



An overview of the proton conductivity of nafion membranes through a statistical analysis



Lunyang Liu, Wenduo Chen, Yunqi Li*

Key Laboratory of Synthetic Rubber & Laboratory of Advanced Power Sources, Changchun Institute of Applied Chemistry (CIAC), Chinese Academy of Sciences, Changchun 130022, PR China

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ABSTRACT

Proton conductivity of Nafion membranes, the key feature for their application in proton exchange membrane fuel cells, has been reported in many works. It becomes necessary to assemble these massive reports to present an overview for further development guidelines. We apply an exhaustive search and retrieve 3539 records from 310 original reports. These records are dumped into a database and a statistical analysis is carried out to establish the overview. The histogram, the trend, the temperature, the relative humidity and fillers related to the proton conductivity of Nafion membranes are investigated. There is not always positive progress in recent 13 years to improve the proton conductivity of Nafion membranes. The proton conductivity can be fitted using a simple exponentially increasing function for relative humidity dependence, and the Arrhenius equation for temperature dependence with acceptable correlation confidence. Water contents in membranes from vapor can be well depicted by Brunauer–Emmett–Teller equation, and they have reasonable correlation with proton conductivities. Inorganic fillers usually provide better enhancement in proton conductivity than organic fillers, which is a result of the former have better water-holding capability. Fillers that can facilitate the formation of percolated water channel with less tortuosity have high probability to significantly improve the proton conductivity of Nafion membranes.

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1. Introduction

Proton Exchange Membrane (PEM) fuel cells have emerged as clean power sources with broad applications. Perfluorosulfonated membranes, especially Nafion[®] [1] membranes, have been regarded as the standard in PEM fuel cells, attributed to its superior thermal, mechanical and chemical stability, and high proton conductivity. On the other hand, Nafion membranes also suffer from many drawbacks, such as insufficient resistance to methanol crossover and inevitable water-control at elevated temperatures, and most prominently, high cost resulting from the complicated processes in manufacture. Currently, the majority of commercial membranes for fuel cells are still based on Nafion, such as N115, N117, N1100 etc., and N117 is the most well established PEM material [2]. To satisfy industrial applications and academic interests, either to overcome its disadvantages or for further performance improvement, Nafion membranes have been studied by a large number of journal papers and their annual numbers are shown in Fig. 1. The number of scientific publications on Nafion gradually

increases in recent 13 years, and more than half of them are involved in fuel cells. However, as a key feature to show the advance of PEM manufacture, the proton conductivity has not been systematically evaluated. It is still not clear whether a newly fabricated PEM has advance and what the upper limit for Nafion based membranes, on the basis of the proton conductivity.

The hydrophilic sulfonic acid group attached to the hydrophobic backbone in Nafion allows proton transport through hydrated ionic clusters. The microstructures especially the percolated channel formed by these ionic clusters which may be sculptured by phase separation [3] and/or colloidal packing [4] is the key factor related to the proton conductivity of Nafion membranes. Though the microstructure can be affected by variant factors, the composition, temperature, humidity, filler and the thickness of membrane etc. may be the most important ones. When a Nafion membrane is dehydrated at elevated temperature, the water content in the membrane diminishes significantly, which results in a sharp decrease in the proton conductivity [5]. For Nafion membranes, the operation temperature is generally limited to about 80 °C because of higher temperature requires water-control to maintain sufficient hydration, which may overwhelm the energy conversion in fuel cell [6].

Fundamentally, proton conduction in aqueous channel follows

* Corresponding author.

E-mail address: yunqi@ciac.ac.cn (Y. Li).

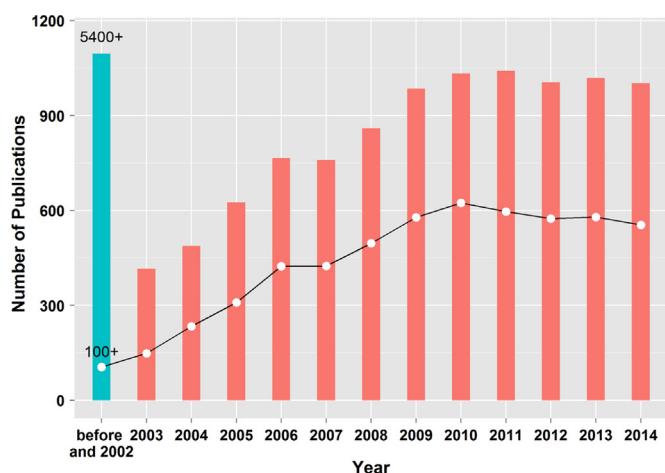


Fig. 1. The histogram of publications retrieved from Web of Science using the keyword “Nafion” (bar plot) and “Nafion and fuel cell” (thin dot line). The first bar was rescaled with annotation of 5400+ and 100+, respectively.

two mechanisms, e.g., the structural diffusion or Grotthuss mechanism, and the vehicle diffusion mechanism. Proton in the structural diffusion can hop in a percolated channel formed by hand-in-hand water molecular string, while in the vehicle diffusion proton translates together with a water molecule/cluster in a form of H_3O^+ , H_5O_2^+ and H_9O_4^+ etc. The structural diffusion allows proton transportation in a much faster rate than the vehicle diffusion [7]. On the basis of Einstein–Smoluchowski relation, Choi et al. [8] suggested that in Nafion membrane, the mean step time for the Grotthuss diffusion is 1.5×10^{-12} s which is around four times faster than that for the vehicle diffusion with a mean step time of 5.78×10^{-12} s. Liquid water is necessary to conduct the diffusion, so proton conductivity in Nafion membranes always sharply decrease or ultimately lose at temperatures lower than 0 °C or higher than 100 °C [9]. Water in Nafion membranes has three forms, the strong bonding, the weak bonding with polymer matrix and the free water. Grotthuss mechanism mainly occurs in the weak bonding water while vehicle mechanism prefers the free water region. To enhance the fraction of water in weak bonding region is a way to increase the proton conductivity of Nafion membranes. It is proportional to the hydration level of membranes. In practice, the hydration of Nafion membrane is generally evaluated by the average number of water molecules per sulfonate group at microscope, and controlled by the humidity or the water uptake under operation environment.

