Chemomechanics of acidic ionomers: Hydration isotherms and physical model

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HIGHLIGHTS

- Hydration isotherms of acidic ionomers described by physical model without any fitting parameter.
- Only two constants related to ionomer properties: deformation and free volume parameters.
- Significance of experimental strategies for improvement of hydration and durability discussed.
- Cross-linking of ionomers reduces swelling at high humidity, but also dehydration at low humidity.

GRAPHICAL ABSTRACT
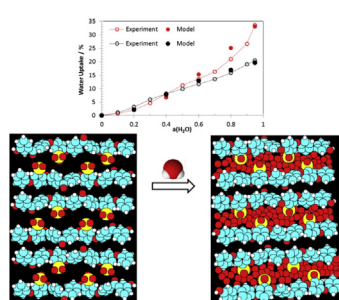
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ABSTRACT

The hydration isotherms of various ionomers (Nafion, Sulfonated Poly-Ether-Ether-Ketone, Sulfonated Poly-Phenyl-Sulfone) were measured and described by a thermodynamic model, assuming ideality and a linear relation between the thermodynamic osmotic pressure and the volume of the internal electrolytic solution. The only two parameters used are related to measurable physical properties: the deformation parameter, inversely proportional to the elastic modulus of the ionomer, and the free volume parameter. The experimental trends are well reproduced by the model, showing that it captures the main physical features and is suitable for semi-quantitative analysis of ionomer hydration. It indicates that the ionomers behave in good approximation like elastic solids in the studied range of water activities ($0 < a(H_2O) < 0.95$). The implications for practical improvement of ionomer properties by thermal cross-linking and annealing treatments are discussed. Cross-linked ionomers do not only better resist swelling at high humidity, but also dehydration at low humidity, which should increase their durability.

1. Introduction

Ion conducting polymers (also called ionomers [1–7]) are a fascinating field of research with many high added value applications, including energy and environment. For example, ionomers can be applied for waste water treatment [8], in proton and anion exchange membrane fuel cells (PEMFC [9–14] and AEMFC

[15,16]), and as separation membranes in redox flow batteries [17,18].

Hydrated ionomers present a subtle nanocomposite structure: ionic conduction takes place in hydrated nanometric channels, percolating through the ionomer matrix, which is made of the highly stable macromolecular backbones and is responsible for the thermal, chemical and mechanical properties of the ionomer [4,19–22]. This particular nanostructure allows decoupling ionic motion from the other properties.

Although water is necessary to allow ionic conduction, it weakens on the same time the mechanical stability of the matrix,

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by reducing the interactions between macromolecular chains, and acts as plasticizer. In fact, dehydration at low humidity or temperatures above 80 °C leads to loss of proton conductivity [21,23], but, on the other hand, the effect commonly known as "swelling" occurs at high humidity, when large quantities of water enter the polymer membrane due to the osmotic pressure [24–27]. This large water uptake is accompanied by an important deterioration of the mechanical properties.

Swelling of ionomers reduces the durability of electrochemical devices, because the contact between the ionomer membrane and the electrodes, where the electrochemical reaction takes place, can get lost in the membrane-electrode assembly. In fuel cells, the large volume expansion or contraction observed on changes of water activity in the surrounding atmosphere leads ultimately to a device failure. Although ionomer swelling and its relation to the osmotic pressure of water are known for quite long time [28–31], they are not yet fully understood. Swelling of ionomer membranes forms part of the new research field of "chemomechanics", which studies the interdependence of compositional changes and mechanical properties in solid materials. Understanding these phenomena requires a general conceptual framework to organize, generalize and extrapolate the experimental observations.

The equilibrium state of the hydrated ionomer is given by the minimum of the Gibbs free energy. The variation of Gibbs free energy during water uptake includes several contributions:

$$\Delta G = \Delta G_{\text{osmotic}} + \Delta G_{\text{elastic}} + \Delta G_{\text{interface}} + \Delta G_{\text{electro}} \quad (1)$$

