On the Use of Pressure-Loaded Blister Tests to Characterize the Strength and Durability of Proton Exchange Membranes

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The use of pressurized blister specimens to characterize the biaxial strength and durability of proton exchange membranes (PEMs) is proposed, simulating the biaxial stress states that are induced within constrained membranes of operating PEM fuel cells. PEM fuel cell stacks consist of layered structures containing the catalyzed PEMs that are surrounded by gas diffusion media and clamped between bipolar plates. The surfaces of the bipolar plates are typically grooved with flow channels to facilitate distribution of the reactant gases and water by-product. The channels are often on the order of a few millimeters across, leaving the sandwiched layers tightly constrained by the remaining lands of the bipolar plates, preventing in-plane strains. The hydrophilic PEMs expand and contract significantly as the internal humidity, and to a lesser extent, temperature varies during fuel cell operation. These dimensional changes induce a significant biaxial stress state within the confined membranes that are believed to contribute to pinhole formation and membrane failure. Pressurized blister tests offer a number of advantages for evaluating the biaxial strength to bursting or to detectable leaking. Results are presented for samples of three commercial membranes that were tested at 80°C and subjected to a pressure that was ramped to burst. The bursting pressures exhibit significant time dependence that is consistent with failure of viscoelastic materials. Rupture stresses, estimated with the classic Hencky's solution for pressurized membranes in conjunction with a quasielastic estimation, are shown to be quite consistent for a range of blister diameters tested. The technique shows considerable promise not only for measuring biaxial burst strength but also for measuring constitutive properties, creep to rupture, and cyclic fatigue damage. Because the tests are easily amenable to leak detection, pressurized blister tests offer the potential for characterizing localized damage events that would not be detectable in more commonly used uniaxial strength tests. As such, this specimen configuration is expected to become a useful tool in characterizing mechanical integrity of proton exchange membranes. [DOI: 10.1115/1.3007431]

Keywords: proton exchange membrane, biaxial testing, biaxial strength, pressurized blister test, ramp to burst, time dependence, viscoelastic behavior, Nafion® NRE-211, Gore™ Select® series 57, Ion Power™ Nafion® N111-IP

Introduction

The long-term durability of proton exchange membrane (PEM) fuel cells depends on a number of factors including the retention of catalyst activity, gas diffusion media structure, and membrane integrity. Considering the dual function of the membranes, their thickness is a compromise: sufficiently thin to readily permit ion transport and yet thick enough to minimize gas crossover, both of which can significantly affect operational efficiency. Practical fuel cell constructions at present often utilize PEMs that are on the order of 25 μm or less in thickness. A number of types of polymers are commercially available now, but sulfonated perfluorinated polymers, such as Nafion®[3], remain popular. With hydrogen and oxygen permeabilities on the order of 10^{-12}cm^3(STP) cm/(cm^2 s Pa) (wet) to 10^{-15} cm^3(STP) cm/(cm^2 s Pa) (dry) [1], these membranes are quite resistant to gas crossover. Over their service life, however, they can degrade through several mechanisms, reducing their resistance to reactant gas permeation. Fluoride release associated with the molecular breakdown of the ionomeric membranes results in membrane thinning [1]. Chemical and mechanical stresses can further degrade the material, resulting in flaws that are generically referred to as "pinholes" [2]. Changing mechanical stresses are induced as a membrane, which is constrained in a typical fuel cell by the bipolar plates, and the diffusion media are subjected to varying temperature and humidity, the latter of which causes significant dimensional changes in unconstrained membranes. Local stress risers may exist within the membrane at the tips of the ubiquitous flaws present in the more brittle catalyst layers and at the termination of catalyst layers, subgaskets, or other layers [3,4], further enhancing the likelihood for damage. Over time, contributing factors such as these can lead to pinhole formation that allows crossover of the reactant gases, reducing overall operating efficiency, and possibly triggering further damage as these gases react in the presence of the catalyst. Mechanical integrity of the membranes is thus seen as an essential feature for the long-term operation of PEM fuel cells.

