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# TEOM: A novel technique for investigating sorption in proton-exchange membranes

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## Abstract

A new technique, namely, the tapered element oscillating microbalance (TEOM) is successfully utilized to investigate the equilibrium water and methanol vapor phase sorption and desorption in Nafion® membrane at different relative humidity (RH) and temperatures. The water sorption was found to increase with temperature from 30 °C to 90 °C. This is explained by the increase in the flexibility of polymer chains via a decrease in Young's modulus of membrane with temperature. The effect of various pretreatments, e.g., heating, vacuum treatment, and hot pressing on the water sorption properties is also investigated. It is observed that the water sorption for Nafion® membrane depends both on the pretreatment of the membrane and on the temperature of sorption. The desorption isotherm exhibits a hysteresis with respect to sorption for both water and methanol. This hysteresis behavior may be attributed to the relaxation or viscoelastic properties of Nafion® membrane. In summary, TEOM appears to be an attractive technique for characterizing sorption–desorption behavior of proton exchange membranes.

*Keywords:* Nafion®; Sorption; Desorption; Equilibrium; Isotherm; Water; Methanol

## 1. Introduction

Recently there has been much interest in polymer electrolyte membrane fuel cells (PEMFC). An important factor determining the performance of the PEM fuel cells is the hydration level of the proton-exchange membrane (PEM) [1–3]. A common PEM is Nafion®, a polymer consisting of a polytetrafluoroethylene (PTFE) backbone with side-chains culminating in $SO_3^-H^+$ groups. It exhibits excellent chemical, mechanical, and thermal stability along with low gas permeability and high proton conductivity when adequately hydrated. The amount of water sorbed in the membrane is critical as the proton conductivity directly depends upon the water content of the membrane [4–6]. The main factors that affect the extent of water sorption in a PEM are the nature of polymer backbone, temperature, ion-exchange capacity, pretreatment, as well as the physical state of external water, i.e., whether it is in liquid or vapor form. Water basically dissociates the acid groups and provides a medium for conduction of protons.

In the operation of a typical PEM fuel cell, the reactant feed gases are prehumidified to provide adequate hydration levels in the membrane. This is supplemented by the water produced at the cathode due to the electrochemical reaction, which also results in a gradient in the activity of water across the membrane causing water to diffuse back from cathode to anode [7]. Further, water is transported from anode to cathode along with the protons, i.e., via the electro-osmotic drag. Thus, water management is critical to successful working of a PEMFC, which necessitates an understanding of water sorption characteristics of PEMs.

Many investigators have studied the uptake of water in PEMs. Several investigations have been done on the hydration, swelling, and drying under different conditions for Nafion®, based on spectroscopic, gravimetric and other methods [7–11]. The adsorption from liquid phase is quicker as compared to that from vapor phase. Further, Nafion® adsorbs around 22 water molecules per acid site from liquid water, while it adsorbs around 14 water molecules from saturated

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vapor [7,8], i.e., the so-called Schroeder's Paradox recently explained by Choi and Datta [12].

An important variable is the pretreatment of a PEM that affects its water sorption. In an early study, the following nomenclature was used to describe pretreatment of Nafion®, namely, "E-form" for a membrane swollen and expanded in high-temperature water, and "S-form" for a membrane shrunk in vacuum at high temperatures [13]. The normal membranes were termed "N-form". It was found that the E-form membrane becomes rubbery when the temperature increases, with a tendency to adsorb more water. However, in S-form membranes, the ionic clusters shrink and the water uptake drops. Kawano et al. [14] studied the stress–strain characteristics of Nafion® membrane for various pretreatments (boiling, soaking in other solvents, heating, etc.). They observed that the slope of stress–strain, i.e., Young's modulus (*E*) of the membrane, decreased for a membrane boiled in water, making them more pliable for higher water uptake.

The sorption of methanol in Nafion® is also of interest in context of the direct methanol fuel cells (DMFC) [15–17]. The 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 kinetics at the cathode, resulting into lower cell performance [18,19].

Consequently, there is a strong motivation to systematically study the water/methanol sorption isotherms for Nafion® and other polymer electrolyte membranes. Experiments with the conventional gravimetric methods are slow, providing data of low accuracy. The sorption data are affected by the flow patterns, bypassing, and incomplete contact of the gas with the sample [20]. Further, the equipment has limited temperature and pressure range. There is also significant reduction in mass resolution at high temperatures. Here, the use of a novel and relatively fast technique, namely the tapered element oscillating microbalance (TEOM) is described to accurately measure equilibrium water/methanol sorption–desorption isotherms for PEMs. The effects of solvent activity or relative humidity (RH), temperature, and various pretreatment protocols on sorption behavior of Nafion® are investigated. Further, this technique can also be utilized to study the sorption behavior of inorganic powder additives in our efforts to develop high temperature proton-exchange membranes by improving water retention at elevated temperatures [21,22].

## 2. Description of the TEOM

The tapered element oscillating microbalance (TEOM) Series 1500 Pulse Mass Analyzer (PMA) purchased from Rupprecht & Patashnick Co., Inc., Albany, NY, was utilized to study the equilibrium solvent sorption–desorption behavior for Nafion® membranes. This offers a novel means of analyzing real-time mass change of sample in a fixed-bed while the gases pass through the sample. It includes a tapered element oscillating microbalance, which is based on inertial forces rather than gravity, to measure the mass change of sample [23]. The TEOM possess certain advantages over conventional gravimetric techniques in measuring sorption in polymer electrolyte membranes:

1. The steady flow of gas through the sample provides complete contact with the test material.
2. High mass resolution ($1 \times 10^{-6}$ g) and a low standard deviation.
3. The experiments can be performed over a wide range of temperatures (25–500 °C) and pressures (vacuum to 60 atm).
4. The microbalance employs a resonant cantilever to measure changes in inertia rather than weight, hence the data obtained is not influenced by flow patterns of gas streams, buoyancy and other aerodynamic factors.

However, there are some limitations in using TEOM. It cannot be used for volatile or fragile samples, which may alter the natural oscillating frequency of the test bed. Also, liquid phase studies cannot be performed using this technique.

The heart of the TEOM is an oscillating tapered test bed in which the sample is packed. This tube containing the sample vibrates constantly at its natural frequency of oscillation. There is a feedback system, which maintains the oscillation of the tapered bed [23]. The frequency is obtained optically with a transmitter and receiver located on the opposite sides of the oscillating test bed. A simplified diagram of the 100 mg (0.1 $\text{cm}^3$) test bed and optics is shown in Fig. 1a [24]. The sample was carefully packed between quartz wool in the test TEOM bed.

The motion of TEOM test bed may be approximated as free undamped vibrations of a cantilever in one of the principle planes of the beam [25,26]. The effects of rotatory inertia and of transverse shear deformation are neglected. The equation of motion for beam of uniform cross section is

$$EI\frac{\partial^2 y}{\partial x^2} + \rho A\frac{\partial^2 y}{\partial t^2} = 0 \qquad (1)$$

where *E* is the Young's modulus, *I* the second moment of area of the cross section, $\rho$ the density, *A* the beam cross sectional area, *y* the displacement from the centerline of the beam at any section *x*, and *t* the time.

For free undamped vibration, the solution is of the form

$$y(x,t) = Y(x)\sin(\omega t + \alpha) \qquad (2)$$

where $\omega$ is the frequency of vibration, and or $\alpha$ is the phase angle.

Substituting this in Eq. (1),

$$\frac{\mathrm{d}^4 Y}{\mathrm{d}x^4} - \kappa Y = 0 \qquad (3)$$