STRUCTURE-TRANSPORT RELATIONSHIP OF PERFLUOROSULFONIC-ACID MEMBRANES IN DIFFERENT CATIONIC FORMS

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Abstract

Perfluorosulfonic-acid (PFSA) ionomers are widely used as solid electrolytes and ion-exchange membranes in electrochemical devices, wherein their properties are impacted by the interactions among the anionic sulfonate groups, mobile counter-ions (cations), and hydration levels. Cation-form and humidity collectively affect the structure/transport-property relationship, yet their interplay is still not well known. In this paper, we report changes in water uptake and conductivity of cation-exchanged PFSA in both vapor and liquid water, which are then correlated with changes in mechanical properties and nanostructure (hydrophilic-domain spacing and phase-separation). It is found that the magnitude of changes brought upon depends significantly on the membrane water content, with a master curve in terms of water volume fraction realized. Moreover, nanostructure and dynamical-mechanical behavior of the membrane is examined to establish structure/transport and transport/stability relationships. It is found that with increasing cation size (radius) and valence, the storage modulus increases, while the water uptake and conductivity decreases. In addition, regardless of the cation type, a universal relationship is found between the conductivity and modulus, indicative of a transport/stability tradeoff. The extent to which the cations impact the transport properties depends on the water content: at low

hydration levels the controlling factor is the cation (and its interaction with the sulfonate sites), at increasing hydration the dominant factor becomes water volume fraction, although it is also controlled by the cations. Similarly, the decrease in hydrophilic domain spacing of PFSA exchanged with larger cations scales with cation radius at low water contents, but with Lewis acid strength (LAS) at higher hydration levels. The findings reported here not only provide valuable insights into the interaction between sulfonate groups, cations and water surrounding these ionic groups, but also for understanding cation contamination in fuel cells and redox flow batteries.

Keywords: Cations; PFSA membranes; Structure-transport; Conductivity; Water uptake; SAXS

1. Introduction

Perfluorosulfonic acid (PFSA) ionomers are widely used as an ion-conducting electrolyte in electrochemical energy devices, such as polymer-electrolyte fuel cells (PEFCs) and redox flow batteries (RFBs) [1, 2], due primarily to their exceptional proton conductivity and chemical/mechanical stability. These ionomers consist of a polytetrafluoroethylene (PTFE) backbone and perfluorinated vinyl ether side-chain terminated with a sulfonate groups (SO_3^-), which are neutralized by another cation, most commonly a proton (H^+) creating sulfonic-acid groups (SO_3H) (**Figure 1**). Upon hydration, these hydrophilic sulfonic-acid groups and water molecules form nano-domains (*ca.* 2 to 4 nm) separated from the hydrophobic backbone, thereby creating a nanophase separated morphology [1, 3]. Thus, both transport and mechanical properties of the membrane are controlled by the morphology, which is governed by the balance between the chemical energy of solvation and the mechanical energy of deformation [4]. While mechanical properties and stability are attributed to the backbone, transport properties are associated with the cation/water interaction energies and the hydrophilic domains, or their size, fraction and connectivity, all of which are interrelated to water content. Thus, it is of importance to delineate the interplay between the humidity-driven changes in water content, and cation-induced changes in water-uptake behavior, and how they collectively influence the ionomer's structure/transport relationship.

The nanomorphology of a PFSA not only provides transport pathways for the cations and water molecules, but also creates a local environment for their interplay, facilitated by the electrostatic interactions between sulfonate group and the protons, and hydrogen bonds formed in the water network (**Figure 1**). While the former controls the dissociation of protons, and therefore their availability for transport, the latter provides additional contribution to water-mediated transport via proton-

hopping mechanism. Hence, transport phenomena in PFSA ionomers encompass a number of complex mechanisms, which are all interrelated in a disordered nanomorphology, thus making it difficult to elucidate the underlying origins of each mechanism.

The literature is rich with experimental and modeling studies on proton transport in PFSA, in particular, the commercial Nafion[®] membrane, as reviewed elsewhere [5-8]. Moreover, the conductivity of Nafion in H⁺ form has been investigated in relation to its humidity-dependent water uptake and nanostructure in many studies [9]. However, most of these investigations have not been fully extended to other cations, where the focus has mainly been on conductivity, self-diffusion, and transference number in liquid water. These studies have revealed the key roles of the size (i.e., radius) of a cation (M^{z+}), its charge number, *z*, and the strength of its interactions with the sulfonate groups (SO₃⁻•M⁺) in controlling its transport and the membrane's water-uptake behavior. Interest in the properties of PFSA in the presence of other cations has grown recently driven by two needs: (i) understanding the effects of cation contamination and leaching (e.g., iron) that could be introduced in electrochemical devices, such as PEFCs and RFBs, in which PFSA are used as solid-electrolyte separator, and (ii) achieving high selectivity of PFSA in relation to all other cations present in a system, such as high H⁺ conductivity but low transport of other redox species (e.g., vanadium (V)) [10, 11]. For example, deterioration of fuel-cell performance and durability is observed when contaminants, such as ammonia and sodium chloride, are introduced [12-15]. Thus, an understanding on the impact of cation on the structure-property relationship of PFSA membranes not only enhances the understanding of the interactions between the ionomer moieties and the cations, but also sheds light on understanding the controlling factors on membrane performance and stability in electrochemical devices.

Overall, cations have been demonstrated to influence a PFSA membrane's conductivity, self-diffusion, water-uptake capacity in liquid water, transference number, permeability, and selectivity [16-29]. In addition, most of these properties have been shown to be interrelated as most of them are influenced by the cation's hydration energy and interaction between the ionic moieties and water molecules. For example, water uptake and hydration number decrease with increasing cation radius, not only in water, but also in other polar solvents [21, 22]. The self-diffusion coefficient of water in a Li^+ -form PFSA is lower than that in a H^+ -form PFSA due to the strong interaction between Li^+ and water [25, 30]. Water-transport behavior is found to be related to the surface-charge density, cation hydration enthalpy, and membrane water content [17-19]. Lewis acid strength (LAS) was also shown to be an important parameter in controlling the interaction between sulfonate groups, cations, and water molecules. At low water contents, when the LAS of an anion and cation are similar, water tends to attach on the outside of the cation, whereas water tends to move between an cation and an anion if their LAS values are different [31]. The thermal stability is found to be highly dependent on LAS. While some researchers concluded that the temperature of decomposition inversely depends on the size of that cation [32-34], others found that the stability effect of the cation largely depends on the LAS, where cations with LAS values lower than the Lewis base strength of the sulfonate group increases the thermal stability, while the opposite condition decreases the thermal stability [35].

Figure 1 Chemical structure of Nafion PFSA ionomer and the cations investigated in this study illustrated according to their radius (scaled). Pictorial description of the phase-separated nanomorphology of hydrate PFSA membrane and changes in its hydration and conductivity upon exchanging its monovalent cation with a multivalent cation, based on the findings in this study.

In addition to the interactions among PFSA (ionic moieties), cations, and water, the overall morphology of the membrane also controls the mobility of cations and hence membrane conductivity [25, 28, 36, 37]. However, despite many studies on PFSA in various cationic forms focusing on transport phenomena or thermal stability, investigations on their morphology is relatively scarce, with a few notable exceptions based on X-ray- and neutron-scattering (SAXS/SANS) experiments. Yeo and Eisenberg compared the domain-spacing of PFSA in H^+ and Cs^+ form [38]. Fujimura et al. [39] and Gierke et al. [40] extended the comparison to other forms such as Li^+ , Na^+ and K^+ . Young et al. examined similar cations but also with solvent effects [41]. Rollet et al. studied morphology of Nafion in various cation forms and

demonstrated that the hydrophilic-domain radius increases linearly with the increase of water volume fractions for cations of the same valence [42]. Also the domain-radius of membranes exchanged with cations of multivalence ($z > 1$) were smaller than those with monovalence ($z = 1$) [42]. Systematic investigations by Xie, Okada, and co-workers identified the importance of cation size in relation to the membrane's nanodomain size on the transport of water molecules, hinting at the role of membrane morphology [28, 37]. Similarly, larger cations have been associated with lower membrane permeability and better selectivity [17, 43, 44]. Page et al. demonstrated how cations impact thermo-mechanical relaxations in PFSA membranes by restricting the local mobility of ionic moieties within the hydrophilic domains (e.g., clusters) and shifting the thermal-transition temperatures [45, 46]. As such, when chain movements are hindered by large or multivalent cations, mechanical properties also improve, as evidenced by higher modulus of elasticity [47-49]. However, the nanostructural changes induced by the inclusion of cations in relation to both transport and mechanical properties have not been thoroughly investigated.

