significant role in allowing the facile proton transport.

REFERENCES

[1] Agmon N. The Grotthuss mechanism. Chem Phys Lett 1995;244:456–62.
[2] Colomban P, editor. Proton conductors: solids, membranes and gels – materials and devices. Cambridge: Cambridge University Press; 1992.
[3] Kreuer KD. Solid State Ionics 1997;94:55.
[4] Berkelbach TC, Lee HS, Tuckerman ME. Concerted hydrogen-bond dynamics in the transport mechanism of the hydrated proton: a first-principles molecular dynamics study. Phys Rev Lett 2009;103:238302.
[5] Tuckerman ME, Marx D, Parrinello M. The nature and transport mechanism of hydrated hydroxide ions in aqueous solution. Nature 2002;417:925–9.
[6] Luzar A, Chandler D. Hydrogen-bond kinetics in liquid water. Nature 1996;379:55–7.
[7] Pomes R, Roux B. Structure and dynamics of a proton wire: a theoretical study of H$^+$ translocation along the single-file water chain in the gramicidin A channel. Biophys J 1996;71:19.
[8] Mairitz KA, Moore RB. State of understanding of Nafion. Chem Rev 2004;104:4535.
[9] Gierke TD, Hsu WY. The cluster-network model of ion clustering in perfluorosulfonated membranes. In: Eisenberg A, Yeager HL, editors. ACS symposium series: perfluorinated ionomer membranes. Washington, DC, USA: American Chemical Society; 1982. pp. 283–307.
[10] Schmidt-Rohr K, Chen Q. Nat Mater 2008;7:75.
[11] Li J, Park JK, Moore RB, Madsen LA. Linear coupling of alignment with transport in a polymer electrolyte membrane. Nat Mater 2011;10:507–11.
[12] Kreuer KD, Portale G. A critical revision of the nano-morphology of proton conducting ionomers and polyelectrolytes for fuel cell applications. Adv Funct Mater 2013:1–8.
[13] Zawodzinski TA, Neeman M, Sillerud LO, Gottesfeld S. Determination of water diffusion coefficients in

perfluorosulfonate ionomeric membrane. J Phys Chem 1991;95:6040.

[14] Hamrock SJ, Yandrasits MA. Proton exchange membranes for fuel cell applications. J Macromol Sci C Polym Rev 2006;46:219–44.

[15] Hamrock SJ, Herring AM. High temperature, low humidity operation of proton exchange membrane fuel cells. In: Kreuer K-D, editor. The encyclopedia of sustainability: science and technology, vol. 11. New York: Springer Science + Business Media; 2012. pp. 8328–47.

[16] Emery M, Frey M, Guerra M, Haugen G, Hintzer K, Lochhaas KH, et al. The development of new membranes for proton exchange membrane fuel cells. Electrochem Soc Trans 2007;11:3–14.

[17] Yandrasits MA, Hamrock SJ. In: Herring AM, Zawodzinski TA, Hamrock SJ, editors. ACS symposium series: fuel cell chemistry and operation I. Washington DC, USA: American Chemical Society; 2010. pp. 15–29.

[18] Paddison SJ, Paul R, Zawodzinski TA. A statistical mechanical model of proton and water transport in a proton exchange membrane. J Electrochem Soc 2000;147:617.

[19] Spencer B, Lundgren J-O. Hydrogen bond studies. LXXIII. The crystal structure of trifluoromethanesulphonic acid monohydrate, H_3O^+ $CF_3SO_3^-$, at 298 and 83 K. Acta Crystallogr 1973;B29:1923.

[20] Wu D, Paddison SJ, Elliott JA, Hamrock SJ. Mesoscale modeling of hydrated morphologies of 3M perfluorosulfonic acid-based fuel cell electrolytes. Langmuir 2010;26:14308–15.

[21] Zawodzinski TA, Derouin C, Radzinski S, Sherman RJ, Smith VT, Springer TE, et al. Water uptake by and transport through Nafion® 117 membranes. J Electrochem Soc 1993;140:1041–7.

[22] Paddison SJ. The modeling of molecular structure and ion transport in sulfonic acid based ionomer membranes. J New Mater Electrochem Syst 2001;4:197–207.

[23] Flach AM, Johnson FE, Cabasso I. Synthesis and characterization of fluorinated polyionomers. Part I: polyperfluoro-sulfonylethoxy propylene vinyl ether sulfonimides containing aryl sulfonic acids. Polym Chem 2013;4:3370–83.

[24] Schlick S, Gebel G, Pineri M, Volinot F. Fluorine-19 NMR spectroscopy of acid Nafion membranes and solutions. Macromolecules 1991;24:3517–21.