Besides the fine control of humidity and temperature to tune the weak bonding water, adding filler is another efficient way to improve the proton conductivity of Nafion membranes. Fillers can be organic or inorganic compounds. Organic fillers with sulfonic acid group, such as sulfonated polyaniline (SPANi) [10], sulfonated poly(propylene oxide) [11], normally provide higher proton conductivity because it can help water-holding and facilitate the formation of percolated water channels. Unfortunately, in some cases, organic fillers were used to block fuel crossover, but they also deteriorate the proton conductivity in these membranes [12,13]. While inorganic fillers spread in various compounds, and they can be divided into proton conductive fillers [14], hydrophilic fillers [15], as well as hydrophilic and proton-conductive bifunctional fillers [16,17]. The majority of inorganic fillers have hydrophilic surface with high specific surface area, which normally provided better water-holding capability than their organic counterpart [18]. The capillary force of such fillers also make the composite Nafion membranes have high level of hydration at elevated temperatures, which allows PEM fuel cells maintain high performance at elevated temperatures.

Statistical analysis can provide an overview and clear correlation relationships among multiple parameters, factors and performance indices based on a comprehensive and representative dataset. Though several empirical rules described above have been widely accepted, such as the increase of the proton conductivity with temperature or humidity increase etc., solid proofs and a panoramic view on the proton conductivity of Nafion membranes are still elusive. Reports about Nafion proton conductivity have accumulated a large number of data source, it provides the feasibility to setup a dataset satisfying the criteria for a reference significant statistical analysis. In this work, we carried out a statistical analysis on the original data accounting for the proton conductivity of various Nafion membranes, attempt to provide an overview in this field. The dataset construction will be described at first, followed by the presentation of the statistical method. Then the statistical results including the trend, temperature, relative humidity and filler associated with the proton conductivity will be discussed. Finally, conclusion will be drawn and we believe this statistical analysis can provide a solid overview for the proton conductivity of Nafion membranes and shed a light for further progress in this field.

2. Datasets and methods

2.1. Datasets construction

Total 310 original reports excluded reviews were retrieved from Web of Science (till Jan. 2015) using keywords “Nafion and proton exchange membrane” or “Nafion and polymer electrolyte membrane”. Fig. 2 shows the distribution of these reports and their citations. The wide spread of journals and the intensive citations indicate the dataset collected in this work is quite representative and suitable for a statistical analysis. Experimental data from these reports was carefully recovered with the help of GetData Graph Digitizer v2.26, and 3435 records with proton conductivity were collected.

Each record has five variables, i.e., proton conductivity, water uptake, inorganic/organic filler, temperature and the relative

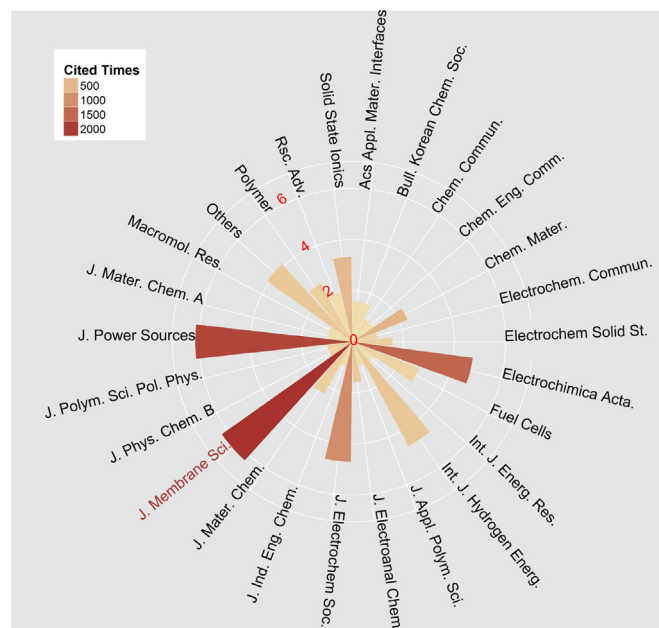


Fig. 2. The distribution of 310 reports studying Nafion membranes in fuel cells from various journals. The height of bar corresponds to the number of publications from a journal, and the color shows total cited times in a roughly way.

humidity. All the variables are normalized: proton conductivity is normalized in the unit of S/m, water uptake (WU, wt%), temperature (T, °C) and the relative humidity (RH, %). The water uptake (WU) is defined as

$$\text{water uptake (WU)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

It accounts the weight increase percentage between wet and the dry membranes, with W_{wet} and W_{dry} are the weight of the wet and the dry membranes, respectively [19]. Fillers enclose three states, inorganic, organic and filler-free Nafion membranes. Temperature and the relative humidity were directly taken or converted (if necessary) from original reports.

2.2. Methods

Four statistical methods including probability density function, boxplot, *T*-test and non-linear regression were used to analyze these data.

The probability density function (PDF) was used to explore the distribution of proton conductivity against one variable along with a set of bins. The distribution of all records and subsets regarding filler types will be studied.

The boxplot [20], also known as the box and whisker plot, can provide an intuitive view on the distribution, diversity and the bias to normal distribution of a set of data. Its elements and typical frame are shown in Fig. 3. This plot enables the direct visualization of the minimum, lower quartile(Q1), median, mean, upper quartile (Q3) and maximum. The minimum and maximum values are determined by $Q1 - 1.5 \times \text{IQR}$ and $Q3 + 1.5 \times \text{IQR}$, respectively. Here IQR equals to $Q3 - Q1$, is the height of the box and proportional to the diversity of the dataset. The distance between the median and the mean values scaled by IQR is a quantitative index to assess the bias from normal distribution. Any data excluded from the minimum to the maximum is classified as an outlier, which is understood as the data is significantly different to the general feature of a given

dataset. An outlier of proton conductivity may derive from several aspects, such the errors in the measurement of membrane thickness and resistance, unappreciated treatment of membrane before measurement (e.g., immerse membrane in acidic solutions) etc. An outlier normally has low repeatability so we excluded them from statistical analysis to provide a robust overview.