Although the H^+ -form of the membrane is widely used and studied, especially its transport properties in liquid water, the impact humidity and interaction between the sulfonate group and different cations on the structure/transport-property relationship is unclear. The objective of this paper is fill this gap by examining the impact of cations on water uptake and conductivity of Nafion membranes, in both vapor and liquid water, and how they are correlated with mechanical properties and nanostructural changes. A wide range of cations were included in this study, including those relevant to PEFC and RFB applications, such as cerium, sodium, and iron. Their role in altering the structure/function relationship of PFSA membranes and the existence of master governing relationships will also be discussed.

2. Experimental

2.1 Membrane preparation

In this study, Nafion[®] 212 membranes with nominal thicknesses of 50 μm were received in protonated (H^+) form from Ion Power Inc. (New Castle, DE). Membranes were cation exchanged by soaking the membranes in 0.5 to 1M aqueous sulfate solutions (from Sigma Aldrich and J.T. Baker, see

Table 1). The membrane dimensions and the volume of salt solutions were selected to ensure that the membrane was exposed to an excess of cations. The specimens were soaked in the solution for at least 48 hours at room temperature (25°C) to ensure that the membranes were fully exchanged.

Afterward, the membranes were rinsed in deionized water twice to remove excess solution on the surface. Membranes were stored in DI water until use.

Table 1 Properties of cations and salts used in this study.

Salt	Cation	Cation Radius ^a / nm
(H ₂ SO ₄) ^b	H ⁺	0.060 (for H ₃ O ⁺)

^a Crystal ionic radii.

Li_2SO_4	Li^+	0.090
Na_2SO_4	Na^+	0.116
K_2SO_4	K^+	0.152
Cs_2SO_4	Cs^+	0.181
MgSO_4	Mg^{2+}	0.086
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	Mn^{2+}	0.081
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Cu^{2+}	0.087
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	Zn^{2+}	0.088
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Fe^{2+}	0.075
$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	Fe^{3+}	0.069
$\text{Ce}(\text{SO}_4)_2$	Ce^{4+}	0.101

2.2 Water uptake

Membrane water uptake as a function of relative humidity (RH) was measured gravimetrically using a dynamic vapor-sorption (DVS) analyzer (Surface Measurement Systems, UK) at 25°C. First, the samples were dried in the DVS at 0% RH and 25°C for 2 hours to set a standard dry state with an initial sample weight, M_0 . The samples were then humidified from 0% to 90% RH with an increasing RH step of 10%, and then 95% followed by 98% RH. Samples were dehydrated back to 0% RH with the same RH values and interval, but in the opposite sequence. Water (mass) uptake of the membrane, ΔM_w , was continuously determined from the weight change with respect to the initial (“dry”) weight, M_0 . At each RH step, the samples were equilibrated for a minimum of 2 hours or until the change in the sample

^b Membrane is received in protonated form and used as-received.

weight, $\Delta M_w/M_0$, was less than 0.005%/min. The water content, λ , the number of water molecules per sulfonic-acid group of ionomer, is calculated based on the measured water uptake, $\Delta M_w/M_0$ as

$$\lambda = \frac{\text{mol}(\text{H}_2\text{O})}{\text{mol}(\text{SO}_3^-)} = \frac{\Delta M_w / 18}{M_0 / \text{EW}} \quad (1)$$

where EW is the equivalent weight of the membrane in g/mol and the molecular weight of the water is 18 g/mol. The residual water, λ_{res} , in the membrane that is present at 0% RH at 25°C was also measured from the weight loss after heating the samples at 120°C for 30 minutes.

2.3 Mechanical properties

Mechanical properties of all specimens were measured using a dynamic mechanical analyzer (DMA) (DMA-Tritec 2000). The sample was tested in tension mode with a frequency of 1Hz. Temperature sweep tests were performed within the range of 25°C to 400°C with a heating rate of 5°C/min. From the collected stress-temperature data, storage modulus (E'), loss modulus, and their ratio, $\tan(\delta)$, was determined and plotted as a function of temperature, as described previously [50].

2.4 Conductivity

In this study, the in-plane and through-plane conductivities of the specimens were measured. The through-plane conductivity was measured as a function of relative humidity at 30°C with a Membrane Test System (MTS) (MTS740, Scribner Associates, Inc.), and the in-plane conductivity was measured in liquid water at 25°C using a four-electrode BT-110 conductivity clamp (Scribner Associates, Inc.). For the through-plane conductivity tests, AC impedance measurements were performed under controlled humidity and temperature with an SI 1260 impedance/gain-phase analyzer (Schlumberger Technologies,

Inc.) and ZPlot software (Scribner Associates, Inc.). Membranes were cut into a rectangular piece with the dimension of 10 mm × 30 mm and were sandwiched between gas-diffusion layers (GDLs) (SGL 10BC). The GDLs were attached to the platinum source electrode with conductive carbon paint. The assembly was compressed with a load of approximately 2.151 ± 0.017 MPa measured by a calibrated force spring and dial displacement indicator. Samples were first kept at 70% RH and 30°C under nitrogen atmosphere for 2 hours at the beginning of the test. Afterward, samples were dried to 20% RH with a step of 10% RH, and then hydrated to 90% with an increment interval of 10% RH, then to 95% and 98% RH, similar to the protocol used for the water-uptake measurements described above. Samples were first preconditioned for 30 min at each step and then the membrane resistance was measured using voltage-controlled frequency-sweep spectroscopy (10 mV_{AC} at 0 V_{DC}, 1 MHz to 1 Hz, 10 steps/decade). The through-plane conductivity was calculated as $\kappa = L/RA$, where L is the thickness of the membrane measured at ambient conditions, R is the resistance derived from the intercept of the high-frequency impedance with the real axis, and A is the overlapping area of the platinum source electrodes (0.5 cm²).

With regard to in-plane conductivity measurement, membranes were cut into strips and placed in the four-electrode conductivity clamp. Prior to measurement, samples were kept in DI water for at least one hour to allow equilibration. The AC impedance was then measured with a BioLogic VSP potentiostat from 20 mHz to 1 MHz at a bias of 100 mV between the outer electrodes. The in-plane conductivity was calculated as $\kappa = L_{IP}/R_{IP}A_{IP}$, where L_{IP} is the distance between inner voltage electrodes (0.425 cm), R_{IP} is the resistance of the membrane, and A_{IP} is the cross-section area of the specimen.

2.5 Small- and wide-angle X-ray scattering

Small/wide-angle X-ray scattering (SAXS/WAXS) experiments were performed in beamline 7.3.3 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). The X-ray wavelength used was $\lambda = 0.124$ nm, with a monochromator energy resolution of E/dE of 100, and the presented patterns were collected using a 2D Dectris Pilatus 2M CCD detector (172 μm x 172 μm pixel size). The scattering wave vector, $q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle, was in the range of 0.001 to 0.04 $\text{\AA}^{-1}$ for SAXS and 0.5 to 3 $\text{\AA}^{-1}$ for WAXS. SAXS experiments were conducted *in-situ* by immersing the cation-exchanged samples in liquid water using custom-designed sample holders with X-ray transparent KaptonTM windows. All of the experiments were carried out at 25°C under liquid-water equilibrium. The collected two-dimensional scattering patterns were azimuthally integrated to generate 1-D intensity profiles, $I(q)$, which were corrected for background scattering. From the SAXS data, hydrophilic-domain spacing and inter-crystalline spacing were calculated using a Gaussian fit to the peaks.

3. Results

3.1 Water uptake

The water-sorption isotherms of Nafion membrane in different cation forms are shown in **Figure 2**. Overall, the water-uptake capacity decreases upon replacing proton with other cations, albeit with different sorption isotherms. The water-sorption isotherm of Nafion-H⁺ membranes exhibits a typical sigmoidal shape. At very low RH (RH < 20%), the sorption isotherm is convex to the humidity axis, corresponding to the Langmuir isotherm that describes water molecules adsorbing onto sulfonic-acid groups due to a strong interaction. These primary-solvation water molecules are termed *bound* due to their limited mobility. At intermediate RH, the quasi-linear sorption isotherm could be associated with Henry-law type sorption, where the molecules are absorbed by the dissolution mechanism. In this

scenario, the slope of the lines represent Henry's coefficient, while their intercept with the y-axis corresponds to the Langmuir capacity constant [21]. The sorption isotherm displays a highly nonlinear upturn at high RH due to the uptake of water molecules that are *free*, i.e., more mobile and less affected by the electrostatic interactions. Upon replacing H^+ with other cations, the sorption isotherms tend to shift downwards, with the most dramatic change being the weaker Langmuir mode at low RH.

