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Numerical modeling of Nafion membranes to predict their performance under different operating conditions

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Abstract. The proton conductivity of Nafion (DuPont) membranes plays a critical role in the performance of Proton Exchange Membrane (PEM) electrochemical cells, as it governs the membrane's ability to transport hydrogen protons (H^+) between the anode and cathode. While numerous studies have been conducted on the conductivity of Nafion membranes, to date, no dedicated experimental campaign has focused on the characterisation of through-plane conductivity of several Nafion membranes, under different operating conditions, to develop a predictive model of their performance. This research work aims to address this gap by investigating the through-plane conductivity of non activated NR212, N115 and N117 membranes. The study was carried out using a Membrane Testing System (MTS), where relative humidity levels (20% to 95%) and temperature conditions (30°C to 80°C) were systematically varied. A new numerical empirical model was developed in the Python programming environment to predict the membranes' performance. In particular, the model was first calibrated using experimental data of NR212 and N117, and then validated using those of N115. The model shows a good reliability for all the operating conditions tested, with a minimum and maximum value of the Root Mean Square Error (RMSE) of 1.1 mS/cm and 4.7 mS/cm at 50°C and 80°C, respectively. Furthermore, to the authors' knowledge, no through-plane conductivity data of non activated N115 and N117 have been published yet, revealing that this is the first research work to fill this scientific gap.

Nomenclature
Acronyms

CNH_2 Centro Nacional del Hidrógeno

EIS Electrochemical Impedance Spectroscopy

EW Equivalent Weight

FRA Frequency Response Analyser

GDE Gas Diffusion Electrode

IP In-plane

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MTS Membrane Testing System

NZE Net Zero Emissions

PEM Proton Exchange Membrane

$PTFE$ Polytetrafluoroethylene

$RESs$ Renewable Energy Sources

$RMSE$ Root Mean Square Error

SD Standard Deviation

TP Through-plane

Geometric and physical variables

σ Ionic conductivity (mS/cm)

A Empirical coefficient (mS/cm)

A_{membrane} Membrane's active area (cm^2)

ASR Area Specific Resistance (cm^2)

b Empirical coefficient ($-$)

c Empirical coefficient ($1/°\mathrm{C}$)

d Empirical coefficient ($1/°\mathrm{C}$)

f Empirical coefficient ($1/cm$)

L Membrane's thickness (cm)

R_{ohm} Ohmic resistance (Ω)

RH Relative Humidity (%)

s Membrane's thickness (cm)

T Temperature ($°\mathrm{C}$)

1 Introduction

It is well known that electrochemical cells powered by Renewable Energy Sources (RESs) are now a significant part of the energy transition. Indeed, according to IRENA's 1.5°C scenario, green hydrogen plays a very important role due to its potential to decarbonise, mainly, hard to abate sectors [1]. This is why the development of cost-effective hydrogen technologies represents an important step towards the Net Zero Emissions (NZE) target.

Among the different available technologies for hydrogen production and use, Proton Exchange Membrane (PEM) is considered one of the most promising. Indeed, it stands out for its high density power and hydrogen purity, high compactness for limited size applications, and easy integration with RESs. However, high costs due to the use of expensive components [2] represent the main limitation to the widespread diffusion of such a technology in the energy global market.

Regarding this, one of the core elements is the Nafion membrane that acts as a separator for the hydrogen and oxygen gases at the electrodes, while allowing the transport of positive ions H^+ between the two cell's compartments. This ability determines its ionic conductivity that, according to the working parameters, directly affects the whole performance of the electrochemical cell.

In such a scenario, it becomes crucial to develop a numerical model capable of predicting its behavior at different operating conditions, in order to optimise the assessment of the system. Most of the relevant models for electrolysers and fuel cells available in the literature are related to the whole cell, giving attention to the overall performance through the modeling of polarisation and efficiency curves. On the other hand, there are limited research works focused on the behaviour of single layers, such as electrocatalysts and membranes [3].