A *T*-test is commonly introduced to determine whether a dataset is significantly different to a specific value or from the mean of another dataset [21]. The *T*-test normally provided *T*-value and *P*-value. The former may be positive or negative, with large absolute value indicates large improvement or deterioration. A *P*-value less than 0.05 is usually used to determine whether two datasets significantly differ from each other.

Nonlinear regression is widely used to setup empirical relationships between variables. It normally applies explicit equation to fit sparse records and the best-fitting solution should has the minimum of the square residual difference [22]. The statistic *R*-square (i.e., the correlation coefficient) and coverage are employed to assess the goodness-of-fit. *R*-square is defined as

$$R^2 = \frac{\sum_i (\hat{y}_i - \bar{y})^2}{\sum_i (y_i - \bar{y})^2} \quad (2)$$

where y_i is the value of the record, associated with a predicted value \hat{y}_i , \bar{y} is the mean value. It ranges from 0 to 1 with higher value indicates better fit and 1 for a perfect fit. The coverage is defined as

$$\text{Coverage} = \frac{\text{Number of records if } |\sigma - \sigma_{\text{fit}}| \leq 2\text{SD}_{\text{res}}}{\text{Number of records}} \quad (3)$$

where σ , σ_{fit} denote the experimental and the fitted proton conductivity, and the SD_{res} refers to the standard deviation of residuals over the whole dataset. We applied the non-linear regression to provide empirical relations for the proton conductivity vs. the relative humidity, and the proton conductivity vs. the operation temperature.

The statistical environment R-project (version 3.0.3, <https://www.r-project.org>) was employed for all the statistical analysis and graphics.

3. Results and discussions

3.1. Distribution of the proton conductivity

The probability density functions (PDF) of the all proton conductivities and the maximal values in each report are presented in Fig. 4. For all proton conductivities, approximately 80.3% of all records, and 87.1% of the highest values of all reports locate in between 1.0 and 21.5 S/m. The USA department of energy (DOE) set a standard of 10.0 S/m at 95 °C [23], which is potentially applicable standard in fuel cell development, about 23.4% of all records, and 37.3% of the highest values of all reports are above this bottom-line. While there is another criterion for commercial Nafion dimensionally stable membranes (DSM™) [23] used in fuel cell, i.e., a proton conductivity of 8.3 S/m at 20 °C, nearly 31.4% of all records and 49.7% of all reports satisfy this criterion. Above the threshold of 21.5 S/m, there are 2.7% of all records, and 8.7% of all reports. So this value may be referred as a criteria for the declaration of advancement for newly fabricated Nafion membranes. Additionally, there are around 0.4% of all records have proton conductivity higher than 30.0 S/m. They are mainly from Nafion membrane with a large amount of zeolites as fillers [20]. Since zeolites are micro-porous minerals and they have extraordinary water-holding capacity, which may not represent the majority of Nafion membranes, these records were excluded from further

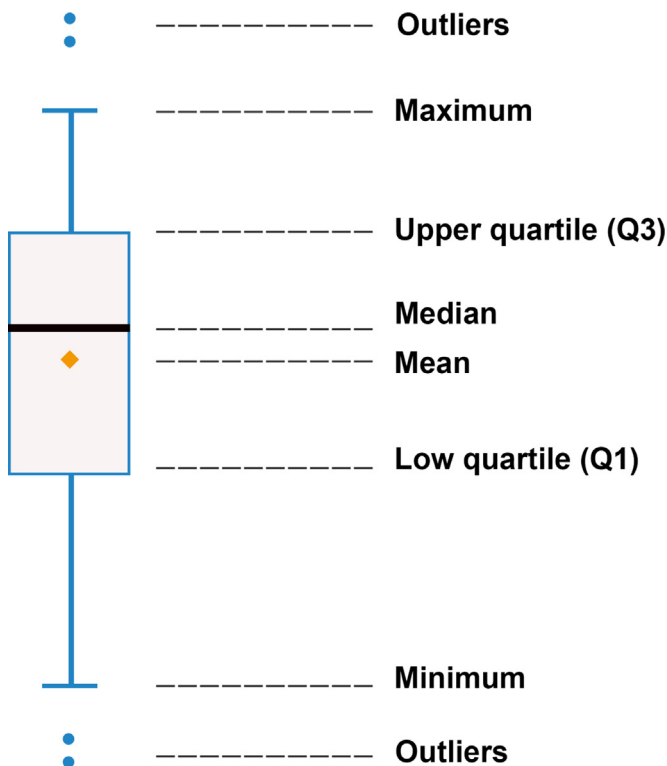


Fig. 3. The schematic boxplot.

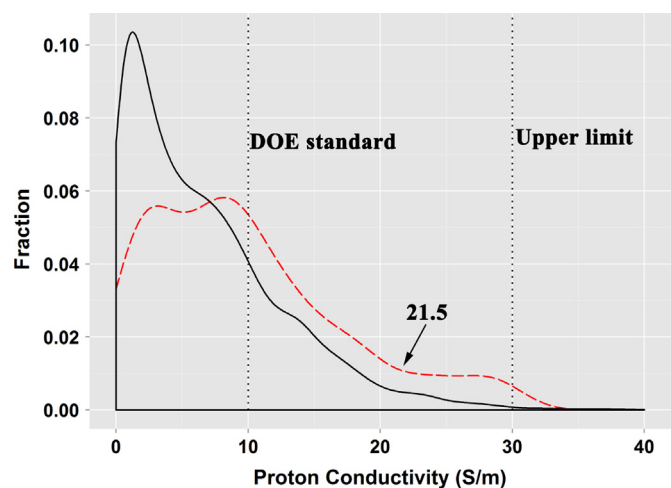


Fig. 4. Probability density function for all reported proton conductivities of Nafion membranes (black line, 3435 values) and the highest value from each report (red line, 310 values). The dot lines are DOE expectation for commercial PEM of 10.0 S/m and the upper-limit of 30.0 S/m. The arrow indicates a value with significant advance at the elevating proton conductivity.

statistical analysis in this work.