It follows from the figure that the water uptake decreases in the order of increasing ionic radius, r_c : $\lambda(H^+) > \lambda(Li^+) > \lambda(Na^+) > \lambda(K^+) > \lambda(Cs^+)$ for monovalent cations (**Figure 2a**). It must be noted that the hydration energy of these cations also decreases in the same order, with Cs^+ having the largest radius and lowest hydration energy. Consequently, the water content of saturated Nafion- H^+ membrane decreases significantly when it is exchanged with Cs^+ , such that the membrane exhibits a Langmuir-type sorption isotherm throughout whole the humidity range (i.e., lacking the free-water regime observed for Nafion- H^+). On the other hand, the water content of Li^+ form membrane becomes comparable with that of a protonated membrane at higher RH ($\lambda(H^+) \sim \lambda(Li^+)$), while at low RH, the water uptake of proton form is higher than that of lithium form ($\lambda(H^+) > \lambda(Li^+)$), which is attributed to the differences in solvation energies of these cations. The hydration energy of proton (H^+) and lithium ion (Li^+) are -1050 and -475 KJ/mol, respectively, [51, 52] which means that it is easier for a proton to dissociate upon solvation and form water complexes. Although comparable water uptake in Li^+ - and H^+ -forms was previously reported in liquid water [30, 40] and in water vapor [21, 22], the results here highlight the key differences between many cations at the low-RH regime, where most of the water is still bound to the SO_3^- sites and the sulfonate/cation interactions dominate. Once the membrane exceeds 70% RH, the additional water absorbed could move freely and is less affected by the cationic interactions.

Membranes exchanged with various divalent cations show almost identical sorption isotherms within the whole RH range (**Figure 2b**). This is not unexpected considering the fact that the cations in the membrane possess the same valence, $z = 2$, and similar cation radii, r_c , (and therefore comparable charge density, z/r_c). At low RH (e.g., below 60% RH), no significant difference in water-sorption isotherms between Li^+ -, Fe^{2+} -, and Fe^{3+} -form Nafion membrane are observed (**Figure 2c**). At higher RH, the water-sorption isotherms of Nafion- Fe^{2+} and Nafion- Fe^{3+} membranes are similar, albeit still with lower uptake than that of Nafion- Li^+ membrane. A noteworthy observation is that, among multivalent cations investigated here, the water-uptake behavior of Nafion in Ce^{4+} form is comparable to that in H^+ form membrane. Even though Fe^{2+} and Fe^{3+} cations have much higher hydration energy than Li^+ , their sorption isotherms at the initial stage are similar, indicating that initial uptake of water and its solvation is less affected by the cation size for multivalent cations. However, for monovalent cations, the impact of cation (size) on the initial sorption regime is more pronounced owing to a large variation in cation size, r_c . Thus, exchanging a Nafion membrane with a monovalent cation of larger size and stronger interaction energy effectively reduces the water uptake. **Figure 2d** illustrates this interplay between the cation size and valence in that water content, λ , at 98% RH increases with increasing LAS (or cation radius, not shown for brevity) monotonically for monovalent cations. However, λ becomes less sensitive to LAS for multivalent cations.

Figure 2 Water sorption isotherms of Nafion 212 membranes at 25°C for (a) monovalent cations; (b) divalent cations; (c) for higher-valence Iron and Cerium. (d) Maximum water content close to saturation as a function of Lewis Acid Strength (LAS) of the cation. Inset shows the residual water at 0% RH plotted as a function of cation radius. The lower and upper symbols for each cation indicate the water content without and with accounting for the residual water, respectively.

3.2 Mechanical properties

Figure 3 compares the dynamic-mechanical properties of dry Nafion membrane in different cation forms. Significant changes are observed for both storage modulus, E' , and alpha-relaxation temperature, T_α . In general, replacing H^+ with another cation increases storage modulus and alpha-relaxation temperature to a great extent due to the stronger electrostatic interactions ($SO_3^- \bullet M^+$) introduced in the PFSA membrane. While storage modulus increases in the order of increasing cation radius, $E'(H^+) < E'(Li^+) < E'(Na^+) < E'(K^+) < E'(Cs^+)$, changes in alpha-relaxation temperature do not follow the same trend. As an example, Nafion in K^+ form membrane exhibits the highest alpha-relaxation temperature, even though Cs^+ has the largest radius among these cations. **Figure 4** displays the storage modulus, E' , of Nafion membrane as a function of the cation radius, r_c , which show a fairly well correlation. A cation with a large radius could hinder the mobility of the chains by forming ion pairs between the sulfonate groups and cations, i.e., ionic crosslinks, thus restricting the local chain movement leading to higher modulus (or resistance to deformation), in agreement with previous findings [47-49, 53]. Interestingly, E' increases almost linearly with increasing r_c , especially for monovalent cations, while cations of higher valence exhibits a different trend with higher modulus. Thus, the changes in storage moduli for different cations appear to be influenced by two factors: the radius and the valence (of the cation). In addition, multivalent cations form ion pairing with more than one ionic site, thereby creating even stronger ionic crosslinks with the sulfonic-acid moieties, further restricting their mobility; thus, the additional increase in modulus at a given r_c (**Figure 4a**). The concentration of multivalent cations is lower than that of monovalent cations, per electroneutrality, leading to a smaller interaction network [54-56]. Hence, the moduli of multivalent cations are affected by these two factors, which compete against each other (concentration vs. strength of the ionic crosslinks). Comparing the changes of modulus with valence and radius, it seems that the storage modulus is more affected by radius and to a less extent affected by

valence, at least when the membrane is not hydrated (i.e. electrostatic interactions are not shielded). This might explain the observation reported in the literature that the cation valence seems to have negligible effect on the membrane modulus [48, 49], which is probably due to the limited surface area of cations that prevent further crosslinks formation.

Figure 3 Dynamic mechanical properties of as-received Nafion membrane in different cation forms: (a) storage modulus and (b) tan delta as a function of temperature

Figure 4 Storage moduli of cation-exchanged Nafion 212 membrane as a function of cation radius. The lines are guides-for-the-eye. (b) Alpha-transition temperature of cation-exchange Nafion membrane plotted in the order of increasing LAS of the cation

The alpha-transition (or relaxation) temperature, T_α , on the other hand, depends more on the interaction energy between the cation and sulfonate group. T_α has been reported to correspond to the

temperature where long-range motion of both main and side chains occur due to destabilization of the electrostatic network [38, 45, 57, 58]. At this temperature, aggregations of ion pairs are disrupted and ion pairs hop from one aggregate to another to relieve local stress, thus facilitating the relaxation of the membrane at higher temperatures [45]. Hence, cations with stronger interactions will serve to retard the relaxation behaviors of the membrane, and thus requiring more thermal energy (higher temperature) for the destabilization of aggregates. The electrostatic interactions between cations and sulfonate groups are much larger than the hydrogen bonding for H⁺-form membrane [59], resulting in an increased T_{α} on cation exchange. The findings on the change in T_{α} with LAS is consistent with previous studies: for cations whose LAS < 0.3, T_{α} values are relatively similar, while for cations whose LAS > 0.3, a sharp increase in T_{α} is observed [60, 61]. This difference has been attributed to the changing interactions between cations and sulfonate groups with the multivalent cations exhibiting stronger interactions, leading to higher T_{α} and therefore thermal stability. Actually, the T_{α} of Nafion exchanged with multivalent cations is so high that it approaches the thermal degradation temperature (~350°C) [60].