Although basic mechanical properties of proton exchange

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membranes have been obtained on free standing membranes [5–7], durability studies have generally focused on performance retention in operating fuel cells under accelerated conditions [2] and ex situ changes in conductivity, gas permeability, strength, and toughness under simulated environmental cycles [8]. As various forms of mitigation agents for chemical degradation are designed into membranes, interest has increased in quantifying the strength and durability of membranes exposed to hygrothermomechanical stresses. Strength, damage, and durability properties have long been necessary inputs for durability models to predict strength retention, life, and reliability for other engineering materials [9]. This paper proposes a simple blister test configuration for characterizing biaxial mechanical properties of membranes over a range of loading profiles and environmental conditions.

In considering appropriate test specimens and damage detection techniques for characterizing fuel cell membranes, several key features of membranes in operating fuel cells are apparent and are likely to be relevant in selecting appropriate test methods. First, the stress state within a membrane of an operating fuel cell is primarily induced by the expansion and contraction of the membrane resulting from temperature and humidity fluctuations. Sandwiched between the diffusion media layers that are compressed by the lands of the bipolar plates, the membranes are nominally constrained in a nearly constant in-plane strain state. Second, the induced mechanical strains and stresses within the membrane are nominally biaxial because of the planar constraint. Third, although in-plane compression of the membrane may occur and even lead to localized buckling in some situations [10], the stress state of primary concern is the biaxial tensile stress state, under which flaws could grow. Fourth, the membrane stresses result not from direct mechanical loading but from hygrothermally driven deformations within the constrained membrane. Because of the temperature and moisture content dependence of the viscoelastic behavior of the membranes, the stresses and environment are inherently coupled; mechanical loading alone might not adequately simulate the actual membrane behavior. Fifth, membrane failure consists not in global mechanical separation of the membrane but by the development of small leaks across the membrane. Damage and failure detection should be tied to changes in permeability rather than the large-scale deformation and tearing that occur in standard tensile specimens, for example, which are often used to characterize membrane properties.

In consideration of these observations, this paper proposes the use of a pressure-loaded blister specimen in which a proton exchange membrane is mounted on a circular aperture and pressurized with air or other media of interest. This configuration is believed to have a number of attributes that make it particularly appropriate for studying the mechanical integrity of PEMs. Before elaborating on these, however, a brief overview of the pressurized blister test is provided.

Pressurized membrane configurations have been extensively studied over the years, both for characterizing the adhesion of membranes to substrates to which they are attached [11] and for studying properties of the membranes themselves. For the latter, blister or bulge tests have been used to measure mechanical properties of membranes [2,12,13], as well as residual stresses [14–16] and burst strength [16]. In the center of a circular pressure-loaded blister, the radial and circumferential stresses are equal. As one moves away from the center, stresses in both directions decrease gradually at somewhat different rates. An exact (large deflection) solution for the stresses within a pressurized circular blister has been given in terms of a power series solution by Hencky [17]. The resulting expressions for the radial, σ_r, and tangential, σ_θ, stresses are given by [17,18]

$$\sigma_r(r) = \frac{1}{4}\left(\frac{Ep^2a^2}{t^2}\right)^{1/3} \cdot \sum_{k=0}^{\infty} B_{2k}\left(\frac{r}{a}\right)^{2k}$$

$$\sigma_\theta(r) = \frac{1}{4}\left(\frac{Ep^2a^2}{t^2}\right)^{1/3} \cdot \sum_{k=0}^{\infty} (2k+1)B_{2k}\left(\frac{r}{a}\right)^{2k} \qquad (1)$$

where E is the Young's modulus of the membrane, p is the applied pressure, a is the radius of the blister, t is the thickness of the membrane, and B_{2k} are the coefficients that can be determined through recursion relationships once the initial B_0 coefficient is known, using

$$B_2 = -\frac{1}{B_0{}^2}$$

$$B_{2k+2} = -\frac{1}{(k+1)(k+2)B_0{}^2}\sum_{m=0}^{k-1}\sum_{n=0}^{k-m}(m+1)(m+2)$$

$$\times B_{2m+2}B_{2n}B_{2(k-m-n)} \qquad (2)$$

The first few series coefficients are

$$B_2 = -\frac{1}{B_0{}^2}, \quad B_4 = -\frac{2}{3B_0{}^5}, \quad B_6 = -\frac{13}{18B_0{}^8}$$

$$B_8 = -\frac{17}{18B_0{}^{11}}, \quad B_{10} = -\frac{37}{27B_0{}^{14}}, \quad B_{12} = -\frac{407}{189B_0{}^{17}}$$