The Gibbs free energy variation due to the osmotic pressure $\Delta G_{\text{osmotic}}$ is the driving force for the water uptake, which is opposed by the elastic deformation energy $\Delta G_{\text{elastic}}$ of the ionomer matrix. The interfacial energy term $\Delta G_{\text{interface}}$ includes the contribution of the hydrated domain-matrix interfaces with the Laplace pressure due to the interface curvature of hydrated domains in the ionomer that can be also included in the elastic term [32,33]. Finally, the electrostatic energy $\Delta G_{\text{electro}}$ takes into account the modification of Coulombic forces between ions during changes of the hydrated channel width [29]. The two last contributions are difficult to assess. The interface term depends on the morphology of the hydrated domains, which are generally considered spherical or cylindrical, but the exact morphology is still a matter of discussion [34,35]. The electrostatic term cannot be expressed by analytical equations and is only accessible numerically [29]. It is therefore difficult to use the complete Gibbs free energy variation for prediction of hydration properties of ionomers. A model for the description of the thermodynamics of water sorption in Nafion was presented some time ago by Datta et al. [36]; although it is rather complete, its practical application seems to be difficult due to the availability of ionomer parameters.

In this work, we will introduce a simplified physical model without any fitting parameter taking into account only the osmotic pressure and the elastic deformation terms. The two parameters used in the model are related to measurable properties of the studied ionomers: the elastic modulus and the free volume. If successful, this approach has the major advantage that predictions for the hydration properties of ionomers can be made.

The general features of the model will first be outlined and the used parameters will be introduced. The model will then be tested on literature data for Nafion and Sulfonated Poly-Ether-Ether-Ketone (SPEEK) and new hydration isotherms of SPEEK and Sulfonated Poly-Phenyl-Sulfone (SPPSU) with various degrees of crosslinking. Finally, the assumptions of the model will be critically assessed and predictions of the model for ionomer improvement will be discussed.

2. Physical model

In the following, the ionomer is considered as an elastic solid, mainly characterized from a mechanical standpoint by its elastic modulus. Furthermore, we make the following assumptions: 1) The system is ideal from a thermodynamic point of view. All activity coefficients are unity and the partial volumes are equal to the molar volumes (a very small negative volume of mixing, $\Delta V_{\text{mix}}/\lambda < -10^{-4}$ L mol^{-1}, was recently reported for SPEEK [22]). 2) The volume of the anions fixed on the macromolecular backbone is considered a part of the ionomer matrix. 3) Protons are completely dissociated (this assumption is reasonable for strong acidic ionomers, such as Nafion or Sulfonated Aromatic Polymers).

2.1. Thermodynamic osmotic pressure

During a hydration experiment, the electrolytic solution inside the elastic ionomer matrix is in contact with a constant water vapor activity. Under these conditions, water passes into the electrolytic solution (at higher water activity) or leaves it (at lower water activity), until the chemical potential of water inside and outside the ionomer is identical. The pressure difference at equilibrium is called the thermodynamic osmotic pressure π, which can be calculated from the expression [37]:

$$\pi = \frac{RT}{V_0} \ln\left(\frac{a(\text{H}_2\text{O})}{x_{0,\text{el}}}\right) \quad (2)$$

In this equation, R is the gas constant, T the absolute temperature and $a(\text{H}_2\text{O})$ is the water activity in the vapor phase. $x_{0,\text{el}}$ is the molar fraction of water in the electrolytic solution inside the hydrated ionomer, $(1 - x_{0,\text{el}})$ being the molar fraction of protons. V_0 is the partial molar volume of water, which can be assumed to be independent of pressure in condensed phases; it is considered equal to the molar volume (0.018 L mol^{-1}).

2.2. Determination of the equilibrium hydration number and water uptake

The volume of the inner electrolytic solution V_{el} is equal to the total measured volume V_{wet} of the wet ionomer minus the volume of the incompressible hydrocarbon matrix, including the anionic groups fixed to the channel walls, V_{matrix}:

$$V_{\text{wet}} = V_{\text{matrix}} + V_{\text{el}} \quad (3)$$

The volume of the inner electrolytic solution V_{el} can be also written:

$$V_{\text{el}} = \sum_i n_i V_i = n_0 V_0 + n_1 V_1 \quad (4)$$

In this equation, n_0 and n_1 are the mole numbers of water molecules and of compensating protons and V_0 and V_1 are their molar volumes ($V_1 \approx 0$). n_1 can be calculated from the ionic exchange capacity (IEC in mol kg^{-1}) and the dry density of the ionomer. One can at this point also include other components in the model, for example solvent remaining from the casting process, by adding other terms in the sum of Equation (4).

A linear relationship is now postulated between V_{el} and the thermodynamic osmotic pressure π:

$$V_{\text{el}} = a\pi + b \quad (5)$$

This expression describes in a general way the elastic properties of a polymer at moderate pressures [28]. The values of a and b depend upon the specific ionomer considered. A change of the mole