An Adjusted Model of Proton Conductivity in Nafion® Membranes

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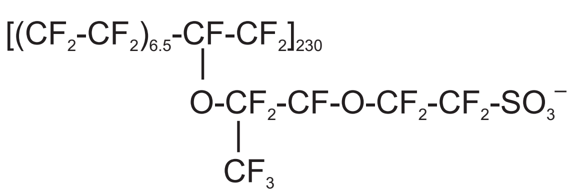
This developed and evaluated an adjusted model for proton conductivity in Proton Exchange Membrane (PEM) electrolyzer systems due to the increasing demand for alternative energy sources and the significance of green hydrogen (GH_2). We performed a logarithmic regression based on experimental data on conductivity and membrane water content to achieve this goal. The main results indicate that the adjusted model shows better agreement with the logarithmic behavior of conductivity when compared to the typical model proposed in 1991. Furthermore, the calculated ohmic overpotential from the adjusted model demonstrated higher accuracy. Therefore, the adjusted model provides a more precise tool for sizing and optimizing (GH_2) production systems using PEM technology.

Keywords: PEM Electrolysis. Proton Conductivity. Nafion. Mathematical Modeling.

With the increasing demand for alternative energy sources to mitigate environmental impacts, green hydrogen (GH_2) emerges as a promising energy option. Among the technologies for producing GH_2, Proton Exchange Membrane (PEM) electrolysis stands out, given its significant advantages in system design, H_2 production rate, purity, and energy efficiency [1].

One of the main differentiating factors of this technology lies in its proton exchange membrane. Composed of PFSA (perfluoro sulfonic acid ionomer, shown in Figure 1) - commercially known as Nafion®, this polymeric membrane acts as the electrolyte in the electrolytic system, meaning that it is responsible for facilitating the transfer of charge between the electrodes (H^+) – from anode to cathode, in this case [2].

Figure 1. PFSA/Nafion® molecular structure.



Therefore, the membrane integrity, besides its protons selectivity and conductivity, are crucial factors in determining the useful life of the equipment, the H_2 production rate, and its purity level. Thus, the importance of developing mathematical models that describe proton behavior in ionomeric systems becomes evident [2]. Among the proton conductivity models available in the literature, the semi-empirical model developed by Springer and colleagues [3] is undoubtedly one of the most widely used (Equation 1). Several authors, such as Görgün [4], Awasthi and colleagues [5], and Kim and colleagues [6], used this model to define the ohmic overpotential of electrolyzers and PEM fuel cells.

According to Springer and colleagues [3], using the Arrhenius equation, this model was developed based on experimental proton conductivity data (σ_{H^+}, from 303 K to 353 K). The pre-exponential term (σ_{303K}) is a function of the membrane water content (λ), which defines the conductivity at a reference temperature of 303 K (Equation 2). The exponential term is a function of temperature,

Equation 1.

$$\sigma_{H^+} = \sigma_{303K} * e^{\left[1268\left(\frac{1}{303}-\frac{1}{T}\right)\right]}$$

Equation 2.

$$\sigma_{K303} = (0.00514\lambda - 0.00326)$$

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allowing for the adjustment of conductivity values under different operational conditions.