Journal of Physics: Conference Series **3143** (2025) 012079 doi:10.1088/1742-6596/3143/1/012079

Yadav et al. [4] presented a correlation to calculate the in-plane (IP) conductivity of Nafion 117 as a function of relative humidity and temperature. In particular, they used Electrochemical Impedance Spectroscopy (EIS) technique to measure the membrane resistance and investigate the effect of the platinum electrode dimension. Results showed that a reduction in the contact area at PEM-electrode interface improves the current distribution, resulting in clearer impedance spectra to obtain the ionic resistance. In addition to this, they found out that Nafion 117 conductivity is strongly related to the temperature and water content, with the latter having a greater influence. Furthermore, when comparing the in- and through-plane (TP) methods, identical Nafion 117 conductivities are obtained. Chandesris et al. [5] designed a 1D numerical model for the membrane degradation of a PEM electrolyser, describing the severe effects of the formation of radicals via Fenton reactions due to the metal-ion impurities and oxygen crossover at the cathode side. The results obtained from the single-cell tests showed the strong influence of the temperature on the degradation rate and the smaller and more complex effect of the current density. Furthermore, the coupling between the performance and the chemical degradation models allows to capture the acceleration of membrane thinning. Slade et al. [6] studied the TP conductivity of a series of extruded Nafion membranes with the same Equivalent Weight (EW) of 1100 using activated samples at 25°C. Results showed that the membrane resistance rises with thickness; in particular, for Nafion 112 and 117 an increase from 0.07 to 0.16 Ωcm^2 is obtained. On the other hand, the conductivity decreases with reducing membrane thickness; indeed, values of 0.083 and 0.16 S/cm have been obtained for N112 and N117. Furthermore, the in-situ conductivity measured in a PEM fuel cell confirms the relatively poor conductivity of the Membrane Electrode Assemblies (MEAs) based on thinner membranes. Cooper [7] has focused his attention on the study of Nafion NR212 taking into account the non-membrane ohmic contributions. In particular, a zero thickness linear regression of the measured high frequency resistance vs membrane thickness has been performed to retrieve the TP conductivity of the membrane at different conditions of Relative Humidity (RH) and temperature. The main result obtained reveals that the conductivity of Nafion NR212 is the same in the through- and in-plane directions.
As it can be noticed, different research works gave attention to the study of Nafion membranes behaviour. However, none of them focused on the development of a predictive model to assess their performance at different operating conditions.
This paper aims to fill this research gap by introducing a new empirical model, developed in the Python programming environment, to predict the Nafion membranes TP conductivity when varying the temperature, RH, and thickness. In particular, experimental results of non activated NR212 (50 μ) and N117 (189 μ) have been used to calibrate the model, while those of N115 (138 μ) have been used to validate it. Furthermore, to the authors' knowledge, no TP experimental data of non-activated N115 and N117 have been published yet, revealing that this is the first research work to fill this literature gap.
This paper is structured as follows: Sec.2 presents an overview of the experimental campaign and model developed, Sec.3 shows the results obtained, and Sec.4 reports the conclusions of the work.

2 Materials and Methods

In this section, a complete overview of the experimental campaign performed together with the numerical model developed is presented.

2.1 Membrane testing system and experimental campaign description

The experimental campaign has been performed at the Centro Nacional del Hidrógeno (CNH_2) in Spain, in the PEM technology laboratory.
Through-plane conductivity measurements for non activated Nafion membranes NR212, N115 and N117 have been conducted with the Membrane Testing System (MTS) 740 from Scribner shown in Fig.1.
It must be specified that NR212 contains a Polytetrafluoroethylene (PTFE) reinforcement layer that slightly modifies the membrane's structure with respect to the homogeneous ones N115 and N117. In this regard, the overall contribution to the ionic conductivity may also depend on the internal morphology. However, this phenomenon has been neglected as it is beyond the scope of this study.
Regarding the experimental setup, membrane samples have been first placed between two Gas Diffusion Electrodes (GDEs - Sigracet 39 BC) located on two platinum electrodes of the cell head shown in Fig.2, and then compressed up to a fixed compression force that guarantees a proper contact membrane-electrode.