The distribution of the proton conductivity of Nafion membranes in recent 13 years illustrated by boxplot was shown in Fig. 5, and the *T*-test between the records reported in each year and the accumulation records before the corresponding year was presented in Table 1. It can be seen that not always positive progress has been achieved. The average proton conductivity of Nafion membranes has a burst progress in 2005, then the enrichment of proton conductivity above 10.0 S/m gradually increases afterwards. The number of records from the year 2002 to 2008 got a steady increase, which is associated with the increase of reports as shown in Fig. 1. The highest values from each report also have the similar trend as that for the mean values. Additionally, the means in all the years are always higher than the medians, and their difference becomes more obvious, suggests the possibility to prepare Nafion membrane with proton conductivity better than random increases.

Regarding a *P*-value of 0.05 as significant based on the *T*-test assessment, the most prominent progress to improve the proton

conductivity of Nafion membranes were achieved in 2005, followed by a slump in 2007 and 2008, then marginal improvement was made from 2012 to 2014. The mean value of proton conductivity in 2014 recovered to the level at 2005 with more than double records. Overall, positive progress has been made to manufacture Nafion membranes with elevated proton conductivity in recent 13 years.

3.2. Temperature and relative humidity dependence of the proton conductivity

The proton conductivity of Nafion membranes as a function of the relative humidity (RH) in 9 bins at different temperatures was presented in Fig. 6. The proton conductivity monotonously increases with RH over the temperatures range from 30 °C to 100 °C. The increasing profile of σ against RH from individual report may be convex [24,25] or concave [26]. The statistical results here show concave upward increase at all temperatures, indicating that the conclusion from the statistical analysis may remarkably different to that drawn from an individual report.

We further use an exponential increasing function to fit the mean values in each RH bin at different temperatures, which is written as

$$\sigma_{\text{fit}}(\text{RH}, T) = \sigma_0 + C e^{\text{RH}/\text{RH}_{\text{ref}}} \tag{4}$$

where $\sigma_0 + C$ can be regarded as the proton conductivity of dry membrane, *C* and *RH_{ref}* are fitting parameters. Alternatively, the proton conductivity of Nafion 117 membranes has been fitted in a polynomial form by Sone et al. [27]

$$\sigma_{\text{fit}}(\text{RH}, T) = a + b \cdot \text{RH} + c \cdot \text{RH}^2 + d \cdot \text{RH}^3 \tag{5}$$

The fitting of the mean values of each RH bins at different temperatures using Eq. (4) was presented in Fig. 6 and fitting parameters were listed Table 2. Accordingly, the fitting using Eq. (5) was provided in Fig. S1 and Table S1 (in supplementary). Though Eq. (5) provided better fitting with higher *R*-square and coverage, the fitting curves exhibit non-monotonic increase dependence. This fluctuation in fitting curves becomes serious for the subsets with a small number of records. Therefore, to present the universal rule for the proton conductivity, we stick on Eq. (4) to describe the RH dependence of the proton conductivity at

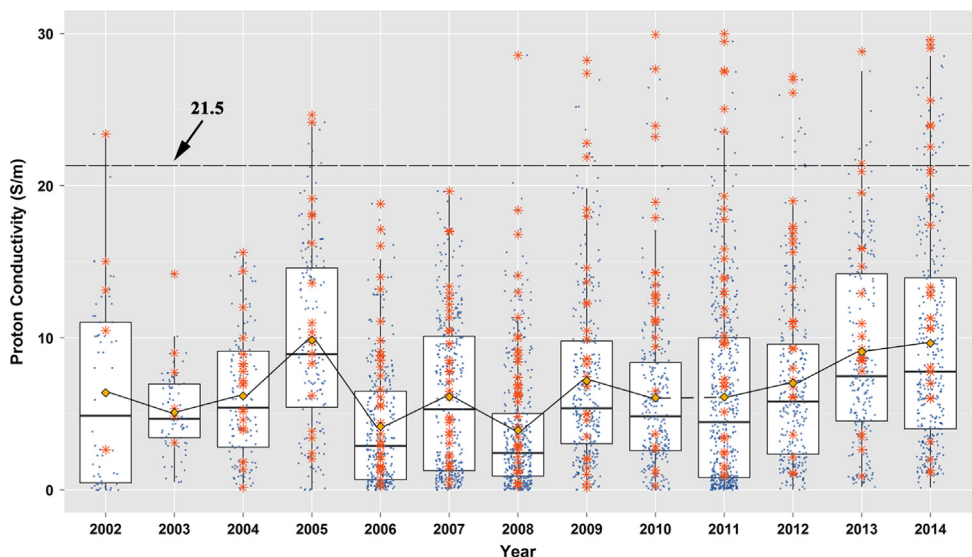


Fig. 5. The trend to improve the proton conductivity of Nafion membranes in recent 13 years. The line across years linked the mean of the proton conductivity over the records reported in the corresponding year. The red stars are the maximum value of proton conductivity reported in each report. The black dash line is the threshold of proton conductivity with 21.5 S/m. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

The T-test of proton conductivity in each year against the accumulation before, the number of records, mean, T-value and P-value. Significant improvement was bolded and deterioration was italic with cutoff of P-value at 0.05.

