

# Moving Beyond Mass-Based Parameters for Conductivity Analysis of Sulfonated Polymers

Yu Seung Kim<sup>1</sup> and Bryan S. Pivovar<sup>2,\*</sup>

<sup>1</sup>Sensors and Electrochemical Devices, Los Alamos National Laboratory, Los Alamos, New Mexico 87545; email: yskim@lanl.gov

<sup>2</sup>Hydrogen Technologies and Systems Center, National Renewable Energy Laboratory, Golden, Colorado 80401; email: bryan\_pivovar@nrel.gov

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\*Corresponding author.

## Key Words

sulfonated polymers, conductivity, water uptake, fuel cells, morphology

## Abstract

The proton conductivity of polymer electrolytes is critical for fuel cells and has therefore been studied in significant detail. The conductivity of sulfonated polymers has been linked to material characteristics to elucidate trends. Mass-based measurements based on water uptake and ion exchange capacity are two of the most common material characteristics used to make comparisons between polymer electrolytes, but they have significant limitations when correlated to proton conductivity. These limitations arise in part because different polymers can have significantly different densities and because conduction occurs over length scales more appropriately represented by volume measurements rather than mass. Herein we establish and review volume-related parameters that can be used to compare the proton conductivity of different polymer electrolytes. Morphological effects on proton conductivity are also considered. Finally, the impact of these phenomena on designing next-generation sulfonated polymers for polymer electrolyte membrane fuel cells is discussed.

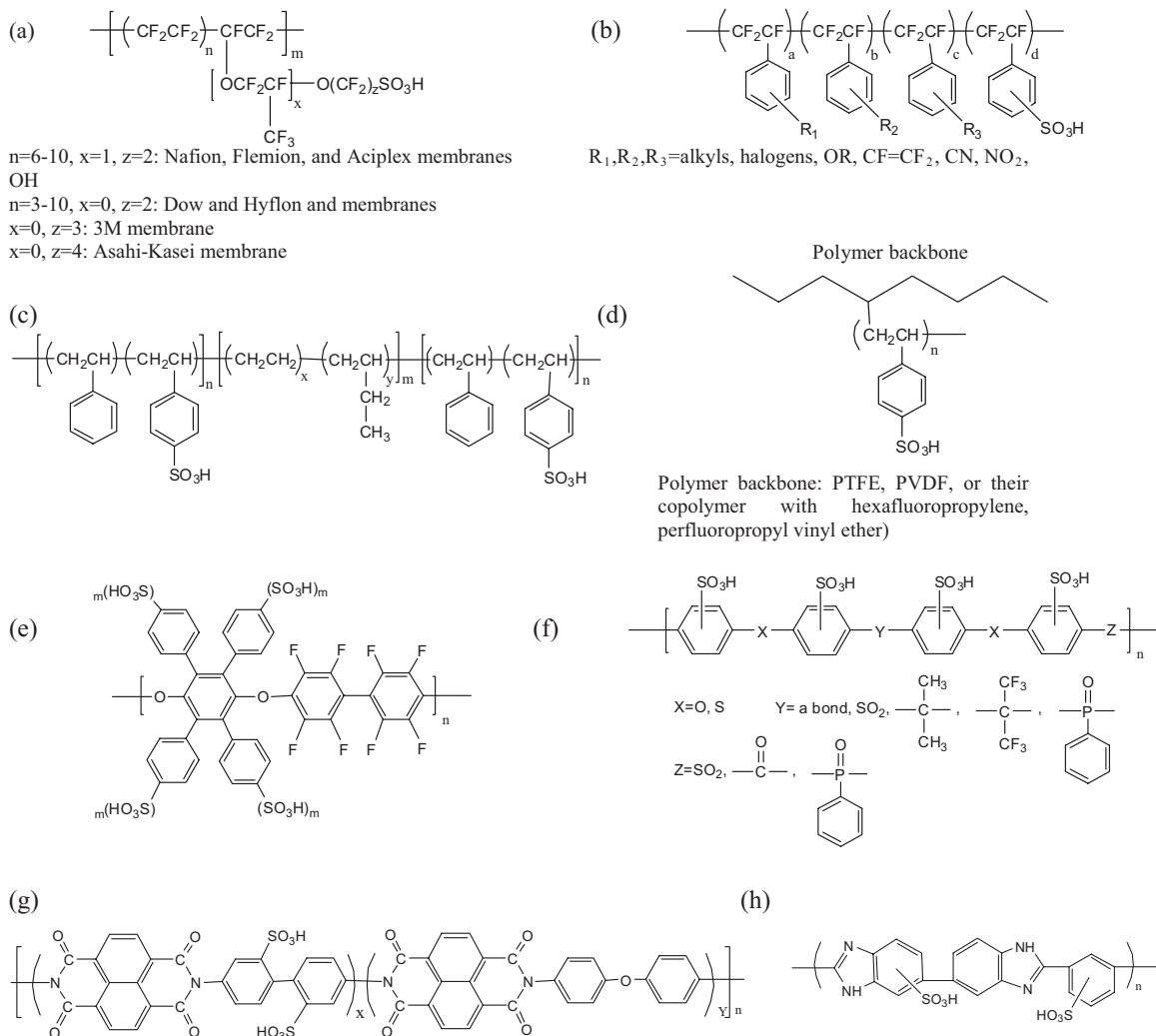
## INTRODUCTION

**PEM:** polymer electrolyte membrane

**PFSA:** perfluoro sulfonic acid

Numerous sulfonated polymers have been developed for potential application in polymer electrolyte membrane (PEM) fuel cells. We group the most highly studied polymers into three categories: (a) poly(perfluorosulfonic acids) (PFSA)s, (b) styrene sulfonic acids (SSAs), and (c) sulfonated aromatic or heterocyclic polymers (1, 2). Representative chemical structures of sulfonated polymers are shown in **Figure 1**.

PFSA)s are copolymers of tetrafluoroethylene and perfluorovinyl ether with a pendant sulfonic acid group. The PFSA Nafion is considered the benchmark of sulfonated polymers for fuel cells



**Figure 1**

Chemical structures of various sulfonated polymers: (a) poly(perfluorosulfonic acids) (PFSA)s, (b) sulfonated polystyrenes, (c) sulfonated polystyrene-*b*-(ethylene-*cobutylene*)-*b*-sulfonated polystyrenes, (d) radiation-induced polystyrene graft polymers, (e) sulfonated polyphenylenes, (f) sulfonated aromatics, (g) sulfonated polyimides, and (h) sulfonated polybenzimidazoles.

(3). Alternative PFSA's such as Flemion, Aciplex, Dow, Hyflon, and 3M share similar chemistry, usually with minor modifications to the ionomeric side chains (4).

Styrene sulfonic acids are sulfonated polymers that replace the tetrafluoroethylene-based backbones of PFSA's with styrene. Styrene sulfonic acid polymers include polymers from the BAM<sup>®</sup> line from Ballard Advanced Materials, Dais Analytic's sulfonated styrene-ethylene-butylene-styrene (SEBS) polymers, and radiation-induced polystyrene graft polymers (5).

Sulfonated aromatic or heterocyclic polymers are based on high performance engineering thermoplastics. Sulfonated polyaromatics include sulfonated poly(arylene ether)s, sulfonated polysulfones, sulfonated poly(ether ether ketone)s, and sulfonated polynitriles (6–8). Sulfonated heterocyclic polymers contain polyimide, polybenzimidazole, or other heterocyclic repeat units (9).

The primary purpose of these electrolytes in fuel cell applications is to transport protons to allow half reactions to occur. It is for this reason that they tend to contain high concentrations of strong acids (typically, sulfonic acid groups). Although proton conduction is the most frequently studied property of these materials, they must also possess other properties such as electronic insulation, impermeability to reactants, and chemical and mechanical robustness. Although most sulfonated polymers are excellent electron insulators and have reasonably low reactant permeability, increasing the proton conductivity of mechanically stable sulfonated polymers remains a technical challenge. Current commercially available polymer electrolyte membranes exhibit proton conductivities of approximately 100 mS cm<sup>-1</sup> under fully hydrated conditions, a level of conduction suitable for most applications. There has been a drive to increase conduction at low relative humidity, however, owing to cost and efficiency implications for high temperature, low relative humidity performance in automotive applications.

Efforts to elucidate the structure-composition-property relationships of polymer electrolytes have aimed at correlating specific metrics (physical or compositional properties of PEMs) to observed performance (for example, proton conductivity as a function of temperature and relative humidity). Here we review the data in the literature specific to proton conductivity in terms of particular parameters including water uptake (WU), ion exchange capacity (IEC) (based on volume and mass), hydration number ( $\lambda$ ), and percent conducting volume (PCV) (a parameter defined and described in detail later). Limitations and advantages of each of these specific metrics are discussed.

Mass-based WU and IEC are two commonly used metrics for studying proton conductivity trends. WU is typically obtained from two simple measurements, the wet and dry weight of membranes. It is therefore one of the easiest metrics to obtain, and is calculated by:

$$WU \text{ (wt. \%)} = \frac{W_{(WET)} - W_{(DRY)}}{W_{(DRY)}} \times 100, \quad 1.$$

where  $W_{(WET)}$  and  $W_{(DRY)}$  are the polymer weight in wet and dry states, respectively.