B_0 is determined by enforcing the boundary condition that the membrane's circumferential strain at the outer edge, $\varepsilon\theta(a)$, must remain equal to the initial (assumed to be equi-biaxial) residual mechanical strain, ε_0. For an elastic material, this boundary condition becomes

$$\varepsilon_\theta(a) = \frac{1}{E}[\sigma_\theta(a) - \nu(\sigma_r)(a)] = \varepsilon_0 \qquad (3)$$

where ν is the Poisson's ratio of the membrane. By inserting Eq. (1) and rearranging

$$\sum_{k=0}^{\infty}(2k+1)B_{2k} - \nu\sum_{k=0}^{\infty}B_{2k} = 4\varepsilon_0\left(\frac{Et}{pa}\right)^{2/3} \qquad (4)$$

Substituting terms into this expression, one obtains

$$(1-\nu)B_0 + \frac{(\nu-3)}{B_0^2} + \frac{2(\nu-5)}{3B_0^5} + \frac{13(\nu-7)}{18B_0^8} + \cdots = 4\varepsilon_0\left(\frac{Et}{pa}\right)^{2/3} \qquad (5)$$

showing that B_0 will be a function of $4\varepsilon_0(Et/pa)^{2/3}$. The residual mechanical strain will vary with temperature and humidity levels, and can be positive or effectively negative (although not physically realizable because buckling of the membrane would likely occur). As such, B_0 can vary as p varies in a test unless ε_0 is zero, in which case B_0 is a constant. Equation (5) can be solved for B_0, and for the case where there is no residual mechanical strain, ε_0 =0, B_0 is only a slowly varying function of ν, taking on values of 1.72433, 1.77683, and 1.84526, respectively, for values of Poisson's ratio of 0.3, 0.4, and 0.5, which cover the range of interest for most polymeric materials. B_0 can be accurately approximated by

$$B_0 \approx 1.6198 + 0.27864\nu + 0.063018\nu^2 + 0.55783\nu^3 \qquad (6)$$

over the full range of positive values of Poisson's ratio.

Figure 1 shows a plot of the radial and tangential stress factors as a function of radial position for a circular blister, illustrating that radial stresses are relatively constant across the entire membrane but that the tangential stresses decrease substantially as one approaches the constrained edge of the specimen, where the tangential strains must be zero (for ε_0=0) and plane strain conditions prevail. The stress factors, when multiplied by $1/4(Ep^2a^2/t^2)^{1/3}$, will provide the actual values of stresses, as given in Eq. (1). The results are shown for the three specific values of Poisson's ratio
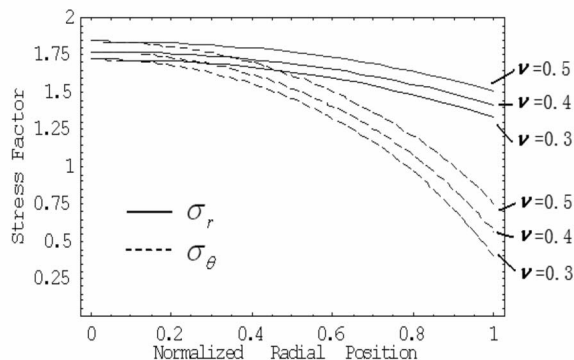
Fig. 1 Plot of radial and tangential stress factors as a function of radial position for a pressurized circular blister

cited above; as the membrane goes from the glassy state ($\nu \approx 0.3$) to the rubbery state ($\nu \rightarrow 0.5$). A common problem in testing many specimen configurations to failure is the possibility of grip failures. Although the nonuniformity shown in Fig. 1 may be undesirable for inducing an ideal uniform stress state, the reduction in stresses near the edges can be advantageous in minimizing the likelihood of grip failures. Figure 2 illustrates the relative uniformity of the stress state, providing a ratio of the tangential to radial stresses as a function of radial position, along with a ratio of the radial stress to maximum radial stress as a function of radial position.