	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Records^a	58	75	127	159	303	351	390	308	274	488	284	225	337
Mean^b	6.391	5.100	6.176	9.843	4.162	6.606	3.916	7.174	6.061	6.114	7.028	9.082	9.643
Acc_mean^c	–	6.391	5.663	5.913	7.405	6.044	6.228	5.611	5.883	5.907	5.947	6.056	6.280
T-value^d	–	1.522	–0.961	–7.171	9.222	–1.621	8.672	–4.441	–0.536	–0.703	–3.073	–7.091	–8.532
P-value^d	–	0.132	0.337	7.7e–16	<i>2.2e–12</i>	0.105	<i>2.2e–16</i>	1.14e–5	0.592	0.482	0.002	1.3e–12	3.3e–16

^a The number of records of proton conductivity for each year in our dataset.

^b The mean proton conductivity for each year.

^c The mean proton conductivity for the accumulation records before the corresponding year.

^d T-test of proton conductivity results between a year and the accumulation before the year.

different temperatures. Though the fittings can provide acceptable correlation relationships and coverage, some of the fitting results are still scarce of rational physical definition, such as the fitting in the temperature of 70 °C and 80 °C. It is a result not only from the number of records in each subset, but also from the diversity of experimental reports deeply originated from the absence of an universal standard for the measurement of the proton conductivity. To explore the influence of temperature on the proton conductivity, we picked out 1727 records with the relative humidity of 100% which accounting to 50.5% of all for further analysis. Fig. 7 shows the distribution and the fitting against different temperatures of these records. When temperature is not higher than 80 °C, the fitting can use Arrhenius equation, which is written by

$$\sigma_{\text{fit}}(\text{RH}, T) = Ae^{-E_a/RT} \quad (6)$$

where E_a , R , and T are the activation energy for proton conduction, the gas constant, and the absolute temperature, respectively. The increase of the proton conductivity is a result of both the diffusivity and ionic mobility [28] increase with temperature elevation. The fit with R-square of 0.774 provides an activation energy E_a 9.6 kJ mol^{–1}. The activation energy for proton conduction in Grotthuss mechanism is about 14.0 to 40.0 kJ mol^{–1} [29], while Nafion membrane with 3 wt% SiO₂ nanoparticle filler show the activation energy value of 11.0 kJ mol^{–1} for filler-free and 8.7 kJ mol^{–1} with filler at RH of 100% [30]. The latter argued that the presence of inorganic fillers can alter the percolated water channel in Nafion matrix and lower down the activation energy. There are ~70% records in our dataset have fillers, so the statistical results may be close to the situation with fillers. Above 80 °C, the proton conductivity significantly drops with further elevation of temperature. It is majorly a result of the loss of liquid water in Nafion membranes. Therefore, the operation temperature around 80 °C probably the most favorable for Nafion membrane based fuel cells.

3.3. Filler effects on the proton conductivity and water uptake

Besides the improvement in stability, mechanical properties and fuel crossover retarding, fillers can be also used to enhance the proton conductivity through the optimization of percolated water channels (in several nanometers) in Nafion membranes.

The distribution of proton conductivity and water uptake against the status of filler are presented in Fig. 8 and the corresponding T-test analysis is summarized in Table 3. Fillers can shift the distribution of the proton conductivity to higher value, and inorganic fillers can significantly improve most Nafion membranes. Though the membrane with organic-fillers has insignificant P-value against filler-free membranes, a portion of them has extremely high proton conductivity indicated from the enrichment of membranes between 20.0 and 30.0 S/m. These fillers include

sulfonated diphenylsilanediol [31], poly(vinylidene fluoride) or histidine functionalized carbon nanofibers [32,33] etc. Organic fillers have hydrogen bond donors that can form salt bridge with sulfonate groups in Nafion and further promote proton conduction. Further, these organic fillers with sulfonated or acetyl side-chain groups, such as the substituted poly(p-phenylene)(POAc) [34] which can form closely packed proton conductive channels through the network of sulfonic acid and hydrogen bonding and greatly improve the proton conductivity. The success of these organic fillers may also contribute to the facilitation of the formation of parallel percolated water nanochannels [35]. Inorganic fillers normally are nonconductive oxide with less proton conductivity (compared with the hydrated Nafion membrane) and hydrophilic surface, such as silica zirconia, titania, sulfonated montmorillonite, sulfonated phenethyl silica [13]. Inorganic fillers can enhance the water retention in Nafion matrix, improve the interconnection of the ionic clusters in the polymeric matrix by providing a preferential pathway for proton hopping and consequently increase the proton conductivity. Thus, inorganic fillers are expected to essentially improve the proton conductivity of Nafion composite membranes.

As shown above, the proton conductivity is positive dependent on the relative humidity and temperature. While the water uptake also has a positive correlation with them [36]. Fillers with higher water uptake capability generally have higher probability to improve the proton conductivity. Fig. 8b shows the influence of fillers on the water uptake of Nafion membranes. Membranes with organic filler have a relative high portion at the value under 20 wt%, which may analogy to such as poly(ether(amino sulfone))(PEAS) with low water-holding capability [37]. One of the major goal for organic fillers is to block fuel crossover, and a P-value of 0.961 indicating almost identical distribution in the proton conductivity between membranes with organic fillers and filler-free become a reasonable result. Inorganic fillers possess absolute advantage comparing with the other two types of membranes at water uptake above 30 wt%. The increasing water uptake may benefit from the presence of homogeneously dispersed inorganic fillers such as hygroscopic inorganic oxides(SiO₂, TiO₂, ZrO₂) and zeolite, etc. with high specific surface area in hydrophilic nature. Meanwhile, a part of inorganic fillers can significantly enhance the water uptake but fail to improve the proton conductivity. It occurs in Nafion composite membranes with a high volume fraction of fillers, which make polymer matrix become rigid and the percolated water channel turn to tortuous [38,39].