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Figure 1: Membrane Testing System for through-plane membranes conductivity measurements.

Figure 2: Cell Head for through-plane membranes conductivity measurements.

After positioning the cell head into the measurement chamber of the MTS 740, a testing protocol has been applied to measure the membranes' through-plane conductivity at different operating conditions of RH and temperature. For each variation, the EIS technique has been used to measure the membranes' ionic resistance in order to calculate their ionic conductivity. In particular, the Newtons4th Ltd Frequency Response Analyser (FRA) has been used to record the spectra, while ZView software has been used to evaluate them.
Nafion samples have been tested between 30 and 80°C and, for each temperature, a RH conditioning process has been performed [8]. Indeed, each membrane goes through a first humidification cycle from 70 to 20% with 10% steps and then a second one from 20 to 95% with the same variation step.
Tab.1 shows the testing protocol applied for a temperature of 30°C.

Table 1: Through-plane conductivity testing protocol at 30°C.

T (°C)	RH (%)	T_{tot} (min)	Hydrogen flow rate $(sccm)$	P_{H_2} (kPa)	$P_{contact}$ (PSI)
30	70	120	500	101	310
30	70	15	500	101	310
30	70	15	500	101	310
30	60	15	500	101	310
30	60	15	500	101	310
30	50	15	500	101	310
30	50	15	500	101	310
30	40	15	500	101	310
30	40	15	500	101	310
30	30	15	500	101	310
30	30	15	500	101	310
30	20	15	500	101	310
30	20	15	500	101	310
30	30	15	500	101	310
30	30	15	500	101	310
30	40	15	500	101	310
30	40	15	500	101	310
30	50	15	500	101	310
30	50	15	500	101	310
30	60	15	500	101	310
30	60	15	500	101	310
30	70	15	500	101	310
30	70	15	500	101	310
30	80	15	500	101	310
30	80	15	500	101	310
30	90	15	500	101	310
30	90	15	500	101	310
30	95	15	500	101	310
30	95	15	500	101	310

As it can be noticed, each RH step is hold for 15 minutes in order to stabilise the operating condition before recording the EIS spectrum. This is valid for each measurement except for the first one when a temperature change is performed; indeed, the first step is hold for 120 minutes to ensure a proper conditioning of the membrane sample when the RH cycle starts.
Furthermore, a constant hydrogen flow of 500 $scmm$ is provided in order to have a well humidified gas flow that allows to reach a steady-state RH within 2 minutes after changing the operating condition [8]. It is worth noting that a fixed pressure of 310 PSI between the electrodes is applied to ensure a good contact with the membrane [7].
From the recorded EIS spectra the membranes' ionic resistance has been estimated and then used to calculate their ionic conductivity, at different conditions of RH and temperature, using Eq.1:

$$\sigma = \frac{s}{ASR_{membrane}} \tag{1}$$

where σ (S/cm) is the membrane's conductivity, s (cm) is the sample thickness, and ASR (Ωcm^2) is the through-plane Area Specific Resistance. The latter is calculated as:

$$ASR_{membrane} = R_{ohm} \cdot A_{membrane} \tag{2}$$

where R_{ohm} (Ω) is the membrane's ohmic resistance determined with a zero-intercept method of the values obtained from the intersection of the EIS spectra with the real axis of the impedance plot, and A_{membrane} (cm^2) is the membrane's active area which corresponds to 0.5 cm^2.

2.2 Membrane conductivity model

As mentioned before, a numerical empirical model to predict the membranes' through-plane conductivity was developed in the Python programming environment. In particular, experimental data of NR212 and N117 have been used to calibrate the model while those of N115 have been used to validate it.

In this case, only the data from 40 to 80°C and from 40 to 95% of RH have been used for the model, since the results obtained at 30°C and 20 and 30% of RH have shown a certain instability probably due to the low humidification condition of the membranes that hinders their capability of conducting ions. This means that the model can be used for the three membranes tested to predict their behavior between 40 and 80°C and 40 and 95% of RH, defining the 3D physical domain depicted in Fig.3.