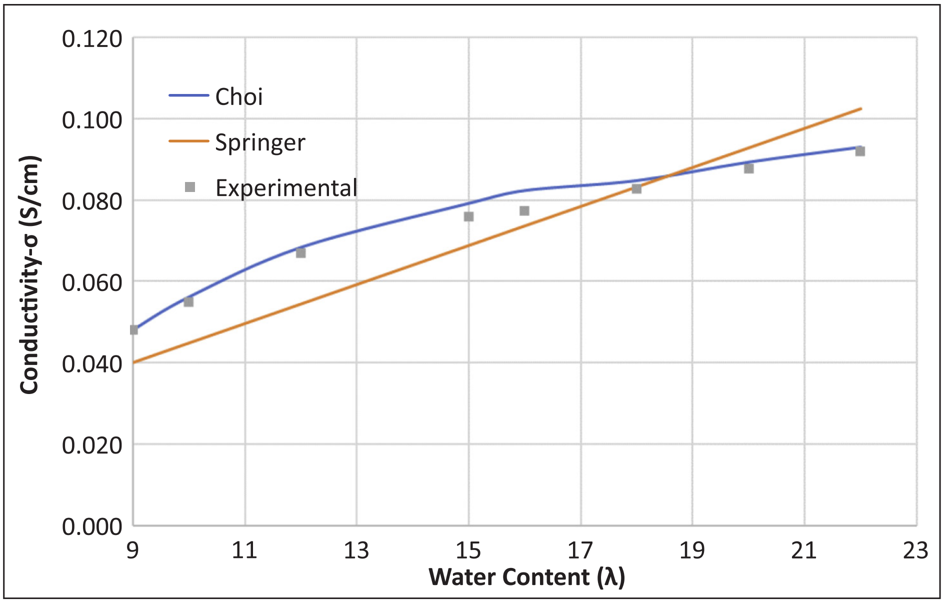
However, despite yielding satisfactory results within moderate ranges of λ (< 18), the model fails to accurately describe the conductivity behavior concerning membrane hydration, portraying it as a linearly increasing profile (first-degree function) due to the empirical pre-exponential term instead of logarithmic behavior shown by most of the experimental data in the literature. An alternative to this is presented in the model developed by Choi [2], which considers proton transport mechanisms in polymeric membranes (Surface, Grotthuss, and Vehicle). However, this phenomenological model exhibits high complexity in its equations and difficulty determining some parameters (not readily available in open literature). Figure 2 compares the aforementioned models and experimental data reproduced by Peckham and colleagues [7].

Therefore, this work aims to develop an adjustment to the mathematical model proposed by Springer and colleagues [3] to achieve a conductivity model that is both straightforward to use – with just one equation and two variables – and more accurate in describing the behavior concerning the hydration of the polymeric membrane. Additionally, an analysis of ohmic overpotential (ηohm) calculation sensitivity concerning the typical and adjusted models will be carried out.

Materials and Methods

As mentioned in the previous section, the main issue with the Semi-empirical model by Springer is its linear function behavior, which differs significantly from the logarithmic behavior observed in the experimental conductivity measurements. Furthermore, as seen earlier, the pre-exponential term of Equation 1 – obtained, according to the author, through regression based on experimental data – is responsible for this specific conductivity (σ_{H^+}) profile as a function of membrane water content (λ). Thus, a literature review was conducted using open-source platforms such as Google Scholar, Web of Science (Clarivate), SciELO, and CAPES, aiming to find experimental data to perform parameter estimation and model fitting. Data on σ_{H^+} and λ comparison – at 303.15 K – are found in Peckham and colleagues [7], Zawodzinski and colleagues [8], Sone and colleagues [9], and Zhang and Edwards [10] (Figure 3).

Figure 2. Comparison between Springer, Choi, and Experimental data.



A logarithmic regression was performed from the acquired experimental data to estimate a new pre-exponential term for the model. For this purpose, a generic logarithmic equation (Equation 3) was assigned.

Equation 3.

$$\sigma_{303K} = a * \ln(\lambda) + b$$

Then, employing the least squares mathematical method, the values of 'a' and 'b' (slope and intercept coefficients, respectively) were estimated, resulting in Equation 4.

Equation 4.

$$\sigma_{303K} = 0.0475 * \ln(\lambda) + 0.0571$$

Finally, the adjusted Springer model can be obtained by replacing the pre-exponential term in Equation 1 with Equation 4 (Equation 5).

Equation 5.

$$\sigma_{H^+} = [0.0475 * \ln(\lambda) + 0.0571] * e^{\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right]}$$

Furthermore, comparative analyses were performed between the models (Springer and adjusted Springer) and the experimental data to evaluate the accuracy of each model and its impacts on ohmic overpotential calculation for a cell working at 298.15 K, current density of 1.35 A/cm^2, and membrane thickness of 0.033 cm. These analyses and the discussion regarding the results can be found in the following section.