3.3 Small- and wide-angle X-ray scattering (SAXS/WAXS)

The morphology of Nafion membrane in various cationic forms are investigated using SAXS, as summarized in **Figure 5**. SAXS profiles of liquid-equilibrated Nafion show the characteristics of a hydrated PFSA membrane with an ionomer peak around $q = 0.15\text{\AA}^{-1}$, corresponding to the spacing between the “wet” hydrophilic domains ($d_w = 2\pi/q \sim 4.2 \pm 0.2$ nm). The most striking effect of the cations is observed in the shape of the ionomer peak in that it becomes broader and less apparent when the membrane is exchanged with larger cations. This finding is consistent with the observations reported by other researchers [39, 40, 42]. Such a change suggests more polydispersity in domain-size

distribution. To quantify the domain-size distribution, or the degree of phase-separation, full-width at half maximum (FWHM) of the ionomer peak is calculated hydrated Nafion exchanged with different cations. There exists a strong linear relationship between the FWHM and cation radius, with the lowest FWHM (narrowest peak) observed for H^+ -form Nafion, whereas the highest values (broadest peak) is attained for Cs^+ -form Nafion. In fact, the ionomer peak of Nafion- Cs^+ is so broad and weak that it almost resembles that of a dry Nafion- H^+ . The ionomer-peak behavior is governed by the hydration-induced increase in size and spacing of hydrophilic domains in the hydrophobic polymer matrix. One could therefore attribute the weak peak of Nafion- Cs^+ membrane to its exceptionally low water content, even in the fully-hydrated state. However, it should be noted that the SAXS peak arises from the electron density difference between the phases, and changing the counter-ion from proton to heavier cations results in a reduced intensity. Thus, it is difficult to clearly distinguish the impact of hydration on ionomer peak behavior from that of cation-exchange. Even at the same λ , the SAXS profiles of Nafion- H^+ and Nafion- Cs^+ do not match. This would indicate that phase-separated morphology of Nafion is not solely controlled by the hydration, but also by the nature of the ionomer-cation interactions, and the latter impact the SAXS spectra as well. Nevertheless, the lack of an apparent ionomer peak in hydrated Nafion- Cs^+ could still be attributed to the large Cs^+ cation's ability to interact strongly with the ionomer moieties and localize between the polymer backbone and sulfonate groups [26], thereby creating a strongly-crosslinked ionic network and disrupting the hydrophilic domains. Such a network uptakes much less water, which, however, is not the cause, but the consequence of the changes in morphology as well as in the cation's solvation energy and interactions with the ionomer moieties.

Figure 5 SAXS profiles of Nafion membrane of different cation forms measured in liquid water, and the corresponding full-width half-max (FWHM) of ionomer peak as a function of cation radius.

Upon cation exchange, the ionomer peak of hydrated Nafion shifts to higher q values, and lower intensities, indicating smaller water-domain spacings, in accordance with the decrease in water content,

λ . It is well established that domain spacing of Nafion- H^+ scales with the degree of hydration,[1, 3, 9, 39, 40, 62-64], which could be mathematically expressed by the relationship, $\Delta d = s_n \lambda$, where s_n is the slope of a $d - \lambda$ curve, representing the nanoscale swelling coefficient.[1, 3, 9, 64] In a similar fashion, the hydrophilic domain spacing of a hydrated Nafion membrane, d_{wet} , in different cation forms are compared in **Figure 6b**. Nevertheless, d_{wet} scales not with λ , which is the number of water molecules per fixed sulfonate anion, but with the λ/z , the number of water molecules per cation. This finding is consistent with the SANS study by Rollet et al.[42] and in qualitative agreement with other works [38-40], which suggest that the charge number of cation, z , along with its size, r_c , must be taken into account when analyzing the nanostructural features of cation-exchanged PFSA. The qualitative agreement between SAXS and SANS also suggests that the SAXS changes are resulting from physical and not only electron-density changes.

There appears to still exist a linear relationship between d_{wet} and λ/z , albeit with a different slope (s_n), which indicates that nanostructure-uptake relationship of Nafion upon cation-exchange is not solely due to change in hydration, but governed by the nature of the cationic interactions. This was further demonstrated in **Figure 6b** inset showing an inverse relationship between d_{wet} and LAS: $d_{wet} = 4.13 - 0.657 \times LAS$. All the cations, regardless of their charge, fall on the same line, with the notable exception of H^+ . LAS is a parameter that reflects the surface of an electron core of an atom and depends on the screened nuclear charge and the ionic radius [65]. Noting that LAS of a cation correlates with its charge density, z/r_c , [24, 35] d_{wet} not only relates to the amount of water in the membrane but also to the state of water, e.g. how the water interacts with the cations or sulfonate groups, as discussed below. A consequence of this phenomenon is that the Cs^+ -form membrane has a large wet domain spacing, d_{wet} , despite having the lowest water uptake (among the cations investigated here). Further evidence

supporting this explanation could be obtained by comparing d_{wet} between Li^+ -form and H^+ -form membranes. Despite the similar cation radius between Li^+ and hydronium (H_3O^+), H^+ -form Nafion has a higher λ , and larger d_{wet} than does the Li^+ -form Nafion, perhaps owing to participation in the hydrogen-bond network.

Figure 6a shows the hydrophilic domain spacing of Nafion in “dry” state, d_{dry} , for different cationic forms. Even though changes in d_{dry} resulting from the cation exchange is relatively small, a strong linear dependence of d_{dry} on cation radius, r_c , and water content, λ , is observed for all cations, again with the exception of H^+ . As opposed to the trend in liquid water, d_{dry} decreases with increasing cation radius (not shown for brevity). Hence, larger cations interact more strongly with the sulfonate ions thereby forming stronger ionic crosslinks, which brings ionic aggregates closer to each other resulting in a smaller domain spacing. As a result, one would expect a higher density in dry membrane, which is in agreement with the density values reported by Gierke et al.[40]. Thus, since no excess (free) water present in the membrane in the dry state, the hydrophilic domain spacing is governed more by the interaction between sulfonate groups and cations. A consequence of this phenomenon is that Nafion- H^+ and Nafion- Cs^+ have the similar d_{dry} at 10% RH, although the former membrane accommodates 3 more water molecules per SO_3^- sites (including the residual water). The unique properties of Nafion- Cs^+ owing to its very low charge density and strong interaction with sulfonate (SO_3^-) sites was discussed previously, and Cs^+ was suggested to be transferred through the interfacial regions, not the ionic domains [26, 29]. In such morphology, one would expect an ill-defined ionomer peak due to weak phase-separation, which agrees with the findings herein, since the Cs^+ -form membrane has almost negligible SAXS signal and very high FWHM.

Figure 6 Hydrophilic domain spacing of Nafion membrane (a) in “dry” state (10% RH), d_{dry} , plotted as a function of its water content including the residual water, (b) in liquid water, d_{wet} , plotted as a function of water content per cation. The inset in (a) shows the inverse correlation between d_{dry} and cation radius, and inset in (b) shows d_{wet} plotted vs. Lewis acid strength of cation. The dotted and dashed lines are fit to the data for hydrated Nafion in cation forms (this work), and for Nafion-H⁺ at various hydration levels (refs.[3, 64]), respectively. The colors and symbols are the same as described in Figures 1-4.

Another morphological feature of interest is the change in the shape and position of the matrix knee, which is an indicator of the spacing between crystallites. Consistent with changes in ionomer-peak position, the position of the matrix knee also shifts to higher q values upon cation exchange, suggesting smaller inter-crystalline spacing, possibly indicating better-packed crystalline domains. Disruption of crystallinity along with a decrease in the matrix-knee intensity upon cation exchange was previously observed [66], and is in good agreement with the morphological picture where the ionic crosslinks result in better-packed ionic aggregates, thereby reducing not only the dry-domain spacing, d_{dry} , but also the inter-crystalline spacing. Interestingly, instead of a broader peak in the H^+ -form membrane, the matrix knee becomes more well-defined in other cation forms, indicating a more uniform distribution of the crystalline domains, perhaps owing to a stronger local order around the hydrophilic domains induced by the ionic crosslinks.

3.4 Conductivity

The conductivity of Nafion membrane in different cation forms as a function of water content, λ , is shown in **Figure 7**. Overall, conductivity exhibits a similar dependence on hydration for all of the cations, albeit with a strong vertical shift in their values. For a given λ , the conductivity changes more than two orders of magnitude, with protonated Nafion exhibiting the highest conductivity. Although not shown, Ce^{4+} exhibited an anomalously high conductivity and is being currently investigated as there could be issues with competing interactions during the impedance measurement or incomplete ion-exchange due to the high valence of Ce^{4+} which requires four sulfonate groups to form crosslinks. However, recent studies have shown cerium-impregnated Nafion exhibiting interesting behavior [67, 68], and thus the

data may be valid but more complete examination is required. Comparing the conductivity of H^+ -form and others, a more than one order of magnitude decrease is witnessed at the same water content, due primarily to the lack of structural diffusion (ion hopping) for the other cations. The conductivity for the cations of the same valence almost overlaps, which indicates a more pronounced effect of charge number than the cation size. In terms of RH, the membrane conductivity for the same valence is governed by the water content, λ . Comparing the cation mobility at infinite dilution for various cation valence, no significant difference is observed [37]. Hence, the difference in conductivity of membranes exchanged with different valence cations is not due to the mobility of the cation itself, but due to the interaction between the cations and sulfonate groups as discussed in more detail below.