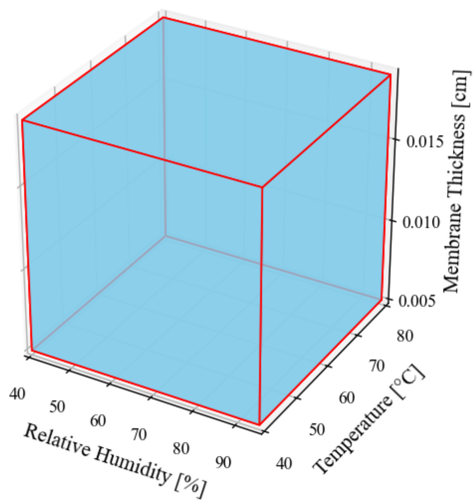

Figure 3: 3D physical domain of validity of the numerical model.

Eq.3 shows the mathematical relation developed in the Pyhton programming environment:

$$\sigma = A \cdot exp^{b \cdot RH + c \cdot RH \cdot T} + d \cdot T + f \cdot L \quad (3)$$

where σ (mS/cm) is the membrane's conductivity, RH is the Relative Humidity inserted as a fraction of 1, T (°C) is the temperature, and L (cm) is the membrane's thickness. As it can be noticed, the model developed contains three main terms: i) crossed effect of humidity and temperature in which the RH has an exponential type predominant influence on the membrane conductivity. This is in line with what reported in the scientific literature [9, 10], ii) linear effect of the temperature [4], and iii) linear effect of the membrane's thickness [6].

The equation presents 3 input variables (e.g., RH, T, and L) and 5 empirical coefficients (e.g., A, b, c, d, and f). The latters are retrieved through an iterative curve fitting process performed in Python, using the experimental data of NR212 and N117 as input, until the algorithm finds the optimal combination of parameters that minimises the sum of the squared differences between the observed data points and the corresponding ones predicted by the model [11]. The objective function to be minimised is the following:

$$\sum_{i=1}^{k} (y_i - f(x_i, p))^2 \quad (4)$$

where p is the parameter vector to be optimised, k the number of data points, x_i and y_i are the coordinates of the i^{th} data points, and $f(x_\mathrm{i}, p)$ is the model prediction given the parameter vector p. It is worth noting that a proper range of variation of the resulting coefficients has to be set to avoid unrealistic values.

Tab.2 reports the empirical parameters obtained with the optimisation algorithm, together with their range of variation.

Table 2: Empirical parameters obtained with the fitting process.

	A (mS/cm)	b (-)	c (1/°C)	d (1/°C)	f ($1/cm$)
Range of variation	0 - 50	-2 - 2	-2 - 2	-2 - 2	0 - 10^3
Numerical values obtained	9.41	1.05	$1.93 \cdot 10^{-2}$	$-2.05 \cdot 10^{-1}$	$3.54 \cdot 10^2$

3 Results and Comments

In this section, the results of the experimental campaign performed together with the numerical model validation are reported.

3.1 Results of the experimental campaign

As mentioned in Sec.2, the TP conductivity of non activated Nafion membranes NR212, N115, and N117 has been studied between 20 and 95% of RH and 30 and 80°C.

Figs.4-9 show the results obtained for all the membranes tested.

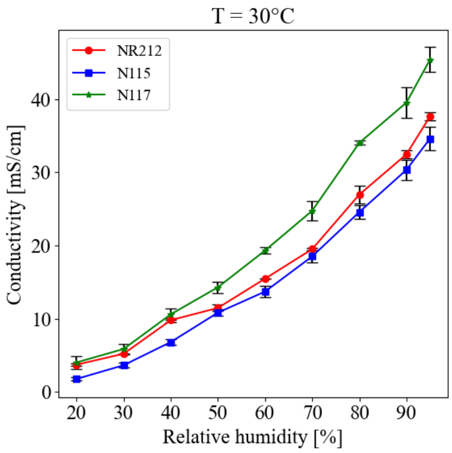

Figure 4: Experimental conductivity at 30°C.