Overall, inorganic fillers can greatly enhance the water-holding capability than their organic counterpart, thus have high probability to improve the proton conductivity of Nafion membranes. Fillers that can regulate the microstructure, facilitate the water uptake and the formation of percolated parallel water channels, as well as promote the fraction of weak bonding water portion at micro-scale should be a rational direction for the selection and

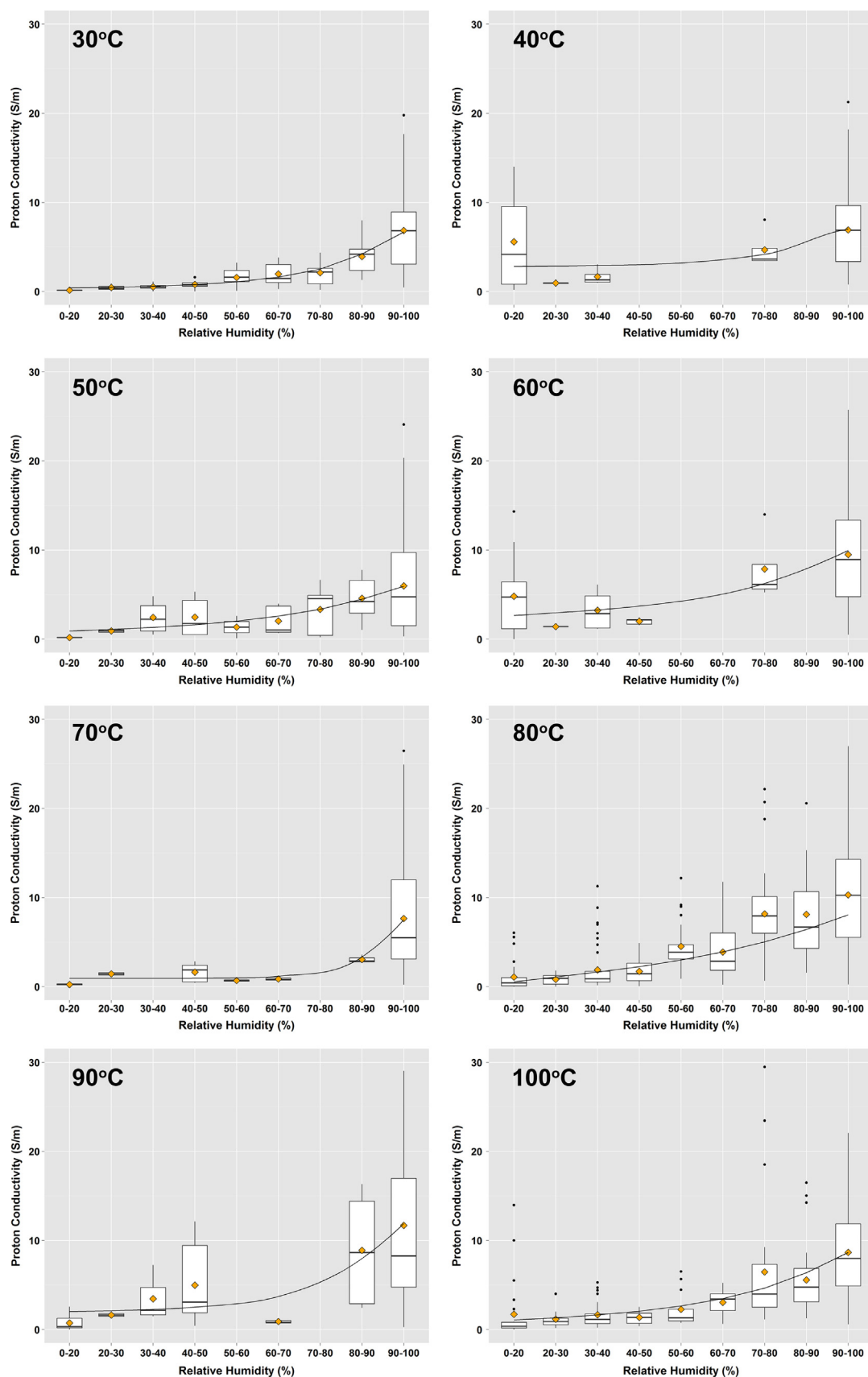


Fig. 6. The relative humidity dependence of the proton conductivity at different temperatures. Black dots are outliers and the diamond is the mean in each RH bin. The black line is the best fit of the means using Eq. (4).

Table 2

Fitting parameters, correlation coefficients and coverage using Eq. (4) for the proton conductivity in RH bins at different temperatures.

Temperature of measurements (°C)	Number of records	σ_0	C	RH _{ref}	R-square	Coverage
30	230	0.325	0.041	18.867	0.982	0.782
40	144	2.772	0.002	18.181	0.496	0.826
50	190	0.569	0.238	31.250	0.875	0.726
60	223	2.139	0.370	31.250	0.757	0.672
70	157	0.931	8.1e-5	8.403	0.965	0.649
80	481	-1.854	1.871	50.000	0.936	0.807
90	174	1.947	0.040	17.241	0.882	0.563
100	281	0.642	0.298	29.411	0.912	0.889

Table 3

The summary of the T-test with significance level of *p*-value 0.05 bolded, for the proton conductivity σ (S/m), and the water uptake WU (wt%).

Test-sample	Records of the former		Mean of the former		P-value		T-value	
	σ	WU	σ	WU	σ	WU	σ	WU
Organic vs. filler-free	817	586	5.881	27.94	0.33	0.96	-0.97	-0.05
Filler-free vs. inorganic	787	1017	6.159	27.97	2.0e-4	2.2e-16	3.72	10.10
Inorganic vs. organic	1614	450	7.058	34.56	4.8e-6	2.2e-16	4.59	9.05

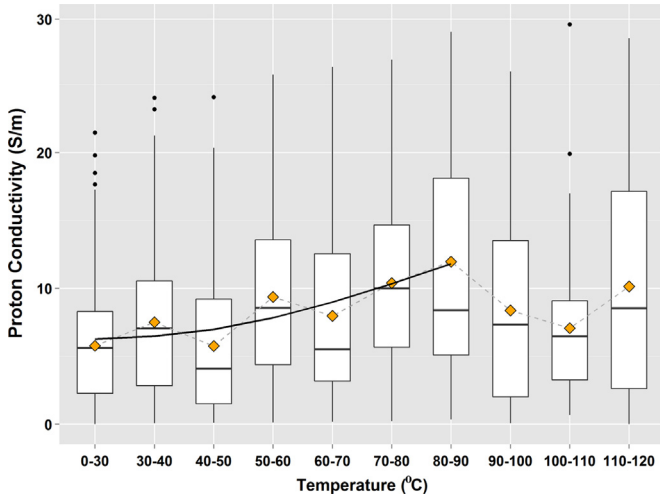


Fig. 7. The temperature dependence of the proton conductivity at the relative humidity of 100%. The dots represent outliers, the line is the best fit using Arrhenius equation, and the dash lines are for eye guide.

manufacture of Nafion composite membranes.