Figure 7 Humidity-dependent through-plane conductivity of Nafion 212 membrane as a function of water content at 30°C. (The colors and symbols are the same as described in Figure 1).

4. Discussion

To assess quantitatively the impact of cationic form on the water-sorption behavior of Nafion membrane, the sorption isotherms are fitted with a dual-mode sorption model [69]

$$C = \bar{C}_p \frac{Aka_w}{(1 - ka_w)(1 - (1 - A)ka_w)} = \bar{C}_p \frac{ka_w}{1 - ka_w} + \bar{C}_p \frac{(A - 1)ka_w}{(1 + (A - 1)ka_w)} \quad (2)$$

where C is the concentration of water and here have the same unit as λ , and a_w is the activity of water in vapor. $\bar{C}_p$ represents the mean sorption capacity of the polymer including the matrix region and the ionic region corresponding to the water molecules that are strongly bound to the ion pairs, forming the first hydration layer of the ion pair. k corresponds to the interaction between the water molecules and the polymer (moieties), and A represents how the interaction of the adsorbed water molecules within the ionic domain change between the first and subsequent adsorption layers. The above equation combines two distinct modes of sorption, where the first and second modes (terms) represent the free and Langmuir-type (bound) sorption, respectively. A higher k indicates a stronger affinity of polymer to uptake water (i.e., hydrophilicity), whereas as A approaches 1, the water molecules have the same hydration enthalpy in multiple adsorption layers, and Eq. (2) simplifies to an upward curve with no bound water. The above expression is adopted due to its simplicity and ability to analyze the uptake curve in the low-RH regime. Even though models based on modified multi-layer absorption Langmuir and Flory-Huggins have been shown to predict accurately the water uptake of PFSA in protonated form [3], their applicability to lower-RH regimes to predict bound water has not been verified. Nevertheless, the above expression has been shown to capture the water-uptake isotherm of Nafion in the presence of Li^+ cations as well as other additives [52, 70].

Table 2 shows the fitting parameters for the sorption isotherms of different cation-form membranes. For membranes exchanged with alkali-metal cations, both C_p and A values decrease with increasing

cation radius, r_c , in agreement with previous observations [52]. The decrease in C_p with increasing r_c implies that less water molecules are associated with the ion pair, which is plausible by considering that alkali-metal cations with larger radii have lower hydration energies. A smaller radius contributes to the larger electrostatic field, which attracts more polar molecules like water, and the larger hydration energy of a cation makes it easier to dissociate – as in the case of H^+ . The parameter A that reflects the upturn curvature at higher water activity also decreases, which could be ascribed to the increased rigidity of polymer network. This is evidenced in **Figure 4**, where the storage modulus of a dry Nafion membrane increases with cation radius. As water sorption behavior is governed by the balance between the hydration energy controlling water uptake through the swelling of the hydrophilic nano-domains and mechanical (deformation) energy opposing them, the higher the modulus of the polymer matrix, the lower the water uptake becomes.

Table 2 Fitting parameters of cationic form sorption isotherms

Membrane	C_p	k'	A
Nafion- H^+	2.671	0.7677	7.269
Nafion- Li^+	2.7	0.8252	3.547
Nafion- Na^+	1.863	0.8116	3.002
Nafion- K^+	0.8972	0.8057	4.432
Nafion- Cs^+	0.6536	0.7946	3.473
Nafion- Mg^{2+}	2.944	0.728	3.125
Nafion- Mn^{2+}	3.332	0.7051	2.766
Nafion- Fe^{2+}	3.322	0.6767	2.993
Nafion- Cu^{2+}	3.278	0.7032	3.001

Nafion-Zn ²⁺	2.882	0.7349	5.938
Nafion-Fe ³⁺	4.114	0.6093	2.962
Nafion-Ce ⁴⁺	3.039	0.7441	5.517

When a Nafion in H⁺- or Li⁺-form is exchanged with multivalent cations, C_p increases slightly while A decreases significantly. Since multivalent cations have much higher hydration energies and energy density, they show higher C_p values. Decrease in A on the other hand implies a downward shift in uptake curves at higher RHs, as shown in **Figure 2**, which can be attributed to the higher modulus of polymer matrix in the presence of multivalent cations, causing a higher resistance to water uptake. Hence, the initial water-sorption stage seems to be only affected by the hydration energy or charge density of the cation and its interaction with the polymer's sulfonate groups, while the high-RH water uptake is affected by the storage modulus and the cation interactions.

To demonstrate this chemical-mechanical balance, the storage modulus of a dry Nafion membrane is plotted as a function of its water content close to vapor saturation (98% RH) (**Figure 8**). It follows from the figure that there is a linear relationship between storage modulus (a measure of mechanical energy) and water-uptake capacity (a measure of chemical energy), confirming the universality of chemical-mechanical balance, regardless of the cation. Such a balance was shown previously for hydration/humidity [3] and hygrothermal ageing [71] effects in Nafion-H⁺ form, and in swelling-modulus correlation of Nafion thin films [72]. Even though the impact of cations on mechanical properties and water uptake have been studied separately before, results herein highlights their correlation. The underlying origin of this inverse relationship can be explained by the fact that cations that form stronger ionic crosslinks increase the storage modulus of the polymer matrix, which, in turn, applies a higher

counter pressure (swelling resistance) to the growing hydrophilic domains, thereby reducing its water-uptake capacity, λ , and hydrophilic domain spacing, d_{wet} (**Figure 6a**).

Figure 8 Relationship between storage modulus and water content (98% RH) of different cation exchanged membranes

Upon water sorption, the hydrophilic domain also swells at the nanoscale, forming a pronounced phase-separated nanostructure. It is interesting to note that the wet-domain spacing (in liquid water) is related to the charge density, and scales with the amount of water molecules per cation (instead of per sulfonate anion), whereas in the dry state it is related to cation radius, regardless of its charge. **Figure 9** shows that the change in hydrophilic-domain spacing from dry to wet state, $\Delta d = d_{\text{wet}} - d_{\text{dry}}$, scales almost linearly with LAS, but still lower than that of H⁺-form membrane, consistent with the trends in water uptake (**Figure 2**). The dependence of Δd on LAS is weaker for multivalent cations, which might be ascribed to their already high LAS screening the interactions controlling the nanostructure-uptake relationship. If H⁺ is excluded from the dataset, the best fit to the data yields an expression of the form:

$$\Delta d = d_{\text{wet}} - d_{\text{dry}} = 1 - \alpha_c LAS \quad (3)$$

where, the coefficient (slope of the d-LAS line) is $\alpha_c = 1.06 \pm 0.02$ [nm].

Figure 9 Change in hydrophilic domain spacing of cation-exchanged Nafion membrane from dry to fully-hydrated state (in liquid water) plotted as a function of Lewis acid strength of the cation.

As dry domain spacing decrease with increasing cation radius and increase with increasing water content, the difference in dry domain spacing between different cations could not be due to cation size but instead the amount of water. Different from the state of water when membranes are placed in liquid water, water molecules in ambient conditions are strongly bound to sulfonate groups. Hence, the more water, the larger the domain spacing. In short, the dry domain spacing is more related to the amount of water molecules while the wet domain spacing is more related to the state of water molecules surrounding cations.

All of these hydration effects also impact the conductivity, which is controlled by tortuosity of the phase-separated network at the mesoscales and the electrostatic and solvation energies at the

nanoscales. To explore these effects, the conductivity data in **Figure 7** are plotted as a function of λ/z in **Figure 10a**. Interestingly, all of the conductivity values overlap and form a master curve, indicating that water content and charge number are the two factors governing the conductivity in a water-vapor environment. This seems to indicate that, as with the water content, the conductivity of cation-exchanged membrane is also dominated by the number of water molecules per charge, instead of water molecules per sulfonic acid group. Since the concentration of SO_3^- groups in the membrane is the same at a given λ , increasing the charge number of cation means a direct reduction in cation concentration, per electroneutrality (**Figure 1**). Exchanging a monovalent cation ($z = 1$) with a divalent cation ($z = 2$) reduces the concentration of the latter by half. Thus, λ/z can also be seen as related to the water volume fraction in these ionomers. These findings indicate a form of *cation/water-uptake superposition*, in which the governing phenomenon is the cation solvation. This master curve also demonstrates that, in this aspect, it is the connectivity of the domains that dominates the conductivity response, which can be more accurately characterized by the water per cation (i.e., λ/z), which accounts for a reduction in water content (due to solvation and interaction effects) and counterions (charger carriers) concentration (see **Figure 1**). In other words, at the same water per charge or volume fraction, the network tortuosity is probably similar and one observes the same conductivity, since their infinitely dilute or innate values are similar [37]. This is counterintuitive since it suggests that for higher valences, one requires more water, which effectively dilutes the cationic charge carriers. The reason is probably due to the screening of the ionic charges and their interactions at higher water contents, which enhances the solvation but reduces the strength of the ionic crosslinks. Such an impact is plausible considering the fact that the symmetric stretching vibration of sulfonate group remained almost unaffected by cation type at higher water content due to the shielding effect of water solvation [73, 74].