IEC is usually obtained from chemical structure (through simple calculation of atomic weight per acid group) and is sometimes verified by measuring acid content by titration. IEC is typically expressed as moles of sulfonic acid groups per gram of dry membrane expressed in the units of milliequivalents per gram. Alternatively, equivalent weight (EW, the number of grams of dry membrane per mole of sulfonic acid groups, the inverse of IEC) is also commonly used.

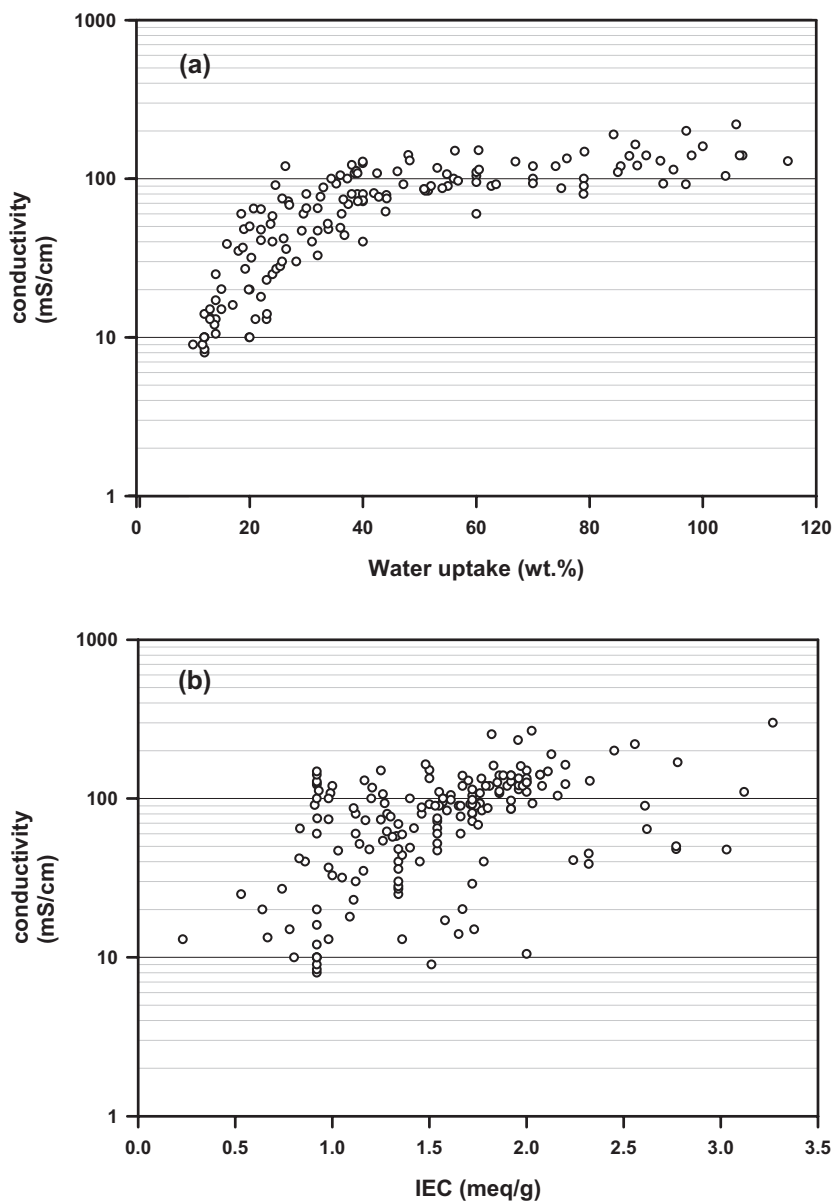
**Figures 2a** and **b** plot proton conductivity versus WU and IEC, respectively, for a large cross-section of sulfonated polymer electrolytes (10–41). (Taken from 32 independent references in the literature, these same data are reproduced in several other figures for different metrics. As an aside, these 32 references were selected from more than 60 references investigated. The references not included either lacked sufficient data or reported values of Nafion conductivity in significant disagreement with the values reported here and widely accepted.) The plots of **Figure 2a** and **b**

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**IEC:** ion exchange capacity (meq g<sup>-1</sup>)

**PCV:** percent conducting volume

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**Figure 2**

Proton conductivity as a function of (a) water uptake and (b) weight-based ion exchange capacity (IEC) of 32 sulfonated polymers. Proton conductivity under fully hydrated conditions at ambient temperature was taken from the literature (10–41).

show a general trend that conductivity increases as WU and IEC increase. These are commonly reported trends and make sense because as polymers contain more acid groups it is reasonable to assume that WU and conductivity should increase. The multiple correlation coefficient,  $R$ , which indicates that how well a regression curve describes data (an  $R$  value of 1 indicates a perfect correlation between independent and dependent variables), was used to quantify data scattering.

The trend exhibited is clearer for WU versus conductivity ( $R = 0.83$ ) than for IEC ( $R = 0.45$ ), but even for WU there is meaningful scatter in the data. At a given WU, conductivity values vary by up to an order of magnitude. The data scatter involved with IEC is much larger, although trends within specific polymer families are often much clearer than the combination of data presented here. Perhaps owing in part to factors illustrated in these plots, WU has been more commonly correlated with physical properties across polymer families whereas IEC is more often limited to use in comparisons within the same family of sulfonated polymers (42, 43).

Both WU and IEC (as presented in **Figure 2**) are mass-based parameters that introduce limitations. One simple reason for the data scatter in **Figure 2** is that polymer systems can have significantly different densities, and the mass of the polymer is less relevant for proton conduction, which happens over length scales that are more appropriately represented by volume-based metrics than mass-based ones. Several scientists (including us) have introduced volume-based parameters, although they still are not commonly reported in relevant studies. The reason for this largely stems from the ease of making mass-based measurements or estimations. Although volume-based measurements are not particularly difficult, they do require more effort, and for most studies in the literature (which focus on a single family of polymers rather than across widely different families of polymers), mass-based trends still allow for insight to be gained. It is only when polymers are compared across families or under “nonstandard” conditions (such as extremely high WU) that mass-based measurements become significantly limited. In compiling the data put forth in this review, one area of concern is that density data for many of the polymers presented in the literature do not exist, and therefore the mass-based measurements cannot easily be converted to volume-related parameters. In this review, we present various volume- (or nonmass-) related parameters for sulfonated polymers and correlate these parameters with proton conductivity. These parameters, although in many ways more appropriate for comparison purposes, are still limited as they do not consider the morphological (structural) features of the polymer systems. We therefore include a brief discussion of the role of structure in properties that highlights issues related to phase continuity and phase contrast. Finally, we discuss the advances made in polymer electrolytes for fuel cell applications and suggest directions for future generation materials.

## VOLUME-RELATED PARAMETERS

We move our discussion to focus on volume-related parameters, including swelling ratio, water volume fraction, volume-based IEC ( $IEC_V$ ), number of atoms per charge (NAC), molar volume per charge (MVC), and PCV, which are all presented in detail in the following sections. Hydration number (the number of water molecules per sulfonic acid site, often represented as  $\lambda$ ), a nonmass-based parameter although not strictly a volume-related parameter, is also presented in terms of relevance for comparison purposes.

### Swelling Ratio

The swelling ratio of a PEM is a widely reported volume-related parameter, but it is usually presented in the context of dimensional stability rather than in correlation with proton conductivity (44–51). The swelling ratio is obtained from a change in thickness ( $\Delta tb$ ) and/or length change(s) ( $\Delta l$ ) between hydrated and dry membranes:

$$\Delta tb = \frac{(tb - tb_0)}{tb_0}, \quad \Delta l = \frac{(l - l_0)}{l_0}, \quad 2.$$

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**NAC:** number of atoms per charge

**MVC:** molar volume per charge ( $\text{cm}^3$  per ionomer or the mol equivalent of the acid group)

**$\lambda$ :** hydration number

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where  $tb$  and  $tb_0$  are the thickness of membrane equilibrated in liquid water and in the dry state, respectively, and  $l$  and  $l_0$  are the width or length of membrane equilibrated in liquid water and in the dry state, respectively.

Swelling ratios allow for anisotropy to be investigated by measuring WU in the in-plane ( $x$  and  $y$ ) and through-plane ( $z$ ) directions, whereas other length scale parameters only measure isotropic properties. Tang and colleagues observed that Nafion has a higher swelling ratio in the through-plane ( $z$ ) direction compared with the in-plane ( $x, y$ ) directions at 30–90% relative humidity (RH) conditions (52). Others have also reported anisotropic swelling ratios for sulfonated polyimides, polysulfones, and Nafion (47, 53–55). The directionally oriented swelling ratio has importance because most conductivity measurements of sulfonated membranes are conducted in-plane whereas through-plane conductivity reflects the transport direction of protons in operating cells. A few reports have also indicated that Nafion has lower conductivity in the through-plane direction than in the in-plane direction (56, 57).