Results and Discussion

Figure 4 illustrates a graphical comparison between the results of the typical Springer model and the adjusted model proposed by this study. Despite the lower coefficient of determination ($R^2 = 0.933$) when compared to the one proposed by Springer and colleagues [3] ($R^2 = 0.954$), the adjusted Springer model provides better fitting results to the experimental data, following the logarithmic behavior of conductivity as membrane hydration intensifies. Other point to be noted is that the typical model exhibits a pronounced deviation from a specific range of membrane water content, indicating higher conductivity values than the actual ones. Indeed, this behavior can be detrimental to the sizing of electrolytic systems for green hydrogen production, as it would lead to fictitious higher values for GH_2 generation.

Figure 3. Experimental data by several authors.

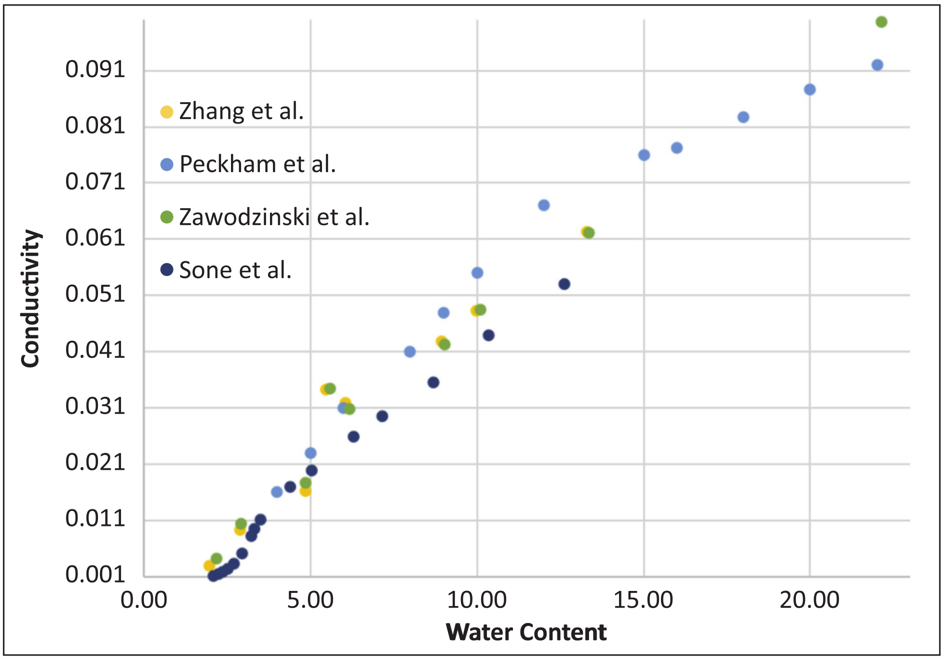


Figure 5 depicts the behavior of ohmic overpotential as a function of the water content provided by each model. As observed and consistent with the aforementioned, at higher values of membrane solvent loading, the typical Springer model describes a system with fewer ohmic losses – less resistant to proton transport.

Furthermore, concerning the prediction of ηohm, the adjusted model showed superior performance, with a coefficient of determination $R^2 = 0.99$.

Figure 4. Comparison between Springer, Adjusted Springer, and Experimental data.