Approach

Much of the prior testing of fuel cell membranes has focused on measurements of viscoelastic properties using small strain loading conditions [6,7], on nonlinear or viscoplastic constitutive properties measured with uniaxial tensile specimens, and on stresses and strains at break in uniaxial tensile tests [5]. While all of these properties can be important in understanding membrane behavior, questions arise as to how these properties can be incorporated into models for predicting long-term membrane integrity in operating fuel cells. Durability predictions may require some types of failure data, yet the large strains and significant plastic deformation encountered in breaking uniaxial tensile specimens may have little relevance to the much more localized damage that results in pinhole formation in operating fuel cells. Mechanical separation, even of environmentally exposed test specimens, bears little resemblance to anticipated fuel cell failure mechanisms and modes, suggesting the need for alternate test techniques that are capable
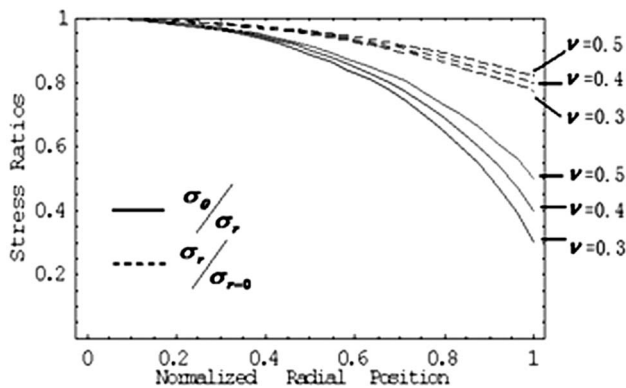

Fig. 2 Plot of the stress state uniformity within a pressurized circular blister, showing the ratio of tangential to radial stresses and the ratio of radial stress to the maximum central stress

of measuring the development of pinholes that can lead to gas cross over. Since the failure mode of interest is leakage, the detection of leaking is believed to be a more relevant failure event for characterizing fuel cell membranes.

In this study, we explore the feasibility of using pressure-loaded blisters to evaluate the mechanical properties and integrity of commercial PEMs. Although the emphasis of this paper is on conducting pressurization tests to burst, subsequent work will report other loading modes for this test configuration, suggesting its versatility. This test geometry is believed to offer a number of advantages for evaluating the properties of proton exchange membranes and membrane electrode assemblies. These include the following:

(1) The simple configuration allows for easy specimen preparation. Suspended membranes can be clamped in place with O-rings or other seals, or can be bonded to substrates. In this paper, we used slightly modified Swagelok®[4] tube fittings to clamp the membrane for pressurization.

(2) The specimen lends itself to miniaturization. This makes it easy to gang multiple specimens on a block that is compact in size so that a great amount of durability data can be obtained simultaneously. In turn, the block can readily fit in an environmental chamber.

(3) Pressurized membranes are well suited for detecting gas leakage through measurements of pressure loss. To avoid stretching of the membrane during a leaking test, a porous solid can be placed on the side of the membrane that is exposed to the atmosphere. This porous solid serves as a support that prevents the membrane from deflecting and stretching while still allows leaked gas to escape. Although not employed for this bursting study, this could prove useful in durability tests.

(4) Pressure-loaded blisters are readily suitable for bubble tests or other methods to monitor the initiation of pinholes. During a bubble test, the pressure-loaded blister is submerged in water and the sites where air bubbles come out are believed to have developed pinholes.

(5) Once a piece of PEM is held onto a front ferrule, it is constrained biaxially. If such a specimen is preconditioned with cycled humidity, the damage induced in the PEM due to the biaxial hygral stresses is similar to that in a fuel cell. Residual strength of the preconditioned PEM can be obtained by a subsequent burst test.

(6) Since air is the medium used for loading, the pressure-loaded blister configuration is a very flexible "loading frame." With the help of digitally controlled valves, stresses can be imposed as any desired function of time, including ramp to failure, static fatigue (creep under sustained pressure), and cyclic fatigue. Thus it provides a platform on which extensive tests can be performed, including tests of membranes removed from operating fuel cells.

(7) Circular specimens result in relatively uniform and equal biaxial stresses across the central portion of the specimen, mimicking the equal biaxial stresses expected in constrained membranes in fuel cells. Other shapes are possible, including long rectangular blisters that result in plane strain conditions throughout most of the specimen.

(8) The stresses decrease toward the edge where the PEM is mechanically gripped. This ideally could eliminate grip failure normally seen in constant width uniaxial tensile tests.

(9) With the failure occurring at the center of the blister, the failure is not affected by artifacts related to sample preparation as can be the case with defects introduced during cutting a uniaxial tensile test specimen, for example.

