

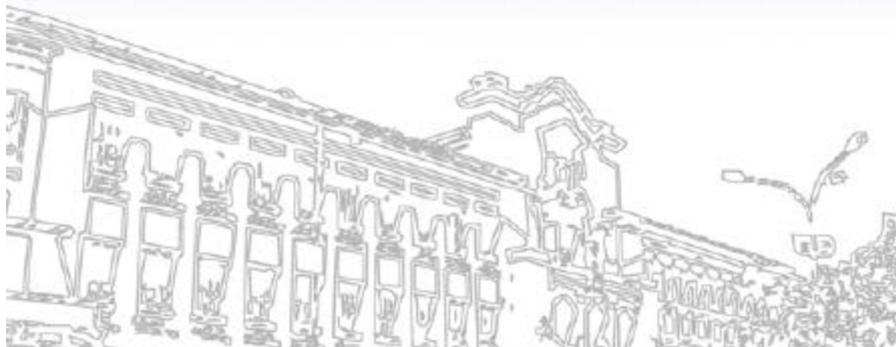
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New expressions to determine the water diffusion coefficient in the membrane of PEM fuel cells

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1 Abstract

Almost all the transport properties of polymeric membranes depend on their hydration, so different flows of matter (protons and water, primarily, but also alcohol in the DAFC) tend to be measured or calculated as functions of the degree of hydration or water content λ in the membrane.

$$\lambda = n_{\text{H}_2\text{O}} / n_{\text{HSO}_3^-} \quad (1)$$

A balance of water flow through the membrane yields an equation which links λ with the ratio β of the flow of water in the membrane to that of hydrogen at the anode [1]:

$$\frac{\beta j}{2F} = n_{\text{drag}}^{\text{SAT}} \frac{\lambda j}{22F} - \frac{\rho_{\text{dry}}}{M_m} D_\lambda \frac{d\lambda}{dz} \quad (2)$$

This equation can be integrated if the value of the diffusion coefficient of water in the membrane D_λ is known. According to [2] and [3], D_λ is the diffusion coefficient of water using a coordinate system fixed to the surface of the dry membrane whose relationship with the intradiffusion coefficient of water in the Nafion membrane D' is [2]

$$D_\lambda = \frac{D'}{(1+s\lambda)^2} \frac{d \ln a_w}{d\lambda} \quad (1)$$

where s is the expansion factor of the membrane due to the absorption of water and a_w the water activity in the environment that is in thermodynamic equilibrium with the membrane. The data in [2,3] show that the intradiffusion coefficient versus the water content of the membrane can be fitted with good precision to a cooperative model, in which the movement of a molecule affects their neighbours (Hill function):

$$D' = C \lambda^m / (k^m - \lambda^m) \quad (4)$$

To solve equation (3) the form of λ as a function of a_w is needed. A polynomial approximation [2] that leads to a D_λ coefficient that is only valid for λ values above 4 is widely used. In addition, the lack of a functional form for situations where the amount of water in the outer membrane environment exceeds the saturation pressure, i.e.,

when liquid water appears, leads to use a linear variation of λ with a_w , at a_w values greater than unity. This implies a discontinuity in the derivative of λ that prevents the correct calculation of D_λ at supersaturation conditions. To avoid this situation, and to improve the fit of the experimental values measured, a new $\lambda = \lambda(a_w)$ function is proposed in this work. The water content in the membrane is modeled as if the wetting of the membrane process was an adsorption process of type IV according to the Brunauer classification [4], using the Langmuir equation to describe the chemisorption process and a Hill function to describe the physisorption cooperative process which produces liquid multilayers until pore filling:

$$\frac{\lambda}{\lambda_{\text{max}}} = A \left(\frac{K a_w}{1 + K a_w} + \frac{B a_w^n}{a_{w,i}^n - a_w^n} \right) \quad (5)$$

As it is shown in fig 1, fitting equation (5) to data in [2], not only the water content in the membrane is predicted for the isopiestic equilibrium data ($a_w \leq 1$), but also the ponding limit value given in [2]. Therefore, the continuity of the fitting function proposed allows to obtain the coefficient of diffusion from the equation (3).

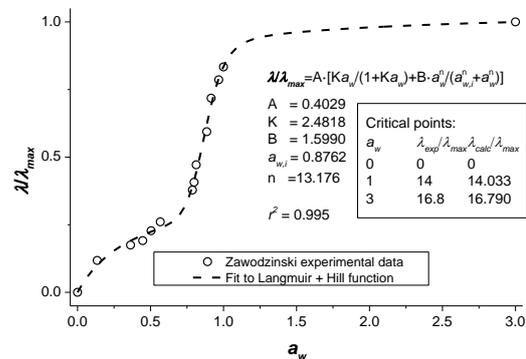


Fig. 1. New expression for the water content in the membrane according to the activity.

2 Acknowledgements

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