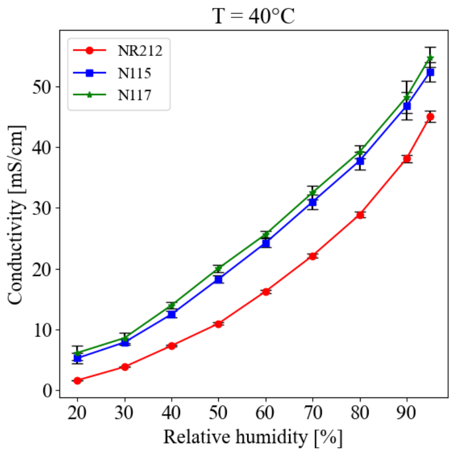

Figure 5: Experimental conductivity at 40°C.

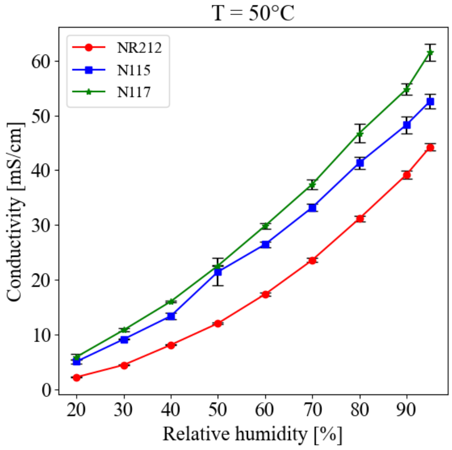

Figure 6: Experimental conductivity at 50°C.

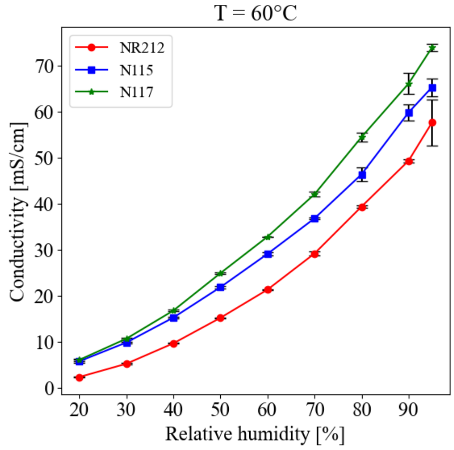

Figure 7: Experimental conductivity at 60°C.

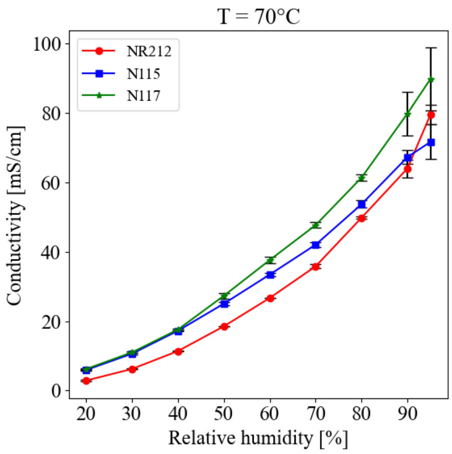

Figure 8: Experimental conductivity at 70°C.

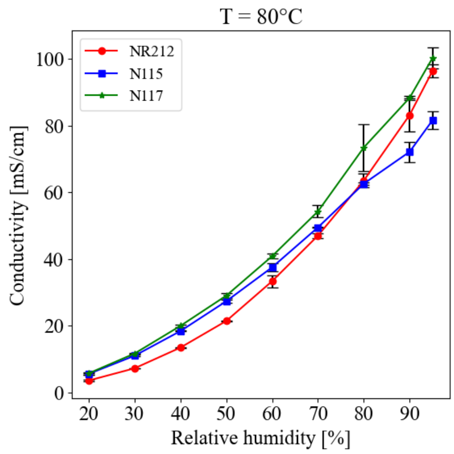

Figure 9: Experimental conductivity at 80°C.