(10) Constitutive properties may be measured through mea-

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[4]Swagelok® is a registered trademark of Swagelok Company, Solon, OH.

surements of deflection as a function of pressure and time. For circular specimens, the biaxial modulus, $E/(1-\nu)$, and for long rectangular specimens, the plane strain modulus, $E/(1-\nu^2)$, can be obtained from pressure and maximum deflection data, where E is Young's modulus and ν is Poisson's ratio.

(11) The specimen can be examined using digital image correlation techniques to accurately capture deflected shapes and other details for characterizing constitutive properties and probing inelastic behavior.

(12) The residual stress within the membrane can also be measured by examining the pressure-deflection behavior.

Along with these promising attributes come several concerns with using pressurized blister specimens for characterizing proton exchange membrane strength and durability. Initial problems involved issues related to leakage around the edges and obtaining sufficiently accurate means to measure deflections that are required to obtain constitutive properties. Significant progress has been made in addressing each of these issues, and results are very encouraging at this point.

Experimental Implementation

Three commercially available PEMs were tested, namely DuPont™ Nafion® NRE-211, Gore™ Select®[5] series 57, and Ion Power™[6]Nafion® N111-IP. They are 25 μm, 18 μm and 25 μm thick, respectively. The Nafion® NRE-211 is homogeneous perfluorosulfonic acid (PFSA) membrane. The Gore™ Select® series 57 membrane has three layers, including the central reinforcing layer that is a composite network of expanded polytetrafluoroethylene (e-PTFE) with PFSA fillers and the outer PFSA layers. The Ion Power™ Nafion® N111-IP is an extruded version of the Nafion® NRE-211.

Subsequent work will report clamping membranes over multi-cell blocks, but in the initial validation studies reported herein, single pressure-loaded blisters were made by mounting bonded membrane samples in slightly modified Swagelok® tube fittings. These proved to be convenient for securing and pressurizing membrane samples over a range of diameters (10–29 mm) corresponding with commercially available Swagelok® reducing unions (tube fittings used to connect tubes of different diameters). In a standard Swagelok® tube fitting, there are two ferrules, the front and back ferrules. When a tube is inserted and the clamping ferrule nut tightened, permanent deformations in the ferrules as well as in the tube lead to an effective mechanical grip and pressure-tight seal. Figure 3(a) shows the components of a Swagelok® tube fitting. In adapting these fittings to facilitate pressure-loaded blister tests, the back ferrule was not used and the head of the ferrule nut was machined to approximately 1 mm thick, just to give sufficient clamping without hindering the PEM from forming a blister. The machining is crucial when testing tough membranes, which strain substantially and form highly stretched blisters larger than a hemisphere.