### Water Volume Uptake

Water volume uptake was introduced at least as early as 1980 (58). The water volume uptake,  $WU_{(VOL)}$ , of a sulfonated polymer is calculated using the density of dry polymer and water according to:

$$WU_{(VOL)} = \frac{(W_{WET} - W_{DRY}) \cdot \delta_{(dry)}}{W_{DRY} \cdot \delta_w}, \quad 3.$$

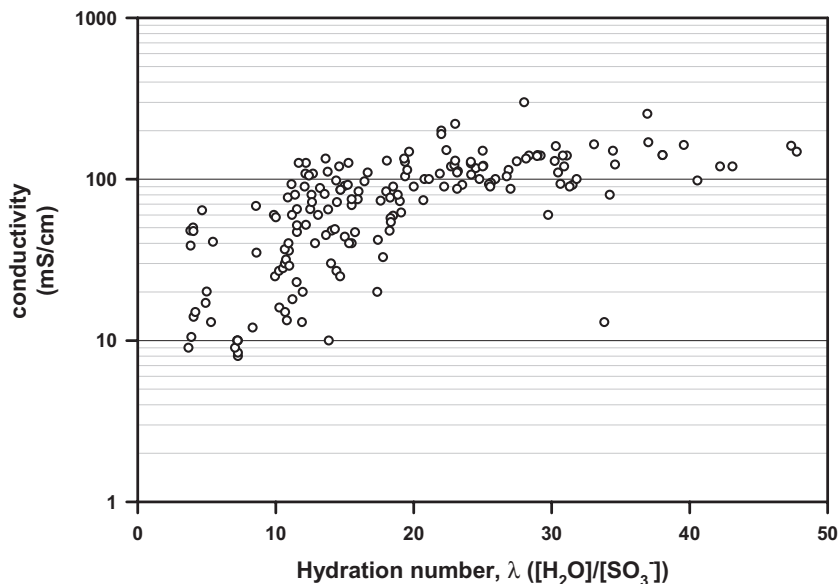
where  $W_{WET}$  and  $W_{DRY}$  are polymer weights in wet and dry states, respectively, and  $\delta_{(DRY)}$  and  $\delta_w$  are the densities of the dry polymer and water, respectively.

In most cases, water volume uptake has been used to standardize proton conductivity (specific conductivity) in models. However, water volume uptake has also been used to evaluate sulfonated polymers (59–62). Scherer et al. compared the proton conductivity of Nafion 117, Nafion 120, and Dow membranes using the number of carriers present per unit volume (63). Pintauro & Tang compared proton conductivity of sulfonated polyphosphazene membranes using specific conductivity (64). Their observations include that (a) the proton volume concentration of fully hydrated PFSA did not always follow the same trends as mass-based IEC, (b) dilution by water molecules affects proton conductivity, and (c) Nafion and sulfonated polyphosphazene have similar dependencies of proton conductivity on water volume fraction.

### Hydration Number ( $\lambda$ )

Hydration number, the number of water molecules per sulfonic acid group (often denoted as  $\lambda$ ), has been widely used to compare properties of sulfonated polymers. Most parameters correlated with polymer electrolyte properties in the literature are focused on mass-based measures that limit comparisons between polymer families. Because hydration number counts the number of water molecules per sulfonic acid group, it can be argued that it avoids some of the limitations of mass-based parameters. This parameter has been used since the early 1960s for sulfonated styrene-based ionomers (65). Since Bunce et al. reported the WU of Nafion using  $\lambda$ , numerous papers have used this parameter for quantifying the WU of various sulfonated polymer systems (26, 27, 66–68).

Hydration number has certain benefits, as it reflects the “acid concentration” in water, assuming that all the water is in a hydrophilic phase and that all the acid groups also reside in this phase. The hydration level of sulfonated polymers under partially humidified conditions is a specific area in which hydration number has been used. Zawodzinski et al. reported that Nafion has two isopiestic sorption regions: (a) a region of relatively little increase in water content ( $\lambda = 2$ –6) with increasing humidity at low RH where the water in the polymer is engaged in strong interactions



**Figure 3**

Proton conductivity as a function of hydration number ( $\lambda$ ) of 32 sulfonated polymers under fully hydrated conditions at ambient temperature.

with the ionic components of the polymer, and (*b*) a region of significantly greater increase in water content ( $\lambda = 6\text{--}14$ ) where water is involved in polymer swelling at high RH (26, 27). Other sulfonated polymers show similar sorption behavior although the  $\lambda$  range in each sorption region varies. This observation motivated studies of the state of water in various sulfonated polymers, and relationships between the state of water, proton conductivity, water diffusion, and methanol permeability have been suggested (68–70).

For other areas, such as electroosmotic drag and water transport (27, 71–74), molecular dynamics modeling (75, 76), and analytical data analysis (77–80) of various sulfonated polymer systems,  $\lambda$  has been preferred over mass-based WU for comparing polymer properties.

Although hydration number has been used as an alternative parameter for mass-based WU or IEC (and in conjunction with them), it also has limits because it does not consider the relative abundance of water (hydrophilic versus hydrophobic phase) in the membrane. Unlike swelling ratio and water volume fraction, for which limited conductivity data are available for multiple classes of polymer electrolytes under liquid equilibrated conditions, significant data for  $\lambda$  versus conductivity exist in the literature. **Figure 3** shows the proton conductivity of multiple sulfonated polymers as a function of  $\lambda$ . The trend of increasing conductivity with increasing hydration number is still clear, but the data scatter is worse ( $R = 0.64$ ) than in the plot of conductivity versus mass-based WU ( $R = 0.83$ ) (**Figure 2a**).

### Volume Ion Exchange Capacity, $IEC_V$

$IEC_V$  represents the sulfonic acid concentration in a unit volume. Dry volume IEC,  $IEC_{V(DRY)}$  is obtained by multiplying the membrane density by the weight-based IEC (81, 82):

$$IEC_{V(DRY)} = IEC \cdot \delta_{(DRY)}, \quad 4.$$

where  $\delta_{(DRY)}$  is the density of the dry membrane.



To account for volume expansion owing to absorbed water, wet volume IEC,  $IEC_{V(WET)}$  is obtained either by direct measurement or by estimating wet membrane density (81–83):

$$IEC_{V(WET)} = IEC \cdot \delta_{(WET)} = \frac{IEC_V}{(1 + WU_{(VOL)})}, \quad 5.$$

where  $\delta_{(WET)}$  is polymer density in the wet state and  $WU_{(VOL)}$  is the water volume uptake.

While water volume uptake can be measured directly from the dimensional change of hydrated polymers, the parameter was often calculated from WU and dry polymer density, which neglects density changes upon mixing.

In a previous report, we showed the strong importance of changing reference parameters from weight-based IEC to  $IEC_{V(WET)}$  in comparing polymer families. In these studies, comparing the WU and conductivity of hexafluoro bisphenol A (6F) and biphenol-based sulfonated poly(arylene ether sulfone)s (BPSHs) showed a strong change in trends as a function of IEC and  $IEC_{V(WET)}$ . The WU data (vol%) are reproduced in terms of both IEC and  $IEC_{V(WET)}$  in **Figure 4a** and **b**, respectively. Of particular note, the WU of the two polymer systems as a function of IEC showed the exact same dependency on WU at a given IEC, which leads to the conclusion that chemistry plays little role in WU. When the parameter was changed from IEC to  $IEC_{V(WET)}$ , however, significant changes were witnessed that demonstrate the importance of chemistry in these systems.

Both the fluorinated and nonfluorinated copolymers exhibit an inflection point (percolation threshold) as the degree of sulfonation increases. The percolation thresholds for 6F and BPSH are similar (~60 mol%). Further increase in the degree of sulfonation reduced  $IEC_{V(WET)}$ , which resulted in reduced sulfonic acid group concentration (dilution of the acid groups) due to substantially increased WU. At this point the mechanical properties of the system become a significant issue. From **Figure 4b** it is apparent that 6F-based copolymers have greater attainable maximum  $IEC_{V(WET)}$  values than biphenol-based copolymers. It is for this reason that they were able to attain higher conductivity values, as we reported earlier.

**Figure 5** contains the data from **Figure 4b** but also adds Nafion (at varying EWs) and cross-linked sulfonated poly(arylene ether) (ESF-BP, at varying sulfonation levels) (13). The PFSA Nafion has a greater attainable maximum  $IEC_{V(WET)}$  than partially fluorinated polymers (6F), whereas ESF-BPs have even higher attainable maximum  $IEC_{V(WET)}$  values. These results show clear trends that sulfonic acid concentration per unit volume of hydrated polymers can be dramatically changed with fluorination and cross-linking.