As it can be observed, conductivity increases with both temperature and RH. This is because in hydrated Nafion membranes, proton transport occurs through interconnected water channels according to the Grotthuss and matrix transport mechanism [12]. This means that as the membrane's hydration increases, more and longer channels will be available for the proton transport, leading to a higher ionic conductivity.

At the same time, as the temperature increases, protons have higher kinetic energy to cross the membrane and the absorbed water is better distributed into the Nafion structure to form more flexible and interconnected water channels. This contributes to increase the conductivity. It should be mentioned that at temperatures above 80°C, ionic conductivity of Nafion is significantly reduced due to the partial evaporation of water that hinders the protons' mobility [12]. This justifies the temperature's upper limit chosen in this research work.

Furthermore, for the same value of RH, the conductivity increases with the membrane's thickness as reported in the scientific literature [6]; indeed, N117 shows the highest conductivity values for all the experimental conditions tested.

This is due to the fact that the larger the thickness, the higher the resistance encountered by the ions that have to travel a longer path to cross the membrane. However, as the ionic conductivity is related to a thickness of 1 *cm*, the larger the membrane, the higher the conductivity thanks to a greater number

of channels available for the ions transport. This condition is always valid except for the temperature of 30°C in which the membrane N115 has a lower conductivity than that of NR212. This could be due to a certain instability of the measurement caused by the low temperature, together with the fact that a higher time of stabilisation is required for thickest membranes. For this reason, the experimental data recorded at 30°C have been neglected when validating the model.
In addition to that, the Standard Deviation (SD) for all the experimental points acquired is also represented. Indeed, due to the testing protocol applied (see Tab.1), a variability of the conductivity values is recorded during the RH conditioning cycle. In this regard, the maximum and minimum values of SD are 9.08 and 0.00052 mS/cm, for N117 and NR212, at 70°C and 95% of RH and 40°C and 30% of RH, respectively.

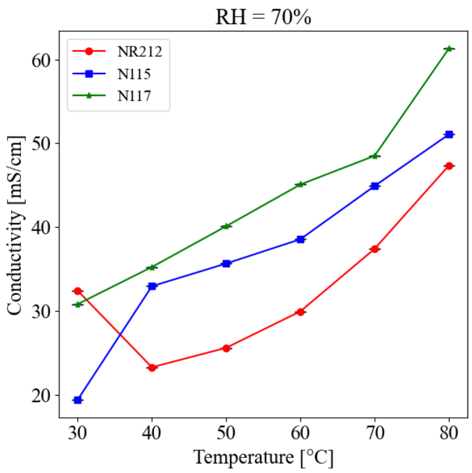

Figure 10: Membranes' conductivity at 70% of RH when varying the temperature.

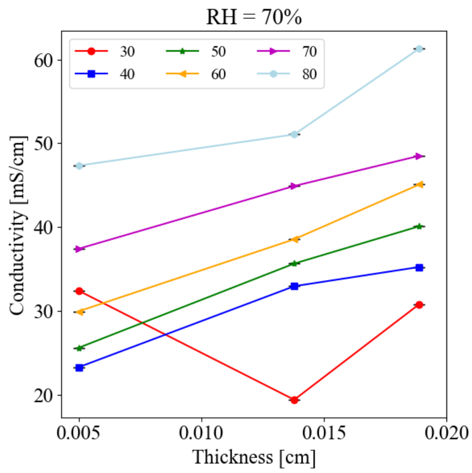

Figure 11: Membranes' conductivity at 70% of RH and different temperatures when varying the thickness.

Figs.10 and 11 show the variation of conductivity with temperature and thickness, respectively, when the RH is kept fixed at the most stable value (see Tab.1) of 70%.
As it can be noticed, a quite linear trend can be attributed to all the experimental conditions if excluding the one corresponding to 30°C in which an anomalous variation is recorded. This is in line with the scientific theory [4, 6]. From the data obtained, it has been found out that this negative effect is amplified at low percentages of relative humidity (e.g., 20 and 30%), justifying the choice of neglecting these values when validating the model. Furthermore, minimum and maximum values of SD of 0.00004 and 0.00203 mS/cm are recorded for NR212 and N117, at 30 and 80°C, respectively. These values are much lower than the ones reported above, highlighting the importance of the stabilisation time as a setting parameter for the measurements.

