Phenomenological methanol sorption model for Nafion® 117

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Abstract

A thermodynamic model is developed to describe methanol sorption phenomena in proton exchange membranes (PEMs). The methanol sorption in the model is determined by the swelling pressure caused within the membrane as a result of stretching of the polymer chains upon methanol sorption. The stretching of the polymer chains is expressed in terms of spring constant \( k \). The swelling pressure exerted within the pores of the membrane is assumed to be linear in solvent uptake. Furthermore, the methanol molecules in the membrane are divided into those that are chemically, or strongly, bound to the acid sites, \( \lambda_i^C \), and others that are free to physically equilibrate between the fluid and the membrane phases, \( \lambda_i^F \). The sorption model can predict the complete isotherm due to methanol vapor sorption by the membrane.

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1. Introduction

Fuel cells are attractive power sources due to their high energy efficiency and environmental compatibility, particularly as compared to combustion engines. Hydrated perfluorosulphonic acid membranes, such as Nafion®, are typically used as the electrolyte in fuel cells because of their excellent chemical, mechanical, and thermal stability, in addition to their conductivities of ca. 0.08 S/cm [1–3]. Recently improved performance has been reported in direct methanol fuel cells (DMFCs) [4,5].

However, two main obstacles that currently limit DMFC performance are the low activity of methanol electro-oxidation catalysts and the crossover of methanol through the polymer electrolyte membrane. It has been observed that methanol crossover to the cathode not only lowers the fuel utilization but also adversely affects the oxygen cathode [6], resulting into lower cell performance. It is therefore beneficial to study the behavior of methanol sorption in Nafion® membranes. At present, little is known about the behavior of these perfluorosulphonate membranes towards methanol. Gates and Newman [7] have shown the methanol uptake in vapor and liquid phase at 60 °C. At this temperature, they reported that vapor- and liquid-phase uptake shows discontinuity just like water uptake. Ren et al. [5] have investigated the methanol uptake of Nafion® 117 membranes equilibrated with methanol solutions up to 8 M at 30 °C to determine the methanol water ratio in the membranes. Until now, none is explained about the methanol sorption mechanism. The present work is intended to report the methanol sorption at 25 °C and a physico-chemical model is proposed to describe methanol sorption in proton exchange membranes (PEMs), which can predict the complete isotherm. Tapered Element Oscillating Microbalance (TEOM) is used to obtain methanol sorption from vapor phase.

2. Theory

The total uptake of solvent by the membrane (number of solvent molecules sorbed/ion exchange site) can be written as

\[ \lambda_i = \lambda_i^C + \lambda_i^F \]  

(1)

When the membrane equilibrates with a vapor phase, assuming that the pressure changes within the condensed...
phase in the pore is caused both due to the stretching of the polymer chains upon solvent uptake, $\Pi_M$, as well as that exerted by the curved vapor–liquid interface within the pores, $\Pi_\sigma$, we get,

$$\ln \frac{a_{\text{i},v}^F}{a_{\text{i},L}} = -\left( \frac{\bar{V}_e}{RT} \right) (\Pi_M + \Pi_\sigma) \quad (2)$$

where the vapor-phase activity $a_{\text{i},v}^F = P_i^F / P_i^{\text{sat}}$ and $\Pi_\sigma$ are provided by the equation of Adamson and Gast \[8\]

$$\Pi_\sigma = \frac{2\sigma \cos \theta}{r_p} \quad (3)$$

where $\theta$ is the liquid-membrane contact angle and $r_p$ is the mean pore radius of liquid-filled pores. For the case of saturated vapor, $P_i^F / P_i^{\text{sat}}$ and Eq. (2) gives

$$\ln a_{\text{i},v}^F = -\left( \frac{\bar{V}_e}{RT} \right) (\Pi_M + \Pi_\sigma) \quad (4)$$

In order to use these results for predictive purposes, it is assumed that the activity coefficients of the physically equilibrated species within the membrane are the same from those as in the vapor phase \[9,10\]. Then, for the vapor-phase sorption in Eq. (4), $a_{\text{i},v}^F / a_{\text{i},L} = \gamma_{\text{i},v}^F \gamma_{\text{i},L} \gamma_{\text{M},v} \gamma_{\text{M},L} \equiv x_{\text{i},v}^F / x_{\text{i},L}$,

$$\ln \frac{x_{\text{i},v}^F}{x_{\text{i},L}} = -\left( \frac{\bar{V}_e}{RT} \right) (\Pi_M + \Pi_\sigma) \quad (5)$$

The mole fraction of the ‘free’ solvent molecules in the membrane is \[11,12\]

$$x_{\text{i},M}^F = \frac{x_{\text{i},v}^F}{\lambda_i} + 1 \quad (6)$$

It is next assumed that swelling pressure exerted within the pores is linear in solvent uptake,

$$\Pi_M = \kappa \epsilon \quad (7)$$

where spring constant $\kappa$ being a function of elasticity of polymer network, degree of cross-linking, energy change of mixing of polymer network and solvent, temperature, and pretreatment procedure and history. Similar linear relations between internal pressure and volume sorbed were found. The pore volume fraction, $\epsilon$, can be obtained as \[11\]

$$\epsilon \approx \frac{\lambda_i}{\bar{V}_M / \bar{V}_i + \lambda_i} \quad (8)$$

where $\bar{V}_M$ and $\bar{V}_i$ are partial molar volume of membrane and solvent, respectively. Finally, it is assumed that the pore radius may be estimated using the parallel pore model,

$$r_p \approx \frac{2\epsilon}{S} \quad (9)$$

The pore-specific surface $S$ here is assumed not to vary substantially with increasing uptake. These assumptions when utilized in the above expressions provide a predictive model for the phase equilibrium between membrane and vapor phase, in terms of common physical properties along with the mechanical spring constant $\kappa$.