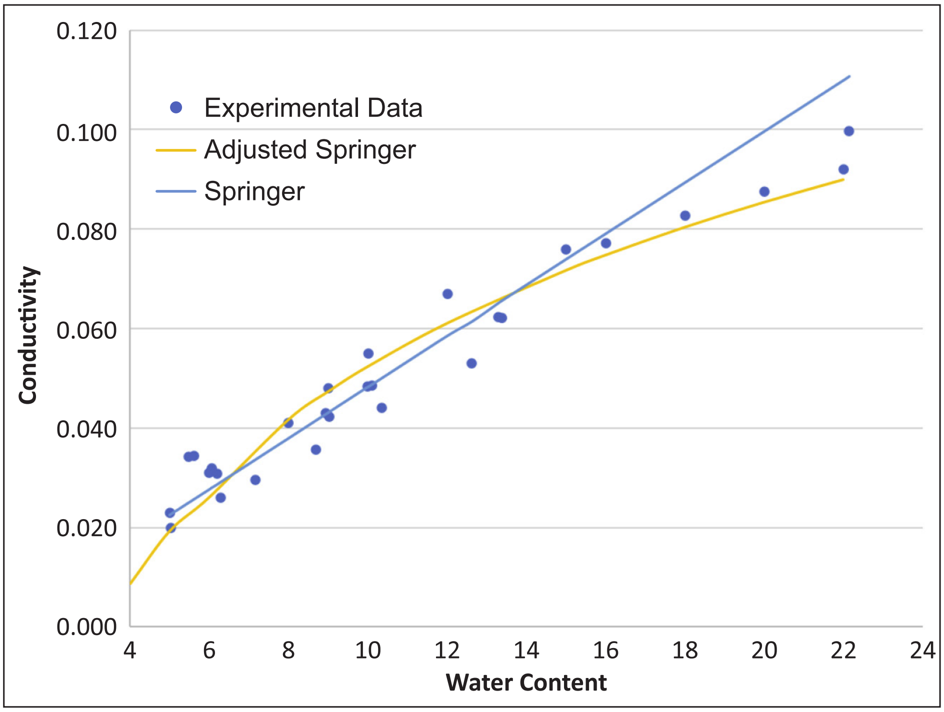
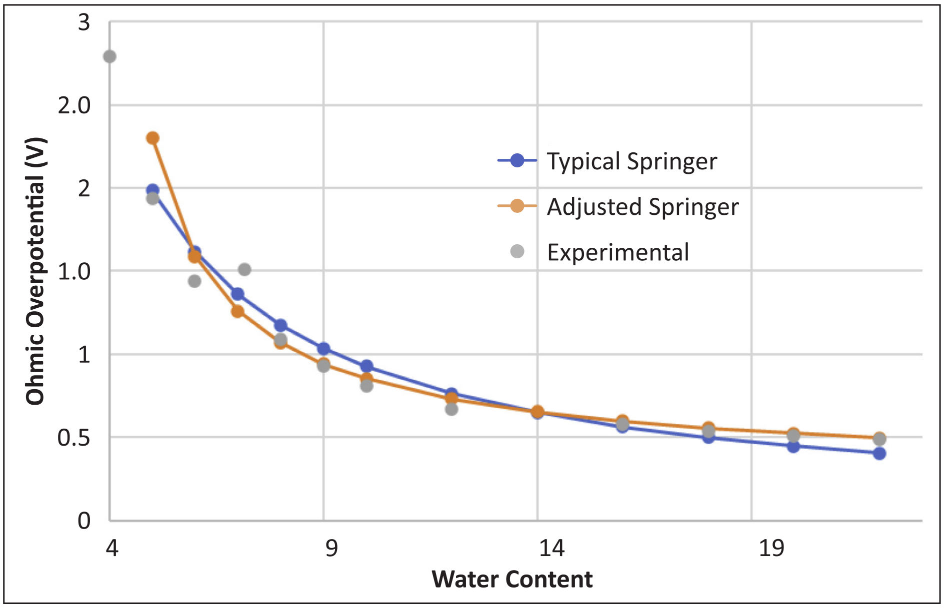


Figure 5. Ohmic overpotential comparison.



However, it is worth noting that, for practical purposes, the results provided by the typical model still exhibit high accuracy, with $R^2 = 0.98$.

Conclusion

An adjusted model for proton conductivity in Proton Exchange Membrane (PEM) electrolyzer systems was developed and evaluated due to increasing demand for alternative energy sources and the significance of green hydrogen (GH_2) in this context, Logarithmic regression was applied based on experimental data of conductivity and membrane water content, resulting in a model that better reflects the logarithmic behavior of conductivity compared to the typical model proposed by Springer and colleagues [3]. The results demonstrate that the adjusted model provides higher precision in estimating ohmic overpotential. This represents a significant advancement in understanding proton conductivity in PEM systems, enabling more efficient sizing and optimization of GH_2 production systems. To drive the viability and widespread adoption of green hydrogen as a clean and renewable alternative for society's energy needs, further research on accurate models and a deeper understanding of ionomeric membrane properties is necessary. Thus, this study contributes to progress in this promising field, paving the way for a more sustainable and environmentally conscious future.

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