3.4. Water in Nafion membranes and problems

Experimentally, water in Nafion membranes may be from liquid or vapor, i.e., immerse membrane in water or keep in air with a given humidity at fixed temperatures. Water content in the former is in a saturated state and solely determined by the temperature, and in the latter is experimentally controlled by the relative humidity (RH). The water uptake of membranes in both

cases can be calculated using Eq. (1). Intrinsically, the water content (λ) in membranes, which is defined as the number of water molecules per sulfonic acid group, i.e., $[H_2O]/[-SO_3]$ [36], is believed to have direct correlations with the proton conductivity. Springer et al [40], has proposed a third order polynomial function for σ as a function of λ based on the study of Nafion 117 membranes. For different membranes, the λ can be converted from WU through

$$\text{water content}(\lambda) = \frac{\text{water uptake(WU)}}{M_{H_2O}} \cdot EW \quad (7)$$

Here M_{H_2O} is the water molecular weight, and EW is the equivalent weight of Nafion that equals to the molecular mass of Nafion per sulfonic acid group. For fuel cells in practical operations, the membrane is surrounding in vapor. In this case, water in membrane can be modeled as gaseous molecules physically adsorbed in the solid membrane with pores and phase separation structures. Therefore, an *n* layer Brunauer–Emmett–Teller(BET) equation [41] can be used to correlate λ and RH, which is written as

$$\lambda = \lambda_m \cdot \frac{[C \cdot RH / (1 - RH)] [1 - (n + 1) RH^n + n RH^{n+1}]}{1 + (C - 1) \cdot RH - C \cdot RH^{n+1}} \quad (8)$$

Here λ_m is the water loading at monolayer coverage, *n* is the total number of water layers in the pores at saturation, and *C* is the BET constant. The best fit against the means for λ at different RH levels is shown in Fig. 9. The fit provides a good correlation coefficient (*R*-square=0.968) with parameters: $\lambda_m = 1.35$, $n = 14.38$, $C = 65.48$. The number of water molecules in saturated adsorption equals $n\lambda_m$ which is 19.41. These parameters seem to be an average of various membranes. For example, Thampan et al. [41] used the BET equation to fit the adsorption isotherm data of Nafion 117 at 25 °C,

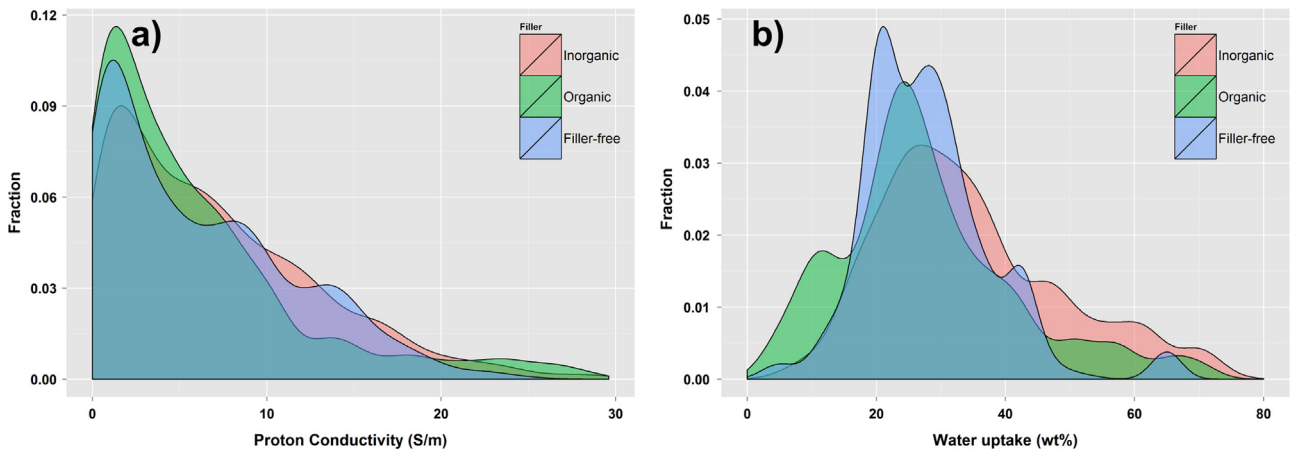


Fig. 8. The probability density function for the proton conductivity (a) and the water uptake (b) regarding to filler types.

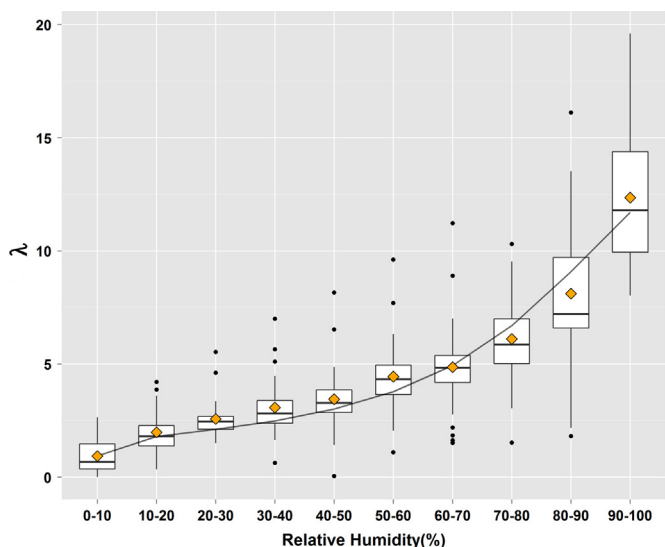


Fig. 9. The relationship between water content (λ) for various Nafion membranes in different relative humidity (RH) levels. The curve is the best fit of BET equation on the mean values.