The role water plays in shielding electrostatic interactions and controlling ionomer properties have been discussed in many studies, but rather in a qualitative manner with a focus on dry and hydrated conditions. Thus, it is of interest to delineate how these interactions and their impact on transport change sequentially by addition of water as a function of humidity.

In an effort to elucidate the interplay between cationic interactions and water (solvation) effects, the measured conductivities are examined in both low-hydration regime (vapor) and high-hydration regime (liquid water) (**Figure 10b**). In liquid water, the conductivity scales very well with the water volume fraction, ϕ_w , regardless of the cation type and valence. As the degree of hydration is reduced, however, the conductivity data begins to deviate from this trend. Cationic-interaction effects appear to manifest themselves especially at low to intermediate humidities (up to 80% RH), where conductivity depends more on the cation's interaction with the sulfonate group, and its dissociation, more so than the water content. Hence, the conductivity of the membrane is influenced by the cation, yet the degree of the impact is controlled by water volume fraction, which reduces the role of cationic interactions, by shielding them, as discussed above. This is especially true for conductivity measured in liquid water, where conductivity almost depends only on water content (or water volume fraction). As hydrophilic-pathway tortuosity is dominated by water volume fraction, it seems that the tortuosity of cation conduction pathways plays a more important role than electrostatic interaction in controlling the conductivity of cations in liquid water. In summary, the mobility of cations is not affected significantly by charge numbers (electrostatic force) in liquid water, but is largely affected in water vapor (especially below 80% RH), implying the effect of water shielding. In addition, while the water per charge and network topology dominates the conductivity response, especially in liquid water, it must be noted that the mesoscale electrostatic and solvation energy balance impacts the absolute value of the water

content and thus conductivity at a given RH. Such findings are useful for understanding the intrinsic processes governing the transport behavior and for guiding membrane and model development and applications.

Figure 10 Humidity-dependent conductivity of cation-exchanged Nafion 212 membrane plotted (a) as a function of λ/z (the colors, symbols and conductivity are the same as shown in Figure 6), and (b) as a function of water volume fraction, where conductivity measured at the same RH are shown in identical colors for all the cations, which are represented by different symbols (the same as in (a)). Line is based on the trend for the liquid-water conductivity data, which is extended to low-RH regime to highlight the deviation from the hydrated conductivity.

5. Conclusions

In this study, the impact of cationic-form of Nafion on various structural and transport properties was investigated, both in liquid water and water vapor (as a function of RH), providing a wider concentration regime than reported previously. A master conductivity curve as a function of water content per charge, which is related to the water volume fraction, was elucidated. The overall properties of the Nafion membrane depended on its water content, which controls the extent of interaction

between cation and sulfonate groups. In the low-RH regime, water-uptake behavior and conductivity of cation-exchange membrane is mainly controlled by the ionic interactions, primarily those by between the fixed sulfonate anion and the cations, due to a lack of solvation. In this regime, the hydrophilic domain spacing depends on the cation size (radius) and storage modulus of dry membrane increases with larger and higher-valence cations owing to the stronger ionic crosslinks formed (by the cation-sulfonate sites) within the hydrophilic domains. Moreover, at the same water content, membranes exchanged with cations of the same valence exhibit similar conductivity, while increasing cation valence (or reducing charge density) tends to reduce conductivity, which is ascribed to the stronger interactions these cations have with the sulfonate groups. However, with the addition of water, especially toward saturated conditions, the conductivity scales linearly with water content, regardless of the cation type, indicating the key role of water amount and resultant mesoscale network connectivity in controlling transport. In this high-RH regime, the impact of cations is diminished as a result of shielding effect of water that solvates the cations and weakens the sulfonate-cation interactions. As such, the hydrophilic domain spacing of a hydrated membrane scales with the Lewis acid strength of the cations, instead of its radius. This study demonstrated how water content influences the interactions between cations, sulfonate groups, and water molecules across the water-content scale. The findings provide a quantitative picture for the shielding effect of water, in that with increasing humidity, the factors controlling the structure-transport relationship of PFSA membranes shift from cation-sulfonate interactions to water content and its solvation effects. These correlations are further substantiated by the fact that the storage modulus correlated with the dry-domain spacing and water-uptake capacity, revealing the underlying structure/transport/stability relationships as the governing phenomena in cation-exchanged ionomer membranes.

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Figure Captions

Figure 1 Chemical structure of Nafion PFSA ionomer and the cations investigated in this study illustrated according their radius (scaled). Pictorial description of the phase-separated nanomorphology of hydrate PFSA membrane and changes in its hydration and conductivity upon exchanging its monovalent cation with a multivalent cation, based on the findings in this study.

Figure 2 Water sorption isotherms of Nafion 212 membranes at 25°C for (a) monovalent cations; (b) divalent cations; (c) for higher-valence Iron and Cerium. (d) Maximum water content close to saturation as a function of Lewis Acid Strength (LAS) of the cation. Inset shows the residual water at 0% RH plotted as a function of cation radius. The lower and upper symbols for each cation indicate the water content without and with accounting for the residual water, respectively.

Figure 3 Dynamic mechanical properties of as-received Nafion membrane in different cation forms: (a) storage modulus and (b) tan delta as a function of temperature

Figure 4 Storage moduli of cation-exchanged Nafion 212 membrane as a function of cation radius. The lines are guides-for-the-eye. (b) Alpha-transition temperature of cation-exchange Nafion membrane plotted in the order of increasing LAS of the cation

Figure 5 SAXS profiles of Nafion membrane of different cation forms measured in liquid water, and the corresponding full-width half-max (FWHM) of ionomer peak as a function of cation radius.

Figure 6 Hydrophilic domain spacing of Nafion membrane (a) in “dry” state (10% RH), d_{dry} , plotted as a function of its water content including the residual water, (b) in liquid water, d_{wet} , plotted as a function of water content per cation. The inset in (a) shows the inverse correlation between d_{dry} and cation radius, and inset in (b) shows d_{wet} plotted vs. Lewis acid strength of cation. The dotted and dashed lines are fit to the data for hydrated Nafion in cation forms (this work), and for Nafion- H^+ at various hydration levels (refs.[3, 64]), respectively. The colors and symbols are the same as described in Figures 1-4.

Figure 7 Humidity-dependent through-plane conductivity of Nafion 212 membrane as a function of water content at 30°C. (The colors and symbols are the same as described in Figure 1).

Figure 8 Relationship between storage modulus and water content (98% RH) of different cation exchanged membranes

Figure 9 Change in hydrophilic domain spacing of cation-exchanged Nafion membrane from dry to fully-hydrated state (in liquid water) plotted as a function of Lewis acid strength of the cation.

Figure 10 Humidity-dependent conductivity of cation-exchanged Nafion 212 membrane plotted (a) as a function of λ/z (the colors, symbols and conductivity are the same as shown in Figure 6), and (b) as a

function of water volume fraction, where conductivity measured at the same RH are shown in identical colors for all the cations, which are represented by different symbols (the same as in (a)). Line is based on the trend for the liquid-water conductivity data, which is extended to low-RH regime to highlight the deviation from the hydrated conductivity.