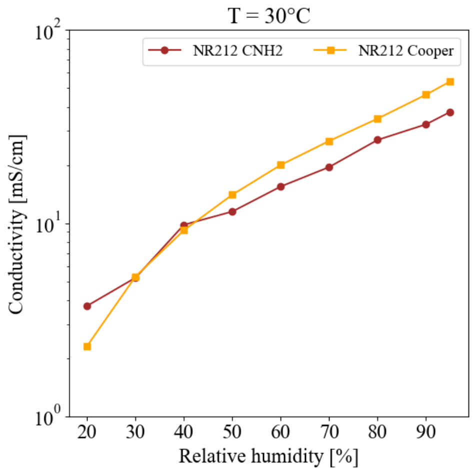

Figure 12: NR212 conductivity comparison between CNH_2 and literature at 30°C.

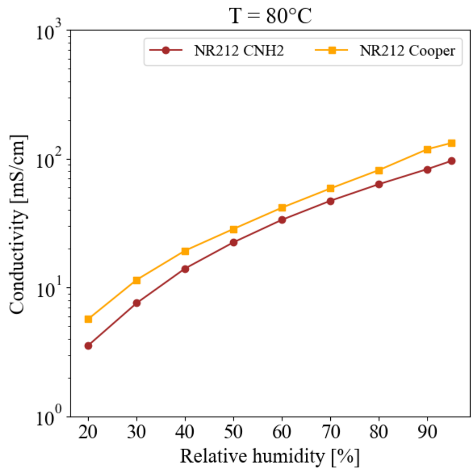

Figure 13: NR212 conductivity comparison between CNH_2 and literature at 80°C.

Figs.12 and 13 show the comparison, for the membrane NR212, between the experimental results obtained in this work and those reported in the scientific literature [7].
As it can be observed, there is a good agreement between the two experimental datasets, confirming the validity of the measurement protocol used. In this case, the SD of the conductivity curves obtained in this work is already represented above (see Fig.4 and 9), while the one related to the curves taken from the literature is hard to extrapolate. However, a maximum deviation of 31.12 mS/cm has been estimated at 95% of RH and 80°C.

3.2 Numerical model validation

As described in Sec.2, the mathematical equation developed has been used in a curve fitting process of the experimental data of NR212 and N117 to retrieve the empirical coefficients that allowed to validate the model for the intermediate membrane N115.
Figs.14-18 show the results of the numerical model validation.

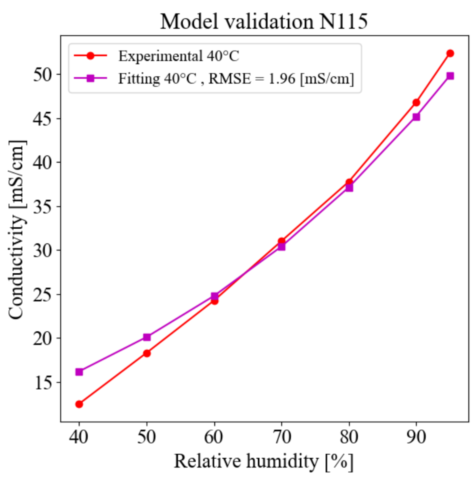

Figure 14: Model validation for N115 at 40°C.

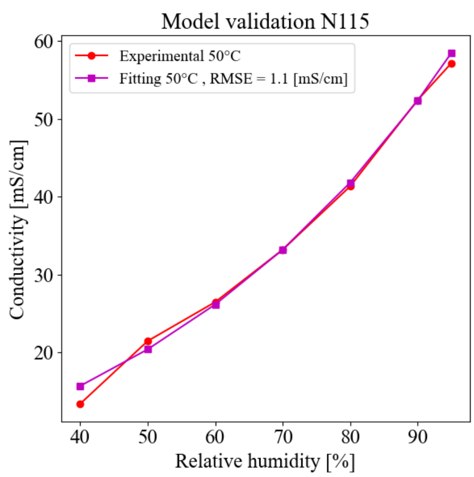

Figure 15: Model validation for N115 at 50°C.