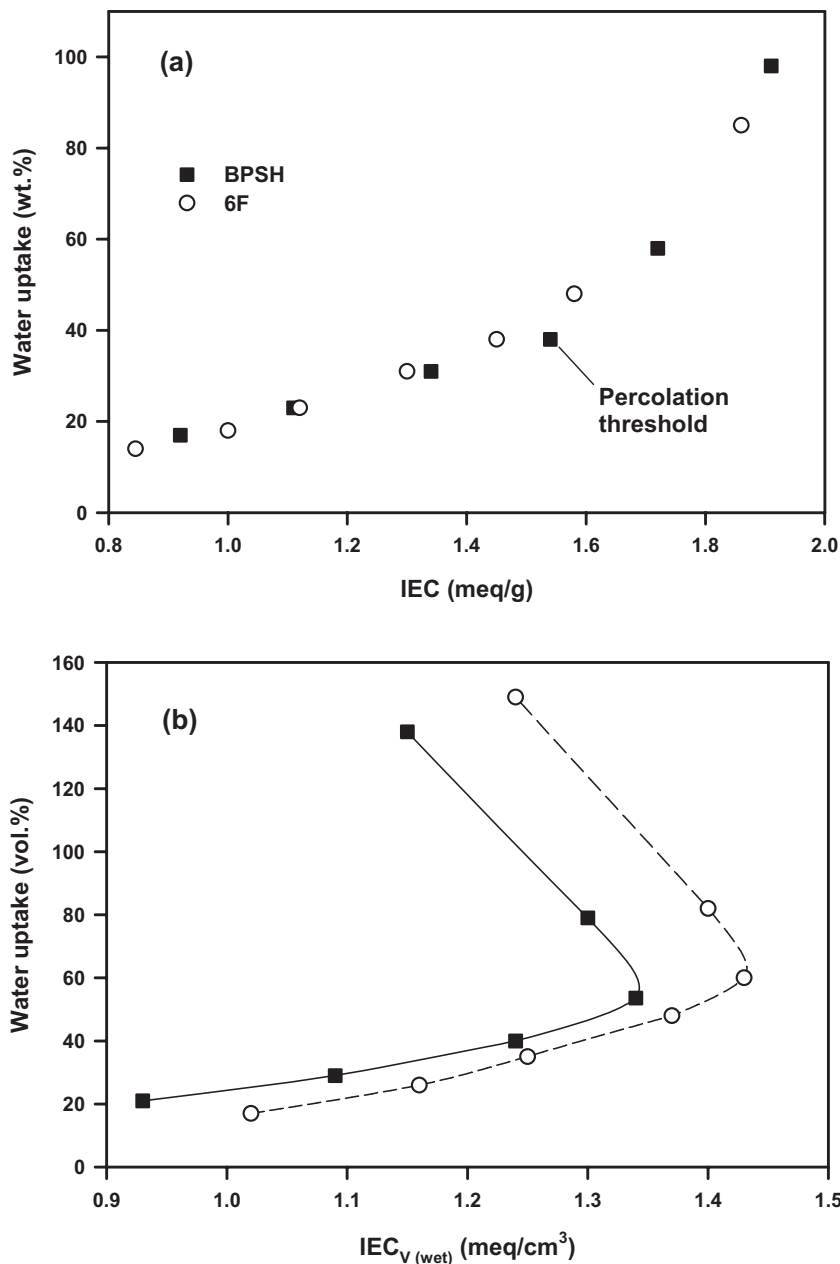
**Figure 6** compares the proton conductivity of BPSH copolymers as a function of (dry, weight-based) IEC and (hydrated, volume-based)  $IEC_{V(WET)}$ . When the proton conductivity of BPSH is plotted as a function of IEC, conductivity increases monotonously until BPSH forms a hydrogel owing to excessive water absorption. At this point, the polymer lacks the ability to resist swelling forces, and eventually, at even higher sulfonation levels, dissolution occurs. This behavior has also been observed in other sulfonated polymer systems such as Nafion (12, 84) and styrene sulfonic acids (85–87). If instead the proton conductivity of BPSH is plotted as a function of  $IEC_{V(WET)}$ , a much different trends appears. At low ion content, conductivity increases with increasing acid content until some percolation limit is reached at which mechanical properties become limited (e.g., modulus changes from 580 to 174 MPa) and swelling significantly increases (e.g., WU changes from 26% to 61%). Hydrogel formation is denoted by the onset of decreased conductivity with further increases in sulfonation level. Even though the highly sulfonated BPSH polymers presented have reasonable conductivity, these hydrogels cannot be used for fuel cell applications because of poor mechanical properties (e.g., the modulus and WU of BPSH-60 are <10 MPa and

**6F:** hexafluoro bisphenol A-based sulfonated poly(arylene ether sulfone)

**BPSH:** biphenol-based sulfonated poly(arylene ether sulfone) H<sup>+</sup> form

**ESF-BP:** biphenol-based cross-linked sulfonated poly(arylene ether)



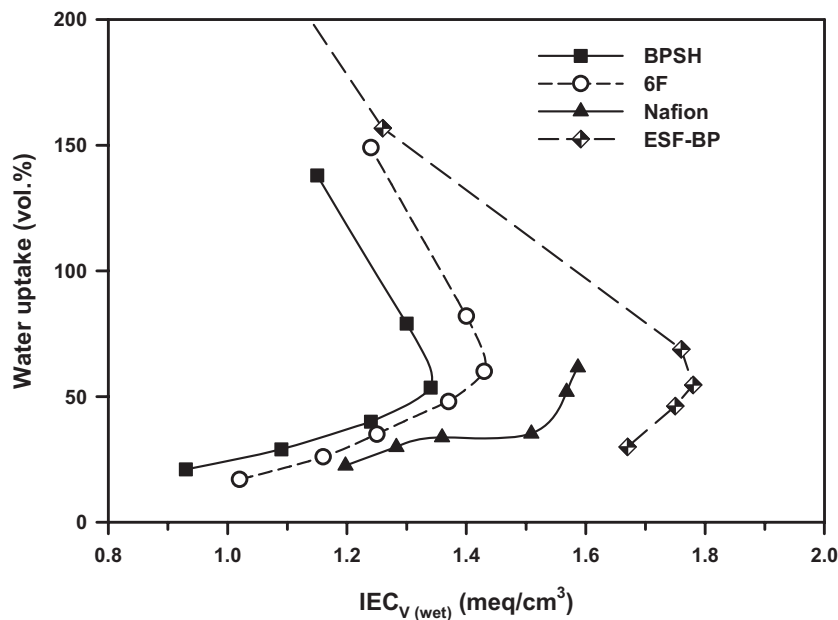


**Figure 4**

Comparison of water uptake (WU) using (a) weight-based IEC and (b) fully hydrated, volume-based IEC ( $IEC_{V(WET)}$ ). Data reproduced from Reference 81.

> 500%, respectively) that are more easily visualized in the plot of  $IEC_{V(WET)}$ . In fact, even polymers above the percolation limit have poor long-term stability under fuel cell operating conditions.

The data presented show the value of  $IEC_{V(WET)}$  as a correlating parameter. Still, it has rarely been used (88), largely because of the lack of density data for sulfonated polymers in the literature owing to the additional experimental requirements/difficulties of measuring volumetric change under fully and partially humidified (or dry) conditions.



**Figure 5**

Effect of fluorine and cross-linking on membrane WU as a function of  $IEC_{V(WET)}$ .

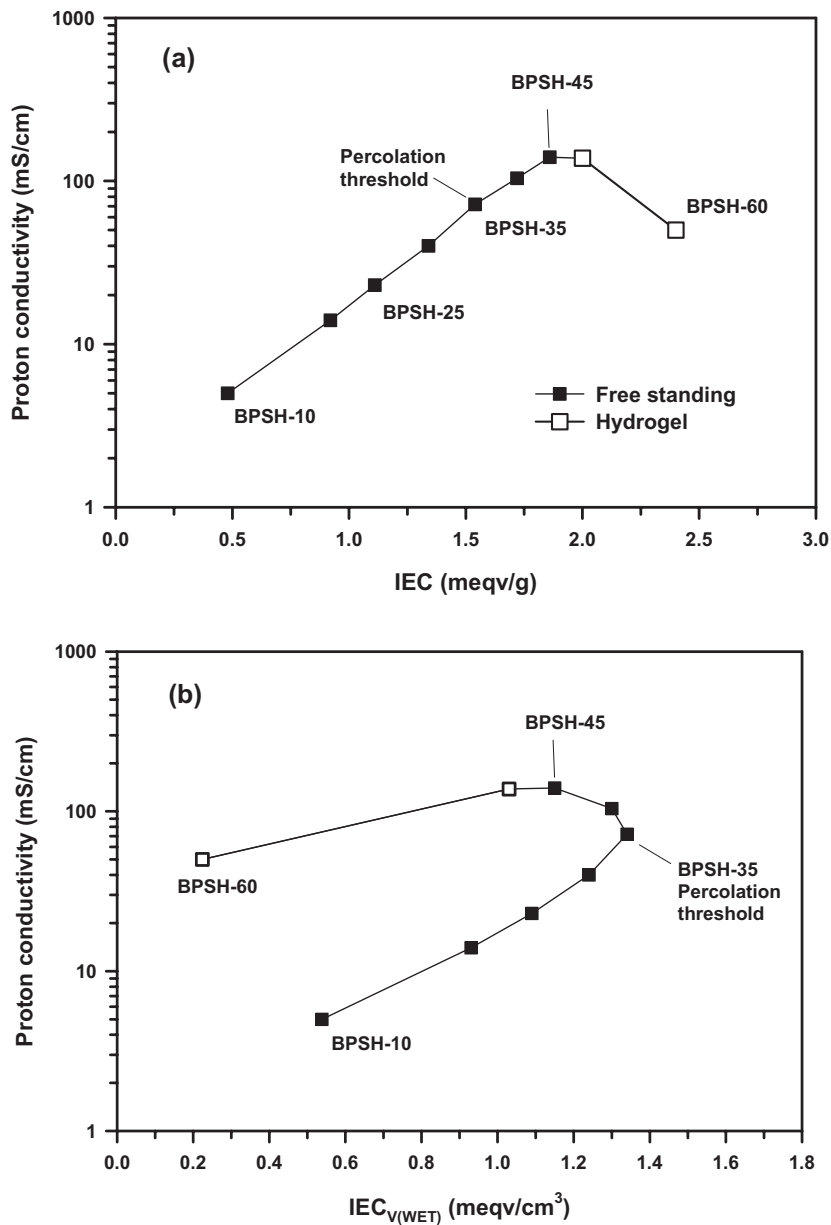
Yeo (89) and Makinnon (90) have used similar quantities based on ion concentration within hydrophilic domains to make similar comparisons.