References

- [1] A. Kusoglu, K.T. Cho, R.A. Prato, A.Z. Weber, Structural and transport properties of Nafion in hydrobromic-acid solutions, *Solid State Ionics*, 252 (2013) 68-74.
- [2] M.L. Perry, A.Z. Weber, Advanced Redox-Flow Batteries: A Perspective, *J. Electrochem. Soc.*, 163 (2016) A5064-A5067.
- [3] A. Kusoglu, S. Savagatrup, K.T. Clark, A.Z. Weber, Role of Mechanical Factors in Controlling the Structure–Function Relationship of PFSA Ionomers, *Macromolecules*, 45 (2012) 7467-7476.
- [4] G.S. Hwang, D. Parkinson, A. Kusoglu, A. MacDowell, A.Z. Weber, Water Uptake and Transport in Nafion®, Meeting Abstracts, MA2012-02 (2012) 1483.
- [5] M.A. Hickner, Water-mediated transport in ion-containing polymers, *J. Polym. Sci., Part B: Polym. Phys.*, 50 (2012) 9-20.
- [6] K.-D. Kreuer, S.J. Paddison, E. Spohr, M. Schuster, Transport in Proton Conductors for Fuel-Cell Applications: Simulations, Elementary Reactions, and Phenomenology, *Chem. Rev.*, 104 (2004) 4637-4678.
- [7] S.J. Paddison, Proton conduction mechanisms at low degrees of hydration in sulfonic acid-based polymer electrolyte membranes, *Annu Rev Mater Res*, 33 (2003) 289-319.
- [8] M.A. Hickner, B.S. Pivovar, The chemical and structural nature of proton exchange membrane fuel cell properties, *Fuel Cells*, 5 (2005) 213-229.
- [9] A. Kusoglu, A.Z. Weber, Water Transport and Sorption in Nafion Membrane, *Polymers for Energy Storage and Delivery: Polyelectrolytes for Batteries and Fuel Cells*, American Chemical Society 2012, pp. 175-199.
- [10] A.Z. Weber, M.M. Mench, J.P. Meyers, P.N. Ross, J.T. Gostick, Q.H. Liu, Redox flow batteries: a review, *J. Appl. Electrochem.*, 41 (2011) 1137-1164.
- [11] A.Z. Weber, R.L. Borup, R.M. Darling, P.K. Das, T.J. Dursch, W.B. Gu, D. Harvey, A. Kusoglu, S. Litster, M.M. Mench, R. Mukundan, J.P. Owejan, J.G. Pharoah, M. Secanell, I.V. Zenyuk, A Critical Review of Modeling Transport Phenomena in Polymer-Electrolyte Fuel Cells, *J. Electrochem. Soc.*, 161 (2014) F1254-F1299.
- [12] M.S. Mikkola, T. Rockward, F.A. Uribe, B.S. Pivovar, The Effect of NaCl in the Cathode Air Stream on PEMFC Performance, *Fuel Cells*, 7 (2007) 153-158.
- [13] X. Cheng, Z. Shi, N. Glass, L. Zhang, J. Zhang, D. Song, Z.-S. Liu, H. Wang, J. Shen, A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms, and mitigation, *J. Power Sources*, 165 (2007) 739-756.
- [14] R. Halseid, P.J.S. Vie, R. Tunold, Effect of ammonia on the performance of polymer electrolyte membrane fuel cells, *J. Power Sources*, 154 (2006) 343-350.
- [15] T. Okada, Effect of ionic contaminants, *Handbook of Fuel Cells*, John Wiley & Sons, Ltd 2010.
- [16] H. Yoshida, Y. Miura, Behavior of water in perfluorinated ionomer membranes containing various monovalent cations, *J. Membr. Sci.*, 68 (1992) 1-10.
- [17] G. Xie, T. Okada, Water Transport Behavior in Nafion 117 Membranes, *J. Electrochem. Soc.*, 142 (1995) 3057-3062.
- [18] G. Xie, T. Okada, Pumping effects in water movement accompanying cation transport across Nafion 117 membranes, *Electrochim. Acta*, 41 (1996) 1569-1571.
- [19] G. Xie, T. Okada, Characteristics of water transport in relation to microscopic structure in Nafion membranes, *Journal of the Chemical Society, Faraday Transactions*, 92 (1996) 663-669.

- [20] M. Lopez, B. Kipling, H.L. Yeager, Ionic diffusion and selectivity of a cation exchange membrane in nonaqueous solvents, *Analytical Chemistry*, 49 (1977) 629-632.
- [21] M. Legras, Y. Hirata, Q.T. Nguyen, D. Langevin, M. Métayer, Sorption and diffusion behaviors of water in Nafion 117 membranes with different counter ions, *Desalination*, 147 (2002) 351-357.
- [22] N.H. Jalani, R. Datta, The effect of equivalent weight, temperature, cationic forms, sorbates, and nanoinorganic additives on the sorption behavior of Nafion®, *J. Membr. Sci.*, 264 (2005) 167-175.
- [23] K. Hongsirikarn, J.G. Goodwin Jr, S. Greenway, S. Creager, Effect of cations (Na⁺, Ca²⁺, Fe³⁺) on the conductivity of a Nafion membrane, *J. Power Sources*, 195 (2010) 7213-7220.
- [24] H.F.M. Mohamed, Y. Kobayashi, C.S. Kuroda, A. Ohira, Effects of Ion Exchange on the Free Volume and Oxygen Permeation in Nafion for Fuel Cells, *J. Phys. Chem. B*, 113 (2009) 2247-2252.
- [25] M. Saito, K. Hayamizu, T. Okada, Temperature Dependence of Ion and Water Transport in Perfluorinated Ionomer Membranes for Fuel Cells, *J. Phys. Chem. B*, 109 (2005) 3112-3119.
- [26] H.L. Yeager, A. Steck, Cation and Water Diffusion in Nafion Ion-Exchange Membranes - Influence of Polymer Structure, *J. Electrochem. Soc.*, 128 (1981) 1880-1884.
- [27] T. Okada, H. Satou, M. Okuno, M. Yuasa, Ion and water transport characteristics of perfluorosulfonated ionomer membranes with H⁺ and alkali metal cations, *J. Phys. Chem. B*, 106 (2002) 1267-1273.
- [28] G. Xie, T. Okada, Characteristics of water transport in relation to microscopic structure in Nafion membranes, *J. Chem. Soc., Faraday Trans.*, 92 (1996) 663-669.
- [29] S. Chaudhury, C. Agarwal, A.K. Pandey, A. Goswami, Self-Diffusion of Ions in Nafion-117 Membrane Having Mixed Ionic Composition, *J. Phys. Chem. B*, 116 (2012) 1605-1611.
- [30] M. Saito, N. Arimura, K. Hayamizu, T. Okada, Mechanisms of ion and water transport in perfluorosulfonated ionomer membranes for fuel cells, *J. Phys. Chem. B*, 108 (2004) 16064-16070.
- [31] S. Quezado, J.C.T. Kwak, M. Falk, An Infrared Study of Water-Ion Interactions in Perfluorosulfonate (Nafion) Membranes, *Can J Chem*, 62 (1984) 958-966.
- [32] D.L. Feldheim, D.R. Lawson, C.R. Martin, Influence of the Sulfonate Counteranion on the Thermal-Stability of Nafion(R) Perfluorosulfonate Membranes, *J. Polym. Sci., Part B: Polym. Phys.*, 31 (1993) 953-957.
- [33] L.G. Lage, P.G. Delgado, Y. Kawano, Vibrational and thermal characterization of Nafion (R) membranes substituted by alkaline earth cations, *Eur Polym J*, 40 (2004) 1309-1316.
- [34] Y.F. Fan, D. Tongren, C.J. Cornelius, The role of a metal ion within Nafion upon its physical and gas transport properties, *Eur Polym J*, 50 (2014) 271-278.
- [35] C. Bas, L. Reymond, A.-s. Danérol, N.D. Albérola, E. Rossinot, L. Flandin, Key counter ion parameters governing polluted nafion membrane properties, *J. Polym. Sci., Part B: Polym. Phys.*, 47 (2009) 1381-1392.
- [36] T. Okada, S. Moller-Holst, O. Gorseth, S. Kjelstrup, Transport and equilibrium properties of Nafion (R) membranes with H⁺ and Na⁺ ions, *J. Electroanal. Chem.*, 442 (1998) 137-145.
- [37] T. Okada, G. Xie, O. Gorseth, S. Kjelstrup, N. Nakamura, T. Arimura, Ion and water transport characteristics of Nafion membranes as electrolytes, *Electrochim. Acta*, 43 (1998) 3741-3747.
- [38] S.C. Yeo, A. Eisenberg, Physical-Properties and Supermolecular Structure of Perfluorinated Ion-Containing (Nafion) Polymers, *J. Appl. Polym. Sci.*, 21 (1977) 875-898.
- [39] M. Fujimura, T. Hashimoto, H. Kawai, Small-Angle X-Ray-Scattering Study of Perfluorinated Ionomer Membranes .1. Origin of 2 Scattering Maxima, *Macromolecules*, 14 (1981) 1309-1315.