and presented the parameters $\lambda_m=1.8$, $n=13.5$, $C=150$ and $n\lambda_m$ is 24.3. Yang et al. [42] fitted Nafion 115 membranes and got parameters $\lambda_m=2$, $n=9.2$, $C=35$, and $n\lambda_m$ is 18.4. The saturation water content is close to the upper limit of $\lambda=22$ immerse in liquid water, and higher than $\lambda=14$ with the 100% relative humidity in vapor for Nafion 117 membranes [43].

Through the water content, we also intend to construct direct correlations between the proton conductivity and the water uptake. Their correlations are presented in Fig. 10, for water content (λ) in liquid calculated using Eq. (7) and in vapor. Water contents from liquid do not show confidential correlation with the proton conductivity (with R -square of 0.659, Spearman coefficient, a ranking order correlation is 0.167). While the correlation has R -square of 0.802 (Spearman coefficient of 0.829) for those in vapor. Therefore, water uptake measured in vapor is a more reliable parameter to correlate the proton conductivity. Further, the same guideline drawn from the selection of fillers can also be observed here, that membranes immersed in liquid have saturated water content, which always present higher proton conductivity (with 18.7% of all data in 10–20 S/m) than those in vapor (with 31.7% of all data in 5–10 S/m). In both cases, when $\lambda < 5$, proton conductivity is negligible. The λ dependence of the proton

conductivity agrees with the consensus summarized by Devanathan [44] for Nafion 117 membranes, small water clusters occur for $\lambda < 3$, size gradually increasing of water clusters for $\lambda < 3-5$ and eventually a percolated water network for $\lambda > 6$. The proton conductivities still monotonously increase with the water contents in membranes from statistical view.

Behind the results reported here, we also collected other features such as the thickness of membrane; the ion exchange capacity (IEC) or the equivalent weight (EW) of composed polymer; conditions of measurements in air, solution or in membrane electrode assembly (MEA); the history of treatment during the fabrication of Nafion membranes like hot pressing; mechanic properties of membranes and the crossover of fuel etc. all may interplay with the proton conductivity. Deeply research into these data and carefully decouple their relationships should be more informative. Unfortunately, the absence of an international standard in the measurement of the proton conductivity results in many uncertainty that create additional challenges for a solid statistical analysis. Further data mining is still undergoing to provide a clearer overview with more informative guidelines.

4. Conclusions

In this study, we performed a statistical analysis on a comprehensive and representative collection of the proton conductivity of Nafion membranes, and a data-supported overview was presented. The advancement to improve the proton conductivity of Nafion membranes in recent 13 years was summarized. A proton conductivity of Nafion membrane higher than 21.5 S/m should be a criterion for advance declaration. The proton conductivity of Nafion membranes can be described using an exponential increase function against relative humidity at different operation temperatures with acceptable confidence. While the temperature dependence can be fitted by Arrhenius equation for temperature lower than 80 °C with a statistical activation energy of 9.6 kJ mol⁻¹. Water content in membranes in vapor, rather than that calculated from liquid, show good correlation with proton conductivities. It supports the consensus for the correlation of water clusters in membranes with the proton conductivities. Fillers that can enhance weak bonding water and facilitate percolated water channel with less tortuosity should be a direction to achieve membranes with higher proton conductivity.

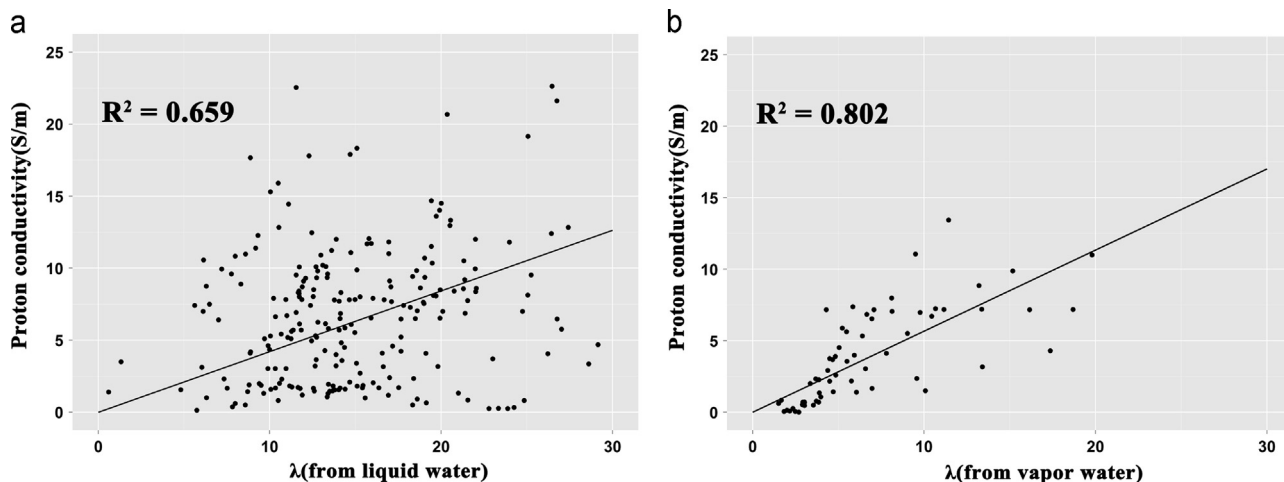


Fig. 10. Proton conductivity dependence of water content from a) liquid water, b) vapor water. The black lines are generated by fitting the data using linear equations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2015.12.065>.

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