### Number of Atoms per Charge and Molar Volume per Charge

As most polymer systems presented in the literature present data based on mass-based measurements and chemical structures, we have chosen to use this data to make estimates of volume-based parameters using different levels of assumptions. Initially considering only the dry polymer, a simple and rather rough estimation of sulfonic acid concentration can be expressed by NAC. **Table 1** compares the atomic masses and van der Waals and covalent radii of different atoms (91). Whereas the masses vary greatly, atomic radii are reasonably similar. For example, the atomic mass of fluorine is 19 times greater than that of hydrogen, but the (van der Waals) atomic radius of fluorine is only 25% greater than that of hydrogen. Because the difference in atomic volume between atoms is much closer than the difference in their masses, the volume calculated by simply counting the NAC (92) should be an improved estimate compared with mass-based comparisons. This dry NAC is analogous to mass-based IEC or EW but offers the potential of more “fair” comparisons between fluorinated and nonfluorinated systems in which density differences are large.

Counting atoms is an exceedingly simple mechanism to improve comparisons that assumes each atom occupies the same volume. It can be further improved by using the group contributions of molar volumes to obtain a MVC (93). Whereas NAC approximates each atom as having the same volume, MVC accounts for the van der Waals volume increments of the component atoms or structural groups:

$$MVC = \sum_i n_i V_i, \quad 6.$$



**Figure 6**

Comparison of proton conductivity using (a) weight-based IEC and (b) fully hydrated, volume-based IEC ( $IEC_{V(WET)}$ ).

where  $V_i$  is the volumetric contribution of the  $i$ th structural group that appears  $n_i$  times per charge.

MVC is an estimate of equivalent volume (cm<sup>3</sup> per ionomer or the mol equivalent of acid groups) based on the summation of molar volume subunits rather than true volume measurements. Table 2 presents the molar volume increments of selected groups used in our calculations (94, 95).

**Table 1** Atomic mass, van der Waals radius, and covalent radius of different atoms (91)

	-H	C <sub>ar</sub>	-N<	-O-	-F	-S-
Atomic mass	1.008	12.01	14.01	16.00	19.00	32.07
Van der Waals radius (nm)	0.120	0.170	0.157	0.136	0.135	0.185
Covalent radius (nm)	0.031	0.070	0.070	0.066	0.064	0.104

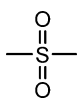
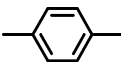
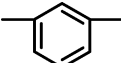
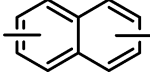



**Figure 7** shows the proton conductivity of fully hydrated membranes as a function of (dry) NAC ( $R = 0.70$ ) and MVC ( $R = 0.73$ ) and can be compared with **Figure 2b** (which has a larger data scatter,  $R = 0.45$ ) to support the use of volume-based parameters rather than mass-based parameters in predicting conductivity trends. Both plots show the expected trends of conductivity increasing with decreasing volume per charge. **Figure 7a** (NAC) has a slightly greater data scatter than **Figure 7b** (MVC), as might be expected owing to the increased level of sophistication in obtaining MVC. Still, the NAC plot shows reasonably clear trends and suggests that counting the number of atoms per charge may be a useful metric for comparing conductivity between polymers.

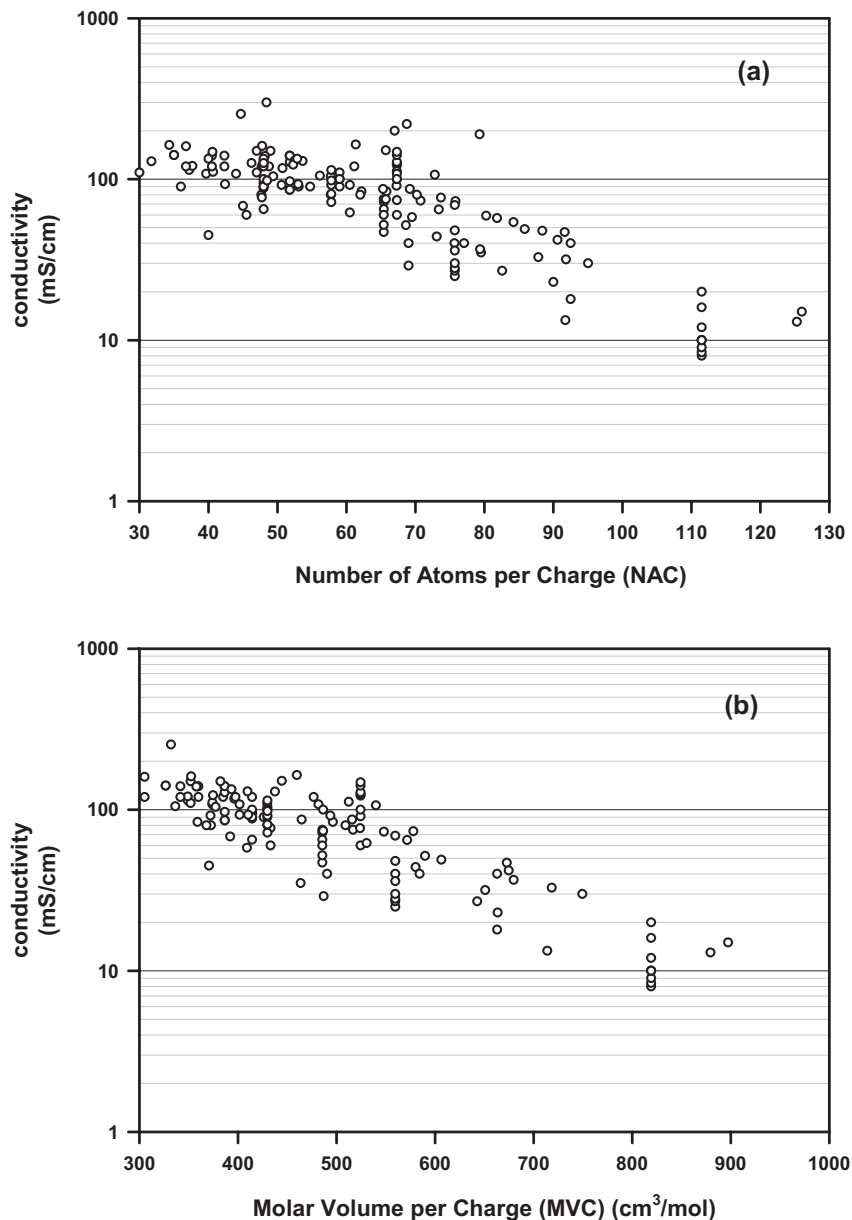
Fully hydrated versions of these properties,  $NAC_{(WET)}$  and  $MVC_{(WET)}$ , can be calculated from the dry-based properties and information on WU:

$$NAC_{(WET)} = NAC + 3\lambda \quad 7.$$

$$MVC_{(WET)} = MVC + 18\lambda, \quad 8.$$

**Table 2** Molar volume increments of amorphous polymers (94)

Groups	V <sub>a</sub> (298) (cm <sup>3</sup> /mol)	Groups	V <sub>a</sub> (298) (cm <sup>3</sup> /mol)
—H <sub>2</sub> — —C—	16.37		32.5
—F <sub>2</sub> — —C—	23.7		
—CH(C <sub>6</sub> H <sub>5</sub> )—	84.16		65.5
—CH(CN)—	30.7		
—CHF—	20.0		69
—C(CH <sub>3</sub> ) <sub>2</sub> —	49.0		
—C(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> )—	100.5		112
—H— —N—	17.3		
—O— (al.)	8.5		5.28
—O— (ar.)	8.0		
N <sub>ar</sub> (pyrid)	8.32		18.72
—SO <sub>3</sub> H	40.5		34.08