- [40] T.D. Gierke, G.E. Munn, F.C. Wilson, The Morphology in Nafion Perfluorinated Membrane Products, as Determined by Wide-Angle and Small-Angle X-Ray Studies, *J. Polym. Sci., Part B: Polym. Phys.*, 19 (1981) 1687-1704.
- [41] S.K. Young, S.F. Trevino, N.C.B. Tan, Small-angle neutron scattering investigation of structural changes in Nafion membranes induced by swelling with various solvents, *J. Polym. Sci., Part B: Polym. Phys.*, 40 (2002) 387-400.
- [42] A.L. Rollet, G. Gebel, J.P. Simonin, P. Turq, A SANS determination of the influence of external conditions on the nanostructure of nafion membrane, *J. Polym. Sci., Part B: Polym. Phys.*, 39 (2001) 548-558.
- [43] A. Steck, H.L. Yeager, Water Sorption and Cation-Exchange Selectivity of a Perfluorosulfonate Ion-Exchange Polymer, *Anal Chem*, 52 (1980) 1215-1218.
- [44] H. Yoshida, Y. Miura, Behavior of Water in Perfluorinated Ionomer Membranes Containing Various Monovalent Cations, *J. Membr. Sci.*, 68 (1992) 1-10.
- [45] K.A. Page, F.A. Landis, A.K. Phillips, R.B. Moore, SAXS analysis of the thermal relaxation of anisotropic morphologies in oriented Nafion membranes, *Macromolecules*, 39 (2006) 3939-3946.
- [46] K.A. Page, J.K. Park, R.B. Moore, V.G. Sakai, Direct Analysis of the Ion-Hopping Process Associated with the α -Relaxation in Perfluorosulfonate Ionomers Using Quasielastic Neutron Scattering, *Macromolecules*, 42 (2009) 2729-2736.
- [47] Y. Iwai, T. Yamanishi, Thermal stability of ion-exchange Nafion N117CS membranes, *Polym. Degrad. Stab.*, 94 (2009) 679-687.
- [48] S. Kundu, L.C. Simon, M. Fowler, S. Grot, Mechanical properties of Nafion [trademark] electrolyte membranes under hydrated conditions, *Polymer*, 46 (2005) 11707-11715.
- [49] R.L. Jia, B.H. Han, K. Levi, T. Hasegawa, J.P. Ye, R.H. Dauskardt, Effect of cation contamination and hydrated pressure loading on the mechanical properties of proton exchange membranes, *J. Power Sources*, 196 (2011) 3803-3809.
- [50] S. Shi, T.J. Dursch, C. Blake, R. Mukundan, R.L. Borup, A.Z. Weber, A. Kusoglu, Impact of hygrothermal aging on structure/function relationship of perfluorosulfonic-acid membrane, *J. Polym. Sci., Part B: Polym. Phys.*, 54 (2016) 570-581.
- [51] Y. Marcus, Thermodynamics of Solvation of Ions .5. Gibbs Free-Energy of Hydration at 298.15-K, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 2995-2999.
- [52] Y.L. Li, Q.T. Nguyen, C.L. Buquet, D. Langevin, M. Legras, S. Marais, Water sorption in Nafion (R) membranes analyzed with an improved dual-mode sorption model Structure/property relationships, *J. Membr. Sci.*, 439 (2013) 1-11.
- [53] A.K. Phillips, R.B. Moore, Mechanical and transport property modifications of perfluorosulfonate ionomer membranes prepared with mixed organic and inorganic counterions, *J. Polym. Sci., Part B: Polym. Phys.*, 44 (2006) 2267-2277.
- [54] K.B. Daly, A.Z. Panagiotopoulos, P.G. Debenedetti, J.B. Benziger, Viscosity of Nafion Oligomers as a Function of Hydration and Counterion Type: A Molecular Dynamics Study, *The Journal of Physical Chemistry B*, 118 (2014) 13981-13991.
- [55] D.S. Bolintineanu, M.J. Stevens, A.L. Frischknecht, Influence of Cation Type on Ionic Aggregates in Precise Ionomers, *Macromolecules*, 46 (2013) 5381-5392.
- [56] R. Tandon, P.N. Pintauro, Divalent/monovalent cation uptake selectivity in a Nafion cation-exchange membrane: Experimental and modeling studies, *J. Membr. Sci.*, 136 (1997) 207-219.

- [57] K.A. Page, K.M. Cable, R.B. Moore, Molecular origins of the thermal transitions and dynamic mechanical relaxations in perfluorosulfonate ionomers, *Macromolecules*, 38 (2005) 6472-6484.
- [58] R.T. Martin, P.D. Kevin, D.L. Katherine, W.M. Charles, Structure and Properties of Short-Side-Chain Perfluorosulfonate Ionomers, *Multiphase Polymers: Blends and Ionomers*, American Chemical Society 1989, pp. 370-400.
- [59] S.J. Osborn, M.K. Hassan, G.M. Divoux, D.W. Rhoades, K.A. Mauritz, R.B. Moore, Glass transition temperature of perfluorosulfonic acid ionomers, *Macromolecules*, 40 (2007) 3886-3890.
- [60] E. Moukheiber, C. Bas, N.D. Alberola, L. Flandin, Infrared and thermal behaviour of proton exchange membrane (PEM) after cationic contamination, *J. Membr. Sci.*, 431 (2013) 105-112.
- [61] C. Bas, L. Reymond, A.S. Danerol, N.D. Alberola, E. Rossinot, L. Flandin, Key Counter Ion Parameters Governing Polluted Nafion Membrane Properties, *J. Polym. Sci., Part B: Polym. Phys.*, 47 (2009) 1381-1392.
- [62] K.D. Kreuer, G. Portale, A Critical Revision of the Nano-Morphology of Proton Conducting Ionomers and Polyelectrolytes for Fuel Cell Applications, *Adv Funct Mater*, 23 (2013) 5390-5397.
- [63] G. Gebel, Structural evolution of water swollen perfluorosulfonated ionomers from dry membrane to solution, *Polymer*, 41 (2000) 5829-5838.
- [64] A. Kusoglu, T.J. Dursch, A.Z. Weber, Nanostructure/Swelling Relationships of Bulk and Thin-Film PFSA Ionomers, *Adv Funct Mater*, 26 (2016) 4961-4975.
- [65] I.D. Brown, A. Skowron, Electronegativity and Lewis acid strength, *Journal of the American Chemical Society*, 112 (1990) 3401-3403.
- [66] D. Damasceno Borges, G. Gebel, A.A. Franco, K. Malek, S. Mossa, Morphology of Supported Polymer Electrolyte Ultrathin Films: A Numerical Study, *The Journal of Physical Chemistry C*, 119 (2015) 1201-1216.
- [67] A.M. Baker, R. Mukundan, D. Spornjak, E.J. Judge, S.G. Advani, A.K. Prasad, R.L. Borup, Cerium Migration during PEM Fuel Cell Accelerated Stress Testing, *J. Electrochem. Soc.*, 163 (2016) F1023-F1031.
- [68] M.C. Tucker, A. Weiss, A.Z. Weber, Improvement and analysis of the hydrogen-cerium redox flow cell, *J. Power Sources*, 327 (2016) 591-598.
- [69] H. Feng, Modeling of vapor sorption in glassy polymers using a new dual mode sorption model based on multilayer sorption theory, *Polymer*, 48 (2007) 2988-3002.
- [70] K. Fatyeyeva, C. Chappay, F. Poncin-Epaillard, D. Langevin, J.M. Valleton, S. Marais, Composite membranes based on Nafion (R) and plasma treated clay charges: Elaboration and water sorption investigations, *J. Membr. Sci.*, 369 (2011) 155-166.
- [71] S.W. Shi, T.J. Dursch, C. Blake, R. Mukundan, R.L. Borup, A.Z. Weber, A. Kusoglu, Impact of hygrothermal aging on structure/function relationship of perfluorosulfonic-acid membrane, *J. Polym. Sci., Part B: Polym. Phys.*, 54 (2016) 570-581.
- [72] K.A. Page, A. Kusoglu, C.M. Stafford, S. Kim, R.J. Kline, A.Z. Weber, Confinement-driven increase in ionomer thin-film modulus, *Nano Lett*, 14 (2014) 2299-2304.
- [73] S.R. Lowry, K.A. Mauritz, An Investigation of Ionic Hydration Effects in Perfluorosulfonate Ionomers by Fourier-Transform Infrared-Spectroscopy, *J. Am. Chem. Soc.*, 102 (1980) 4665-4667.
- [74] K.M. Cable, K.A. Mauritz, R.B. Moore, Effects of Hydrophilic and Hydrophobic Counterions on the Coulombic Interactions in Perfluorosulfonate Ionomers, *J. Polym. Sci., Part B: Polym. Phys.*, 33 (1995) 1065-1072.

Phase-separated morphology of cation-exchanged PFSA ionomer impacts its conductivity, which scales with hydration per cation