New simple electrochemical method for measuring the water vapor transmission rate and diffusion coefficient of polymer membranes

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ABSTRACT

In this paper, we present a new electrochemical method for measuring the water vapor transmission rate, the permeability coefficient and the diffusion coefficient of polymer membranes. This method is based on the electrical conductivity of an electrolyte layer, which depends on the water content inside the layer. We describe the calibration process and show exemplary measurements on polymer membranes in good agreement with literature values.

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1. Introduction

Water vapor transmission through polymer membranes is an important area of research in the packaging industry, especially in association with products that are susceptible to moisture, where good barrier performance concerning water vapor is required [1–3]. On the other hand, good water vapor transmission is favorable for functional breathable clothing [4] and biomedical applications [5]. While many methods to measure the water vapor transmission rate have previously been described in the literature [6], the current standard method is ASTM standard E 96/E96M-10 [7], which involves gravimetrically measuring the loss of water through a test polymer membrane under controlled conditions [7].

In literature the water vapor transmission rate is given for a large number of polymers [8–10]. It is shown that for highly permeable polymer films the ASTM standard becomes imprecise [11].

In this paper, we describe the use of indirect electrochemical measurements to obtain the water vapor transmission rate (WVTR) through polymer membranes, the water permeability of the membranes, and the diffusion coefficient of water through the polymer membranes. The method involves coating the test membrane with a hygroscopic electrolyte, and measuring how the electrical conductivity of the electrolyte layer changes as water diffuses through it.

Such a hygroscopic electrolyte layer is already used in electrochemical devices called nanofilm processors, where a nanoscale aluminum layer is oxidized laterally by the anodic dissolution of a nanoscale aluminum film [12–16]. This process requires water, which the functional electrolyte layer can harvest from the surrounding atmosphere [17,18]. A similar procedure is applied for humidity sensing devices, where the conductivity of an electrolyte layer is related to its water content, which in turn depends on the water activity of the ambient water vapor phase [19–21].

2. Theory

The permeation of gas molecules through a membrane, driven by a pressure difference between the opposite sides of a membrane, takes place in three steps. The first step is adsorption of gas molecules at the surface of the membrane that is exposed to higher pressure. The second step is diffusion of the adsorbed gas molecules through the membrane against the pressure gradient, and the third step is desorption of gas molecules at the surface of the membrane that is exposed to lower pressure.

For the ideal case, where the diffusion coefficient and the solubility coefficient are constant, Fick's law describes the diffusion through the membrane and predicts a linear dependence of equilibrium concentration of gas molecules on the membrane surface in the first and third step to the gas pressure. If the pressure at the first and third steps of the gas permeation process is known,
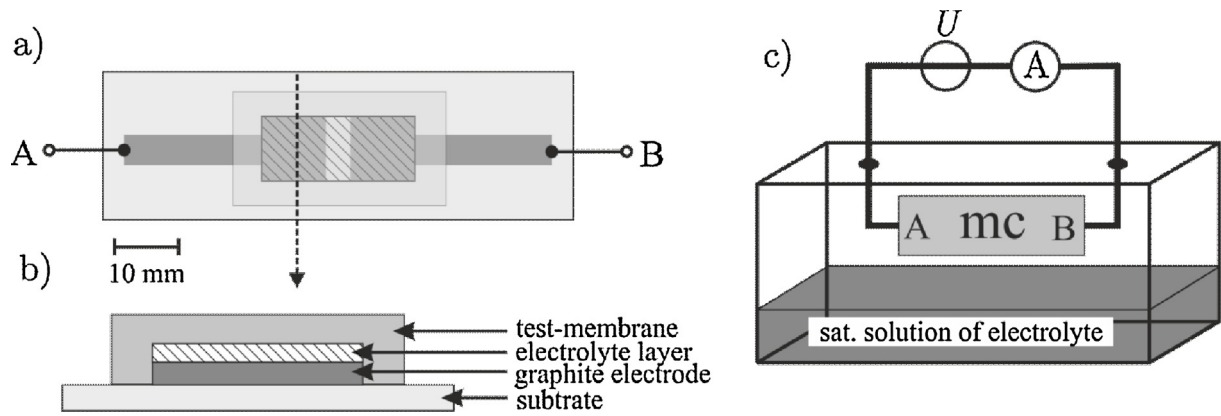
Fig. 1. Schematic layout of the measuring cell. (a) Top view. (b) Cross-sectional view. (c) Complete setup for the measurement, showing the air-tight box, saturated aqueous solution of electrolyte, measuring cell (mc) and electric circuit.

the gas permeation through a non-porous polymer membrane is describable by the solution-diffusion model [22] as in Eq. (1),

$$P = DS, \tag{1}$$

where P is the permeability, D the diffusion coefficient and S the solubility coefficient.