To bond PEMs onto a front ferrule, a piece of packaged PEM, which allows eight to ten samples to be made, was cut from a batch on a cutting mat and laid flat on the mat. Since the Nafion® NRE-211 and and Gore™ Select® series 57 membranes are sandwiched between two backings, one backing must be removed (this step was skipped for Ion Power™ Nafion® N111-IP membranes, which only have one backing), leaving the PEM on top of the remaining backing. Retaining the second backing is beneficial in preventing the PEM from wrinkling during bonding. Then, a small amount of thoroughly mixed Devcon®[7] two-part 5 min epoxy adhesive was applied onto the flat face of a front ferrule with a
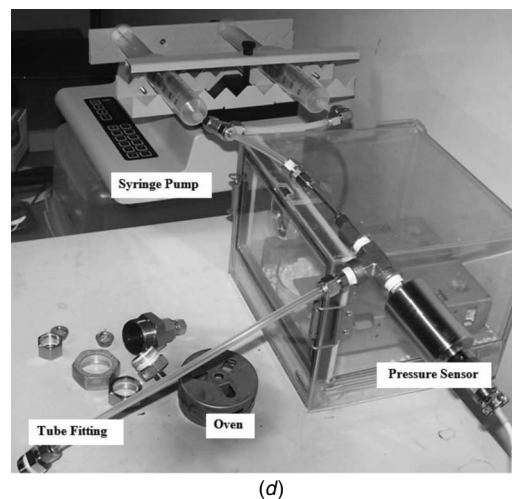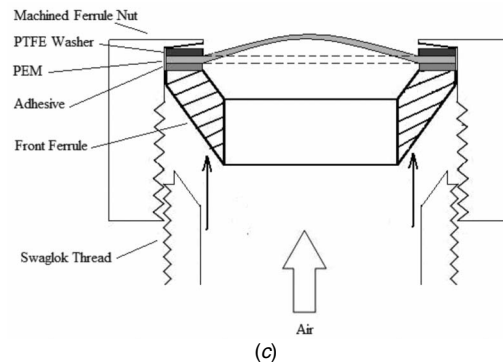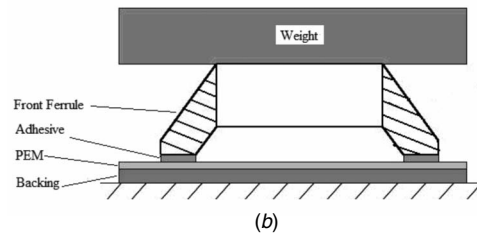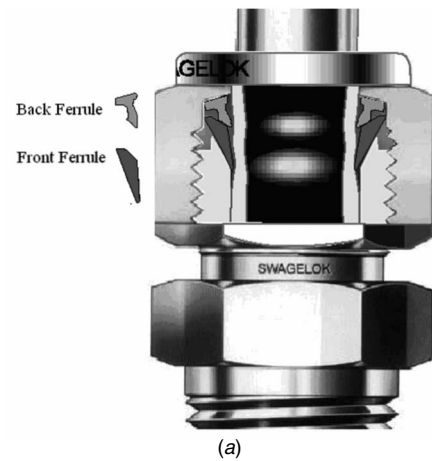

(a)

(b)

(c)

(d)

Fig. 3 Illustrations of (a) **a standard Swagelok® tube fitting (adapted from animations available at http://www.swagelok.com);** (b) **a cross-sectional diagram describing the sample preparation process (not to scale);** (c) **the clamping and pressurizing of a sample with the modified fitting (not to scale), and note the machined ferrule nut;** (d) **the connections involved in a blister test. After the specimen was clamped onto the tube fitting, it was inserted into the oven from the top.**

[5]Gore™ Select® is a trademark of W. L. Gore & Associates, Inc. of Newark, DE.
[6]Ion Power™ is a trademark of Ion Power, Inc. of New Castle, DE.
[7]Devcon® is a registered trademark of ITW Devcon, Danvers, MA.

pushpin. Caution must be taken not to apply more than enough to form a thin layer of adhesive. Each ferrule was then inverted and gently dropped vertically onto the PEM from about 1 mm above. The fast curing epoxy adhesive has a pot life of several minutes, allowing one to make four or five samples at a time. Repeating these steps with another batch of adhesive, eight to ten samples can be fabricated from a piece of PEM within 15 min. A small weight was placed on top of each ferrule for 2 h while the adhesive cured. Finally, individual blister test specimens were completed by cutting around the perimeter of each ferrule and removing the second backing layer. Figure 3(b) schematically illustrates the preparation of a sample (not to scale).

In preparing to conduct a pressurized blister test, a sample is clamped within the tube fitting. A thin PTFE washer (1 mm thick) was placed in front of the specimen to enhance sealing as well as to reduce friction that could shear or wrinkle the membrane. Figure 3(c) schematically illustrates the clamping and pressurizing of a specimen.

Figure 3(d) illustrates the setup the authors have used to conduct the blister test results reported herein. Pressurized air was supplied to the fitting by a KDScientific®[8] 230 series syringe pump, whose displacement rate could be varied. Two 60 ml Becton Dickinson®[9] plastic syringes were connected in parallel (to increase the flow rate) and driven by the pump. The pistons of the syringes were initially withdrawn to 60 ml and the volume of infusion (which determines the maximum achievable pressure) and the rate of infusion (which determines the time it takes to burst the sample) were set up with the touch pad. After clamping the PEM-ferrule specimen in place and setting up the syringe pump, the other end of the reducing union was connected to the syringes on the syringe pump with a 6.3 mm o.d. nylon tube. A Sensotec®[10] pressure sensor was connected in line to monitor the pressure. The analog signal from the pressure sensor was conditioned and recorded with a LABVIEW®[11] VI at 5 Hz. The specimen assembly was inserted through the access hole on the top of a Fisher Scientific™[12] convection oven, which was equilibrated at 80°C. After soaking the specimen for 10 min, the data collection VI was started and the syringe pump began to pressurize the blister until an audible pop was heard from the oven, which indicated bursting of the blister. The 10 min soaking was arbitrarily chosen but could be crucial, since the change of environment from ambient to elevated temperature and reduced relative humidity will lead to residual stresses in the membrane, which are time dependent. This has not been rigorously studied, but all results reported herein represent a consistent 10 min thermal soak. After bursting, the reducing union was taken out of the oven to visually check whether the rupture of the blister initiated from the center of the blister. Blisters that ruptured from the center give meaningful data, while those ruptured due to failure of bonding or shearing during clamping are discarded, as one would do with a grip failure during a uniaxial tensile test.