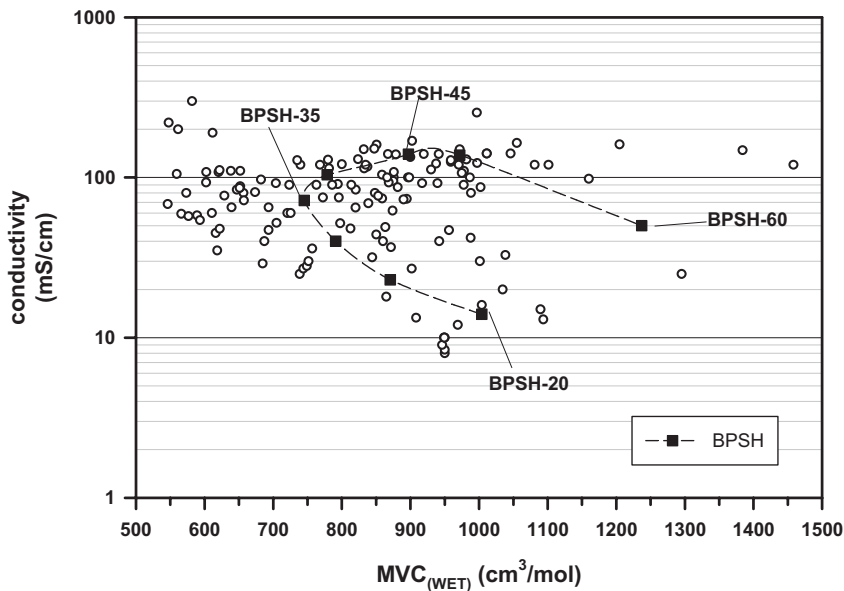


**Figure 7**

Proton conductivity versus (a) dry number of atoms per charge (NAC) and (b) dry molar volume per charge (MVC) of various sulfonated polymers under fully hydrated conditions at ambient temperature.

where 3 is the number of atoms in a water molecule, and 18 is the molar volume of water in cm<sup>3</sup> mol<sup>-1</sup>.

**Figure 8** shows the proton conductivity of BPSH and other sulfonated polymers as a function of  $MVC_{(WET)}$  ( $NAC_{(WET)}$  shows similar trends and was therefore excluded). As the degree of sulfonation of BPSH increased from 20% to 35%,  $MVC_{(WET)}$  decreased, then it increased with further



**Figure 8**

Proton conductivity versus  $MVC_{(WET)}$  for sulfonated polymers [biphenyl-based sulfonated poly(arylene ether sulfone)s (BPSH) polymers are highlighted] under fully hydrated conditions at ambient temperature.

sulfonation. This behavior mirrors that in **Figure 6b** for  $IEC_{V(WET)}$  and reflects the percolation threshold and hydrogel formation that appear at 35% and 45% sulfonation, respectively. This suggests that  $MVC_{(WET)}$  (and/or  $NAC_{(WET)}$ ), which can be calculated from data commonly reported in the literature, can be considered as an alternative to  $IEC_{V(WET)}$ , which is more difficult to obtain experimentally and often not reported in the literature. This is not surprising as  $MVC_{(WET)}$  is an estimate of equivalent volume, and equivalent volume is the inverse of  $IEC_{V(WET)}$ . Whereas trends within a polymer family are discernible, the scatter of conductivity data as a function of  $MVC_{(WET)}$  (or  $NAC_{(WET)}$ ), and therefore likely  $IEC_{V(WET)}$  is high, which leaves these parameters as poor predictors of conductivity.

### Percent Conducting Volume

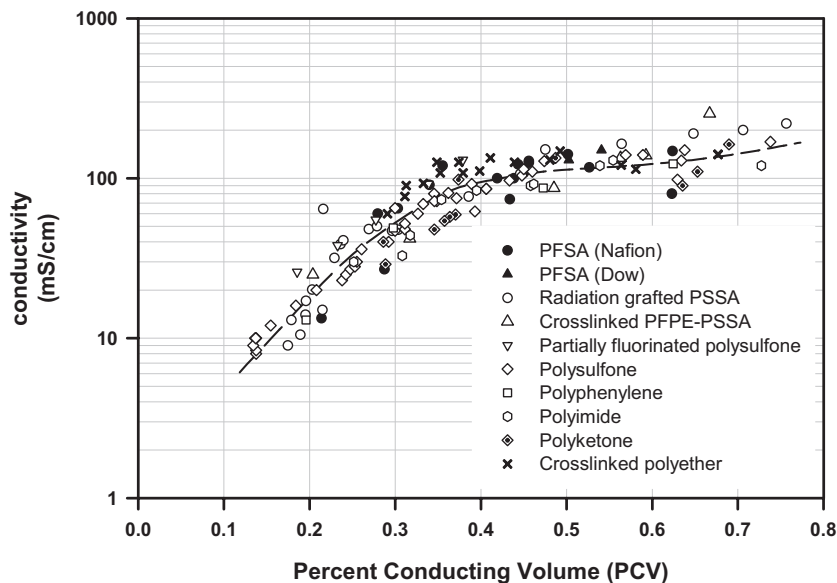
$IEC_{V(WET)}$ ,  $NAC_{(WET)}$ , and  $MVC_{(WET)}$  correlate poorly with proton conductivity, perhaps because water is only considered as a volume element for concentration purposes rather than being the phase through which conduction occurs. We present an alternative parameter, PCV, that focuses on the conducting (hydrophilic) domain (93).

We define PCV as

$$PCV = \frac{V_{H_2O} \cdot \lambda}{MVC_{(WET)}}, \quad 9.$$

where  $V_{H_2O}$  is the molar volume of water,  $18 \text{ cm}^3 \text{ mol}^{-1}$ .

The numerator of Equation 9 is an estimate of the volume of the aqueous (hydrophilic) phase per acid site, and the denominator is an estimate of the volume of the hydrated membrane (both hydrophilic and hydrophobic phases) per acid site. PCV is essentially a ratio of the volume of



**Figure 9**

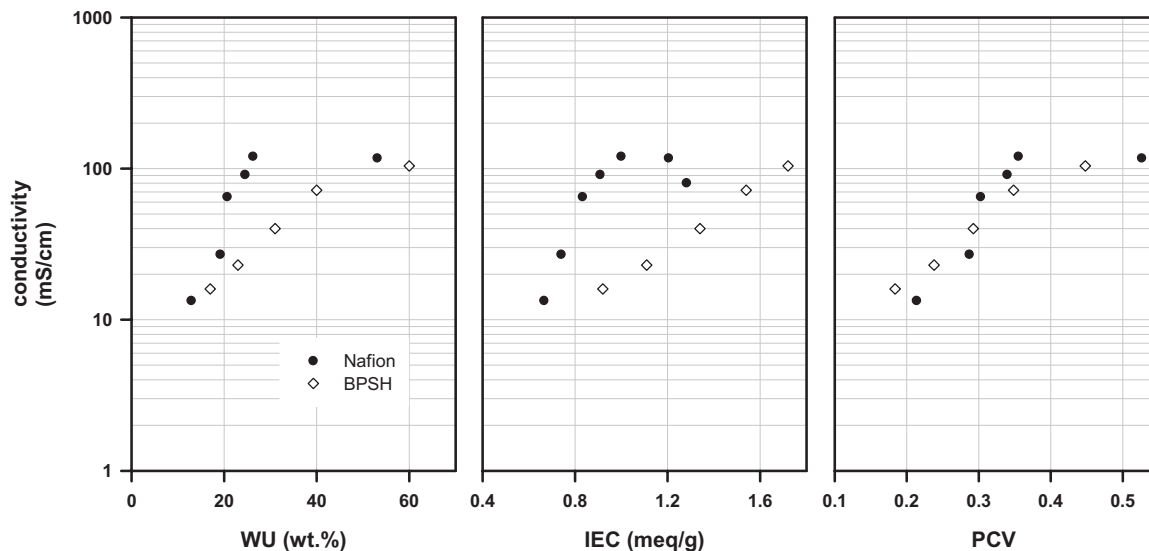
Proton conductivity versus percent conducting volume (PCV) of various sulfonated polymers under fully hydrated conditions at ambient temperature.

the hydrophilic phase to the hydrated membrane analogous to the conducting volume of the membrane (which could be estimated experimentally, but is rarely reported).

**Figure 9** shows the proton conductivity of 32 sulfonated polymers under fully humidified conditions as a function of PCV. A stronger correlation is seen between proton conductivity and PCV compared with any of the other approaches discussed here. The  $R$  value for the universal curve in the PCV plot is 0.89, which makes it a relatively good predictor of proton conductivity in fully hydrated samples. Proton conductivity increases significantly with PCV values from 0.1 to 0.4 and then only marginally above 0.4. These results suggest targeting PCV values of  $\sim 0.3$ – $0.4$  where conductivity is high (ca.  $80$ – $120$   $\text{mS cm}^{-1}$ ) but mechanical properties are better retained owing to the higher hydrophobic domain content and corresponding limited WU. In fact, many “optimized” polymer systems fall in this range. In most cases, “optimized” flexible PFSA or radiation-induced polystyrene graft polymers exhibit less WU ( $\sim 30\%$  by mass) than rigid sulfonated aromatic or heterocyclic polymers ( $\sim 60\%$  by mass).