The *WVTR* is typically obtained according to the ASTM standard E 96/E96M-10, in which gravimetry is used to measure the loss or gain of water through a membrane where the partial pressure of water differs on the opposite sides of the membrane. The gain or loss of water is plotted versus time.

The water vapor transmission rate *WVTR* is determined by Eq. (2) [23],

$$WVTR = \frac{a}{A}, \tag{2}$$

where A is the exchange area of the membrane and a is obtained by plotting the water gain or loss over time, fitting this plot to a line, and measuring the slope of the linear fit.

The permeability for water vapor P_w is expressed by Eq. (3) [24],

$$P_w = \frac{WVTR \cdot d}{p_2 - p_1} \tag{3}$$

where d is the thickness of the membrane, and the partial pressure of water on the opposite sides of the membrane is represented by p_1 and p_2.

Upon making the substitution $p_i = a_{W,i} \cdot p_{W,sat}$, Eq. (3) becomes Eq. (4),

$$P_w = \frac{WVTR \cdot d}{p_{w,sat}(a_{w,2} - a_{w,1})}, \tag{4}$$

where the saturation water vapor partial pressure $p_{w,sat}$ is temperature-dependent and is calculated by the Magnus equation [25], where ϑ is the temperature in degrees Celsius (Eq. (5))

$$p_{w,sat}(\vartheta) = 611\,\text{Pa} \cdot \exp\left[\frac{17.1 \cdot \vartheta}{234.2\,°\text{C} + \vartheta}\right]. \tag{5}$$

At room temperature, the saturation partial pressure of water is $p_{w,sat}\,(20\,°\text{C}) = 2346\,\text{Pa}$, so that Eq. (4) can be rewritten as Eq. (6)

$$P_w = \frac{WVTR \cdot d}{2346\,\text{Pa}(a_{w,2} - a_{w,1})}. \tag{6}$$

Referring once again to the plot of water gain or loss versus time, the point at which the time axis intersects with the linear fit of this plot is called the time lag, which is used to calculate the diffusion coefficient of water across the test membrane (D_w) by Eq. (7) [26],

$$D_w = \frac{d^2}{6L} \tag{7}$$

where d is the thickness of the test membrane and L the time lag. This process is usually called the time-lag method.

3. Experimental

3.1. Devices

A function generator is used as the AC power supply (Velleman, $2 \times 12\,\text{MHz}$ PC Scope + Function Generator PCSGU250). AC current was measured with a multimeter (Agilent 34410A).

3.2. Measuring cell

Graphite electrodes are applied to a wet thickness of $150\,\mu\text{m}$ on a glass substrate, by stencil printing of a graphite lacquer from a mixture of acrylic resin (Wilckens) and graphite powder GSI 70 (weight ratio 3:7). The graphite electrodes are dried for 1 h at room temperature. The electrolyte layer is prepared by mixing poly-acrylic acid and 1.25 M sodium bromide solution (weight ratio 1:19) and stirring for 60 min at room temperature, and then applied by stencil printing at a wet thickness of $150\,\mu\text{m}$ and dried for one hour with a molecular sieve. To the test membrane, a heat seal-ing adhesive (Lascaux® Heißsiegelkleber 375 with toluene, weight ration 1:1) is applied by Mayer bar, to a wet thickness of $50\,\mu\text{m}$, and dried for one hour at room temperature. Then the test mem-brane is affixed to the measuring cell by heat sealing. The complete measuring cell is depicted in Fig. 1. If the test membrane is already adhesive, the last preparation step is ignored.

3.3. Calibration of the measuring cell

For calibrating the measuring cell without the test membrane, we measure the equilibrium current around the measuring cell, at different water activities of the ambient vapor phase, using the setup in Fig. 1(c) with an AC power source ($U = 1.0\,\text{V}/f = 100\,\text{Hz}$). The measurement is carried out in an air-tight box. The water activity of the vapor phase inside the box is adjusted by placing in the box a saturated aqueous solution of an electrolyte (sodium bromide: $a_w = 0.58$ [27], cupric(II) chloride: $a_w = 0.68$ [28], sodium chloride: $a_w = 0.75$ [27], potassium chloride: $a_w = 0.84$ [27]).

The water uptake of the electrolyte layer is measured in an air-tight box of known volume, where the water activity of the vapor phase inside the box is also known. The electrolyte layer, having a wet thickness of $150\,\mu\text{m}$, is applied by Mayer bar onto a polypropylene substrate and dried with a molecular sieve. The electrolyte layer on the polypropylene substrate is cut to a defined area and placed in the box. During the measurement, the change