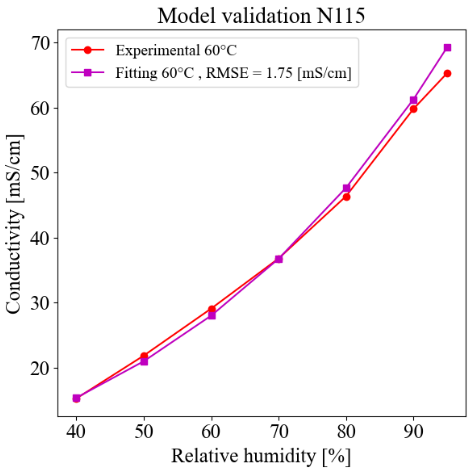

Figure 16: Model validation for N115 at 60°C.

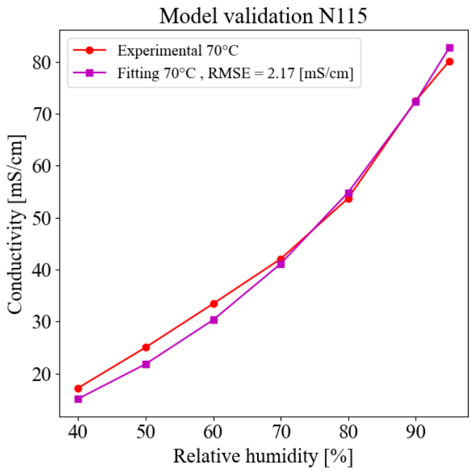

Figure 17: Model validation for N115 at 70°C.

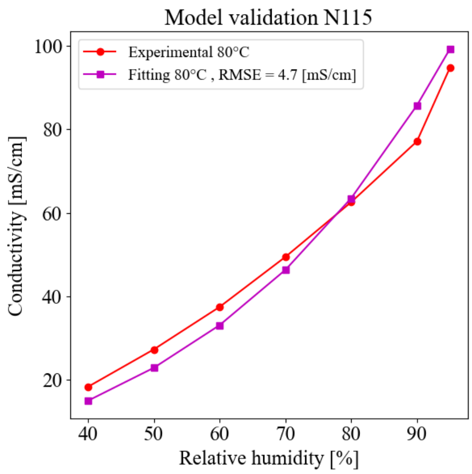

Figure 18: Model validation for N115 at 80°C.

It can be observed that the model developed has a good reliability for each experimental condition used in the validation process. This is also confirmed by the calculation of the Root Mean Square Error (RMSE) that has a minimum value of 1.1 mS/cm and a maximum value of 4.7 mS/cm at 50°C and 80°C, respectively.

4 Conclusions

This study aims to give insights on the Nafion membranes' ionic conductivity at different operating conditions of RH and temperature. In particular, the through-plane conductivity of NR212, N115 and N117 between 30 and 80°C and 20 and 95% of RH has been calculated from the EIS spectra performed during the experimental campaign. A comparison between the values obtained in this work and those reported in the scientific literature for NR212 shows a good agreement, confirming the validity of the measurement protocol used. In addition, to the best of the authors' knowledge, there are currently no published through-plane conductivity data for non-activated N115 and N117 membranes, highlighting that this study is the first to address this gap in the literature. An original data-driven numerical model was implemented using Python to estimate the conductivity of the membranes based on RH, temperature, and thickness. The model has been first calibrated with the experimental results of NR212 and N117 and then validated with those of N115, showing a good reliability for all the operating conditions tested. Indeed, RMSE minimum and maximum values of 1.1 mS/cm and 4.7 mS/cm at 50°C and 80°C, respectively, are obtained. Future developments of this work involve a more extended experimental campaign to retrieve through-plane conductivity data of other Nafion membranes, and the implementation of the numerical model developed as a forecasting tool of a PEM electrochemical cell's performance.

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