**Figure 10** compares the proton conductivity of Nafion and polyaromatic BPSH as a function of WU, IEC, and PCV. Nafion and sulfonated polyaromatics have similar proton conductivity at a given PCV under fully humidified conditions, which is in stark contrast to the significantly higher conductivity reported for PFSA compared with sulfonated polyaromatics when compared using mass-normalized WU or IEC. This plot suggests that the conductivity difference between PFSA and sulfonated polyaromatics under fully humidified conditions is a secondary effect when compared using a volume-based metric. Furthermore, clear, systematic differences in conductivity that depended on the acidity of the acid group, microphase separation, hydrophobicity, chain rigidity, distribution of sulfonic acid groups, and/or the various polymer architectures investigated were not apparent. Multiblock copolymers, random copolymers, graft copolymers, and crosslinked systems all exhibited conductivity within a relatively narrow range at a given PCV; although meaningful deviations from the average existed, the data all appear within a fairly narrow spread.





**Figure 10**

Comparison of the proton conductivity of Nafion and BPSH as a function of WU, IEC, and PCV.

These data suggest, somewhat surprisingly, that structural or morphological effects seem to be secondary when comparing proton conductivity under fully humidified conditions, perhaps due to the continuity of conducting domains under fully hydrated conditions.

**Table 3** summarizes the features of the various parameters presented here in terms of ease of acquisition, factors accounted for, and correlation with proton conductivity for liquid equilibrated polymer membranes. Although mass-based parameters are the most commonly reported, they have significant limitations in their applicability, whereas nonmass-based measurements offer

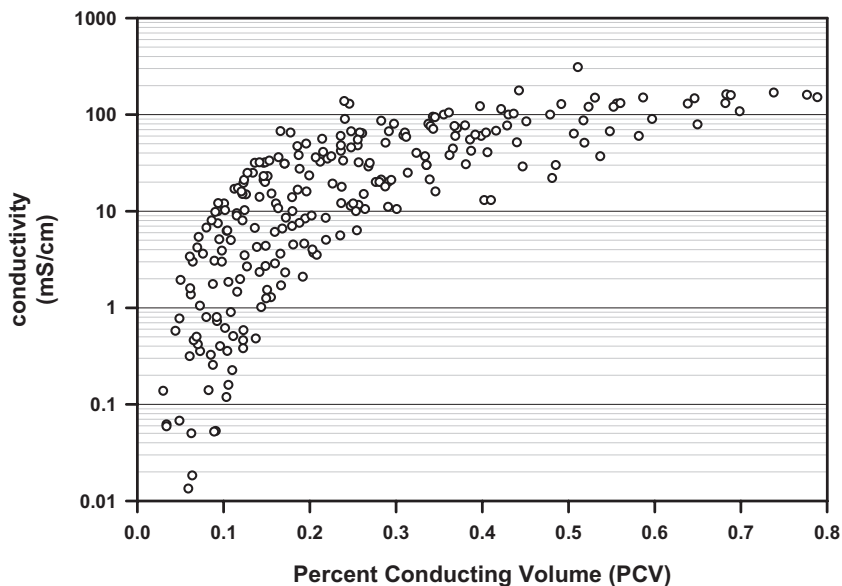
**Table 3 Comparison of mass and length scale parameters**

Parameter	Ease	Factors accounted for <sup>a</sup>		Correlation with conductivity <sup>b</sup>	
		Water content	Sulfonic acid concentration		
Mass based	Water uptake (WU)	Easy	Yes	No	Medium high
	Ion exchange capacity (IEC)	Easy	No	Yes (dry state)	Poor
Non-mass based	Swelling ratio	Easy	Yes	No	NA
	Water volume fraction (WF <sub>(VOL)</sub> )	Medium	Yes	No	NA
	Hydration number ( $\lambda$ )	Easy	Yes	No	Poor
	Volume ion exchange capacity (IEC <sub>V</sub> )	Difficult	No	Yes (dry/wet state)	NA
	Number of atom per charge (NAC)	Easy	No	Yes (dry/wet state)	Medium (dry) Poor (wet)
	Molar volume per charge (MVC)	Easy	No	Yes (dry/wet state)	Medium (dry) Poor (wet)
	Percent conducting volume (PCV)	Easy	Yes	Yes (wet state)	High

<sup>a</sup>All parameters do not account for morphological features.

<sup>b</sup>Correlation with conductivity is determined based on  $R$ ;  $>0.85$ : High;  $0.8-0.85$ : Medium high;  $0.7-0.8$ : Medium;  $<0.7$ : Poor.

NA: Not available.



**Figure 11**

Proton conductivity versus PCV of various sulfonated polymers under partially hydrated conditions at ambient temperature as taken from the literature (23, 35, 96–106).

advantages when making specific comparisons. Swelling ratio, water volume fraction, and hydration number take into account the volume of water absorbed in sulfonated polymers. IEC<sub>V</sub>, NAC, and MVC parameters express sulfonic acid concentration in dry and wet conditions, with the wet volume-based parameters providing useful information on the percolation and hydrogel formation of sulfonated polymers. PCV showed the strongest correlation with proton conductivity and was obtained through information available in the literature for many different families of polymers. Although each of these parameters has utility, they also all have limitations; even with PCV the data show meaningful scatter, and the cases thus far presented only represent liquid equilibrated membranes.

Under partially hydrated conditions the data scatter of proton conductivity versus PCV increases substantially, as shown in **Figure 11** (23, 35, 96–106). PCV of sulfonated polymers changes as  $\lambda$  decreases with reduced RH, which is accompanied by a corresponding change in conductivity. The data in **Figure 11** are limited to the cases in the literature in which conductivity is reported as a function of  $\lambda$ .

It is immediately apparent that PCV is not as good of a gauge for conductivity at less than full hydration. A likely explanation for the greater data scattering in **Figure 11** compared with **Figure 9** is the morphological differences in polymer systems under full and partial humidification. Most sulfonated polymers are visualized as having phase separated structures owing to hydrophobic (nonsulfonated) and hydrophilic (sulfonated) polymer segments. Because proton conduction occurs in hydrophilic domains, morphological differences should affect conductivity both in fully hydrated and partially hydrated conditions. However, a greater impact is observed under low humidification. This suggested that morphological features of each polymer system diminished with abundance of water. As polymers dehydrate, the number of water molecules per sulfonic acid group decreases, which affects the hydrophilic domain size and likely, in many cases, the continuity of the proton conduction pathways. The data presented in **Figure 9** and **Figure 10**

suggest that these factors are not particularly important under full humidification, but the data in **Figure 11** suggest that under partial humidification they can play a large role, perhaps owing to conducting domains becoming more isolated in samples with lower degrees of phase separation and an increased importance of morphology at subsaturated hydration levels.

## MORPHOLOGICAL EFFECTS

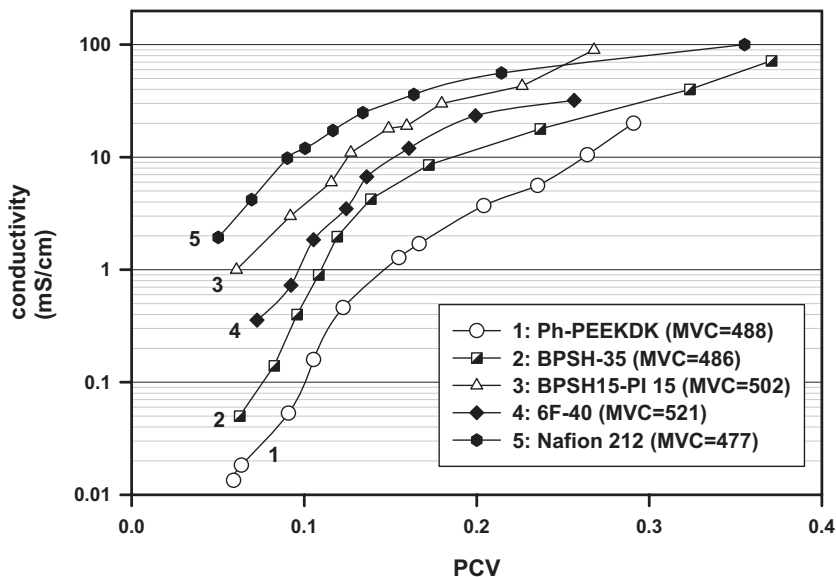
Morphological effects can include many aspects of polymer structure such as ion aggregation, domain size, domain connectivity, and water channel size (107–114). Although structural information is difficult to quantify, we promote phase contrast and phase continuity as qualitative aids in interpreting the impact of structural effects on observed properties. **Figure 12** illustrates 2D renderings of these two parameters (phase contrast and continuity) in schematic diagrams of phase-separated polymers. Filled circles represent hydrophilic polymer segments (or water), and empty circles represent hydrophobic segments. Phase contrast is meant to define the extent of phase separation between the hydrophilic and hydrophobic domains (not necessarily the difference between the hydrophilicity and hydrophobicity of the polymer domains themselves, although increased differences in hydrophobicity would be expected to lead to increased phase contrast). Polymers having lower phase contrast (**Figure 12a**) have less defined phase separation than those having higher phase contrast (**Figure 12b**).

PFSAs such as Nafion exhibit highly phase-contrasted structures, presumably owing to the extreme hydrophobicity and flexibility of the perfluorinated ethylene backbone combined with the mobility and hydrophilicity of the sulfonic acid-containing side chain. The large driving force for phase separation in these polymers is evidenced by the solubility parameter. PFSAs have larger differences in solubility parameters for hydrophobic and hydrophilic segments compared with nonfluorinated polymers (e.g.,  $16 \text{ J}^{1/2} \text{ cm}^{-3/2}$  for Nafion versus  $9 \text{ J}^{1/2} \text{ cm}^{-3/2}$  for sulfonated poly ether ketone) (115, 116). The high phase contrast impacts structure and thereby affects observed properties, as has been reported elsewhere in significant depth (68, 108, 117–119).