The strongly sorbed molecules of methanol to the SO$_3$ group in Nafion® membrane, was determined using molecular simulation study of Nafion® membrane solvation in methanol \[12\]. On average, each SO$_3$ group formed four hydrogen bonds to methanol. In the model, thus the chemically sorbed molecule of methanol is taken as 4. Combining Eqs. (5)–(9) with $\lambda_i^C = 4$ gives an implicit expression of solvent loading for the case of vapor-phase sorption as:

$$\{ \lambda_{\text{i},v} - \lambda_i^C \}^{-1} = a_{\text{i},v}^F \exp \left\{ \frac{\bar{V}_e}{RT} \left[ \frac{\kappa \lambda_{\text{i},v}}{\varepsilon V_{\text{M}} / \bar{V}_i} + \frac{V_{\text{M}}}{\bar{V}_i} \right] \right\} - 1 \quad (10)$$

For given $\bar{V}_e$, $\kappa$, $S$, $\sigma$, $\theta$, and $V_M$, the sorption isotherm, namely $\lambda$ versus $a_i$ can be determined for vapor-phase sorption.

### 3. Experimental

A technique known as tapered element oscillating microbalance (TEOM Series 1500 PMA Reaction Kinetics Analyzer, Rupprecht and Patashnick Albany, NY) has been developed to study the water/methanol sorption by Nafion® membranes.

#### 3.1. Pretreatment of Nafion® sample

Commercial-grade Nafion® 117 was purchased for Aldrich. It was boiled with 3% H$_2$O$_2$ for half an hour. Then boiled in 0.5 M sulphuric acid solution for half an hour. After boiling, the membrane was washed thoroughly with DI water to remove excess of acid. It was then dried at room temperature. The dried membrane was then heated in vacuum at 110 °C for 1 h. The experimental methanol sorption is reported in terms of

| Table 1 Parameters employed in the model for the sorption of methanol in Nafion® membrane |
| --- | --- | --- |
| Symbol | Value | Unit |
| $\bar{V}_M$ | 537 | cm$^3$/mol |
| $\bar{V}_i$ | 42 | cm$^3$/mol |
| $S$ | 210 | m$^2$/cm$^3$ |
| $\lambda_i^C$ | 4 | dimensionless |
| $\sigma$ | 26.2 | mN/m |
| $\theta$ | 98 | dimensionless |
| $\kappa$ | 85 | atm |
λ. It is defined as ratio of moles of methanol to the moles of SO₃H acid group.

4. Discussion

The methanol sorption was measured at 25 °C. Because we were unable to find methanol sorption data for Nafion® in the literature, we reproduced our data to ensure its reliability. The parameters used in the sorption model are given in Table 1. The value of spring constant was determined using liquid sorption which is a special case of vapor sorption with no surface energy terms. Hence, using Eq. (10), the liquid-phase sorption is given as:

\[
\lambda_{i,L} = a_{i,L}^{-1}\exp\left(\frac{V_i}{RT}\left(\frac{\kappa\lambda_{i,L}}{\lambda_{i,L} + \frac{V_M}{V_i}}\right)\right) - 1
\]

(11)

The liquid sorption \(\lambda_{i,L}\) was found to be around 18. This was determined by simply taking the weight difference between the dry sample and sample soaked in methanol for 24 h. Using this value and Eq. (11), the spring constant was calculated as 85 atm. Then, Eq. (10) was solved for activity of methanol ranging from 0.1 to 1. It has been reported that the contact angle of water in Nafion® membrane varied systematically with hydration level. Thus, for a completely dry membrane, \(\theta=116^\circ\), which is the same as PTFE, indicating substantial hydrophobicity [13]. The contact angle decreases gradually at first with \(\theta\), and then somewhat more sharply, reaching \(\theta=98^\circ\) for vapor-saturated membrane. For the contact angle of methanol in Nafion®, a similar value is assumed in this model.

Fig. 1 shows the predicted isotherm of methanol in Nafion®, the solid line, as well as two experimental data sets obtained utilizing TEOM. The simulations were done using Matlab 6.1. Similarly, vapor-phase sorption of water was investigated. As reported in literature, the value \(\lambda\) (i.e., moles of solvent per mole of acid group) for water in saturated vapor conditions is 14 [13]. However, for methanol, a value of 12 is observed experimentally. The model thus predicts the sorption of methanol in Nafion® quite precisely throughout the entire range of vapor phase activity. It predicts the high initial slope, gradual increase of the slope after the sorption of the first few molecules, and high slope at higher activities of about \(a_{i,V}=0.7~0.8\) as observed experimentally. Moreover, because the partial molar volume of methanol is higher than water, membrane swells much more in methanol and greatly affects its spring constant \(\kappa\).

5. Conclusions

A theoretical model is developed for the sorption of methanol in proton exchange membrane. This model predicts complete isotherm for methanol in Nafion® quite precisely and provides insight into the sorption phenomena in the ion exchange polymer. The sorption isotherm is a result of equilibrium conditions that are established between the elastic forces of the polymer matrix and swelling pressure in the membrane. The swelling pressure is derived from the solvent activity inside of the polymer membrane. The future modeling efforts will be focused on replacing the spring constant \(\kappa\) with Young’s Modulus based on polymer properties for any given solvent.

References