Phase continuity is meant to reflect the connectedness of ion-conducting (hydrophilic) domains, and is also illustrated in **Figure 12**. Although **Figure 12c** shows relatively poor phase contrast, it shows enhanced phase continuity compared with **Figures 12a** and **b**. Phase continuity is necessary to provide pathways for proton conduction.

Phase continuity can be probed by microscopy and has been reported upon for multiblock and graft copolymer architectures (112, 120–122). **Figure 13** shows the tapping mode-atomic force microscopy (TM-AFM) micrographs of five sulfonated polymers that have similar MVCs at 50% RH: (a) nonfluorinated random copolymer (BPSH-35), (b) partially fluorinated random copolymer (6F-40), (c) perfluorinated random copolymer (Nafion 212), (d) nonfluorinated alternating polymer (Ph-PEEKDK), (e) nonfluorinated random copolymer (same as a, reproduced to aid visual interpretation), and (f) nonfluorinated multiblock copolymer (BPSH-PI 15k-15k). It is expected that phase contrast increases from a to b and from b to c owing to increased backbone fluorination and backbone flexibility. (This is not apparent in **Figure 13**, however, because of the arbitrary nature of the color scale used. In general, all three AFM images show qualitatively similar domain size and phase continuity.) Samples d, e, and f show clear trends with phase continuity increasing from d to e and from e to f owing to differences in copolymer architecture. The multiblock copolymer, f, has excellent phase continuity whereas the alternating homopolymer, d, has basically featureless phase structure absent of clear microphase separation.

We use the generalities put forward in our discussion of **Figure 13** to evaluate the proton conductivity of these sulfonated copolymers under partially hydrated conditions, which is plotted as a function of PCV in **Figure 14**. **Figure 14** shows clear trends of proton conductivity increasing



**Figure 14**

Proton conductivity versus PCV of Ph-PEEKDK, 6F-40, Nafion 212, nonfluorinated random copolymer, and nonfluorinated multiblock copolymer: PCV changes with RH.

with fluorination. For example, the proton conductivity of perfluorinated Nafion is greater than that of partially fluorinated 6F-40, which in turn has a higher conductivity than nonfluorinated BPSH-35 across the range of PCV values reported. More than an order of magnitude of conductivity difference exists at some PCV values, and we suggest that phase contrast is playing a critical role at low RH. We also examined the proton conductivity of other PFSA membranes including short side chain PFSA and different EWs of Nafion, which show quite similar conductivity at a given PCV (plot omitted for brevity). **Figure 14** also shows the trend that the proton conductivity of multiblock copolymers is greater than that of random copolymers and alternating homopolymers, which indicates phase continuity is another critical parameter for low RH conductivity. The trends for phase continuity across polymer families are consistent with other studies within a polymer family as a function of increasing sulfonation level (123–125).

## A DESIGN PERSPECTIVE ON SULFONATED POLYMERS FOR FUEL CELLS

From our studies of the wide range of polymers presented in the literature, we have found that under fully humidified conditions, proton conductivity is predominantly influenced by factors that can be expressed by a single parameter, PCV. These findings suggest that at high hydration levels, factors such as morphology, acidity, and backbone hydrophobicity have only secondary impacts on proton conductivity.

At lower levels of hydration, where membranes are being developed for high-temperature, low-RH applications, factors such as phase continuity and phase contrast have been presented as properties that can be exploited for improved conduction. Increased levels of fluorination and the use of multiblock copolymer architectures are two routes that resulted in increased conductivity at given PCV values.

From the analysis presented it can be suggested that for low-RH fuel cell operations, sulfonated polymers require highly localized (maximizing phase contrast), highly continuous hydrophilic phase domains as well as high local sulfonic acid concentration. This mirrors the direction of much of the research community where there is a push for increased acid content within the conducting phase and clearer separation from the structural phase. As many of these materials are intended for transportation applications in which there is a need to start under cold, wet conditions and operate under hot, dry conditions, issues relating to RH and temperature cycling are also critical. To date, the rubbery nature of PFSA ionomers has led to enhanced durability compared with hydrocarbons and wholly aromatic polymers.

## DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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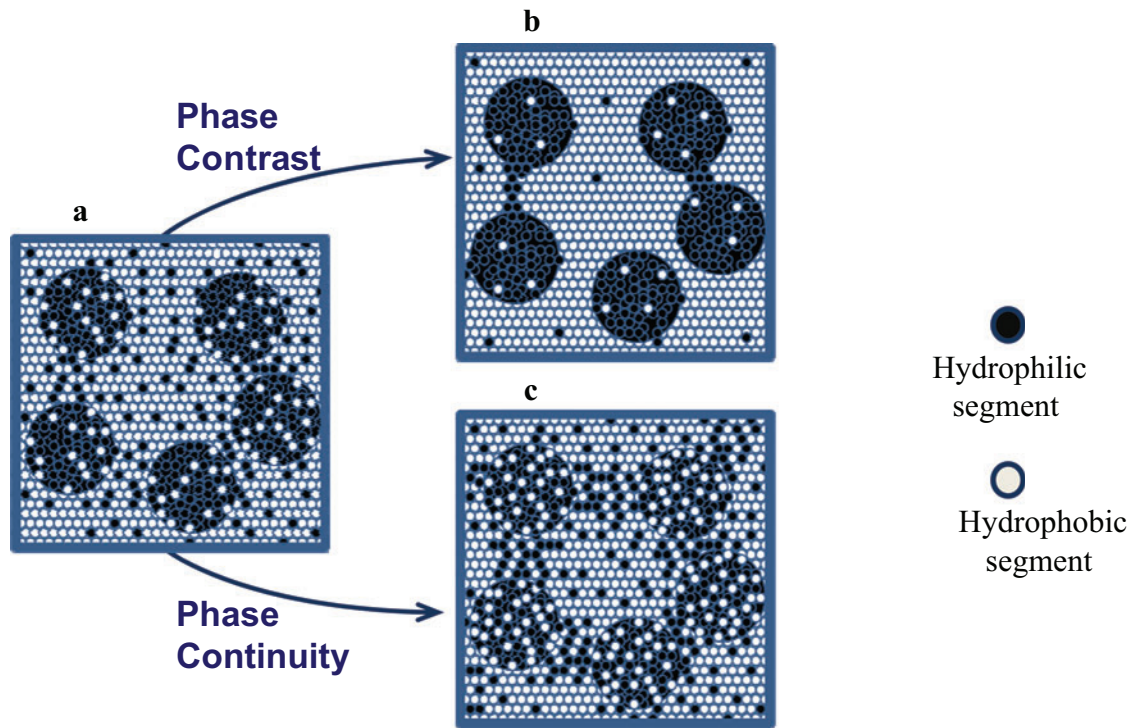


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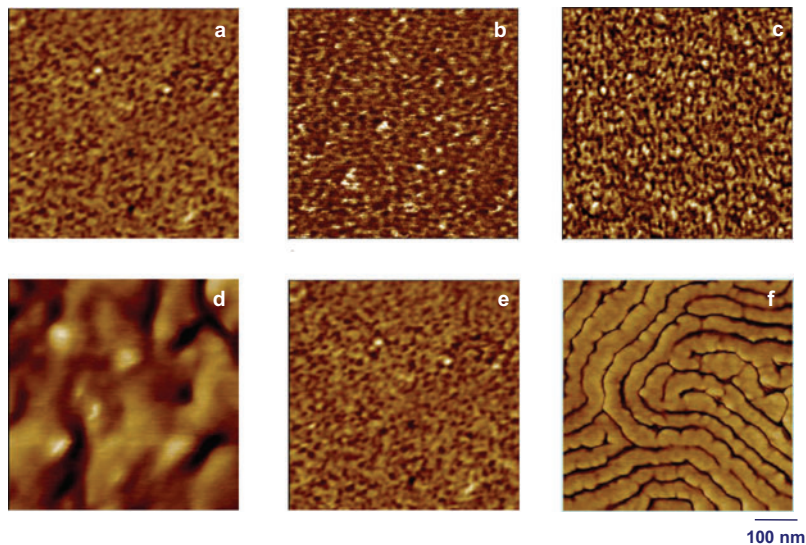
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**Figure 12**

Schematic representations of phase contrast and phase continuity.



**Figure 13**

Tapping mode atomic force microscopy (TM-AFM) images of (a) nonfluorinated random copolymer (BPSH-35), (b) partially fluorinated random copolymer (6F-40), (c) perfluorinated random copolymer (Nafion 212), (d) nonfluorinated alternating polymer (Ph-PEEKDK), (e) nonfluorinated random copolymer (BPSH-35), and (f) nonfluorinated multiblock copolymer (BPSH-PI 15k-15k).





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## Errata

An online log of corrections to *Annual Review of Chemical and Biomolecular Engineering* articles may be found at <http://chembioeng.annualreviews.org/errata.shtml>