Figure 4 shows the frames taken with a high speed camera as a pressurized membrane bursts at room temperature, confirming that failures appear to initiate within the more highly stressed central region of the blister specimens. Although high speed photography could not be performed on specimens tested at elevated temperatures, observations suggested that these failures also initiated in the central region of the blister specimens.

Analysis

The raw burst pressures can be obtained for blister specimens of a given diameter, but to be useful for comparison with blister
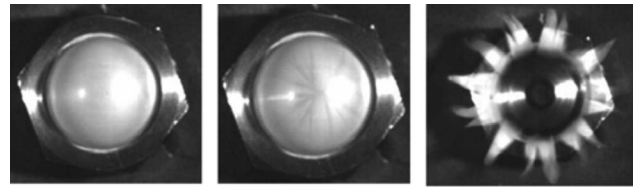

Fig. 4   High speed photographs of a Gore™ Select® series 57 membrane rupturing at room temperature measured at 5500 fps

specimens of other diameters or, more importantly, to use this information to gain knowledge in membrane strength, the rupture pressures must be converted to stresses. Hencky's solution outlined earlier is limited to linear elastic materials, yet time dependence and inelastic behavior were observed in the membranes pressurized to bursting. Nonetheless, a finite element analysis has provided insights into more complex behavior and confirmed the relative accuracy of Hencky's solution for our purposes [19].

Assuming that the initial residual mechanical strain is zero, Eq. (1) becomes

$$\sigma_r = \sigma_\theta = \frac{B_0}{4}\left(\frac{Ep^2a^2}{h^2}\right)^{1/3} \tag{7}$$

at the center of the blister where the maximum principal stresses exist. This relationship will be used to estimate the biaxial stress state within the central portion of the blister, where membrane bursting is believed to initiate. For the purposes of this paper, Poisson's ratio was assumed to be $\nu = 0.4$ for all membranes tested, resulting in a value of $B_0 = 1.777$, which was used throughout the subsequent analyses. Poisson's ratio would be expected to increase slowly with time for these viscoelastic materials, but the modulus changes with time are expected to be much more significant.

Because of the viscoelastic nature of the membrane, no single modulus is appropriate for the stress calculation, but the quasielastic estimation method [20] was employed for simplicity. For a linear viscoelastic polymer that exhibits slow creep or relaxation behavior in the sense that the maximum slope of its log-log relaxation modulus is less than about 0.25, the quasielastic estimation method can be used by starting with the elastic analog problem and simply replacing the elastic material constants with their viscoelastic counterparts as functions of time. In this spirit,

$$\sigma_b = \frac{B_0}{4}\left(\frac{E(t_b)p(t_b)^2a^2}{h^2}\right)^{1/3} \tag{8}$$

where t_b is the time at burst. For this study, the viscoelastic relaxation moduli of the membranes were obtained from Refs. [21,22], in which master curves were produced from uniaxial tensile relaxation tests that were performed using a TA Instruments™[13] Q800 dynamic mechanical analyzer (DMA).

Results and Discussion

Specimens were pressurized at selected rates determined by the speed of the syringe pump, the number and diameter of the syringes that were manifolded together, and the volume of the air column. Pressure was recorded at a rate of 5 Hz resulting in typical pressure traces, as illustrated in Fig. 5(a). For most specimens, bursting was clearly evidenced by the rupture sound and by a catastrophic loss in pressure. In other cases, however, leakage from around the perimeter prevented the pressure from reaching sufficient levels to burst the specimen; the resulting pressure traces exhibited a plateau and such specimens were not included
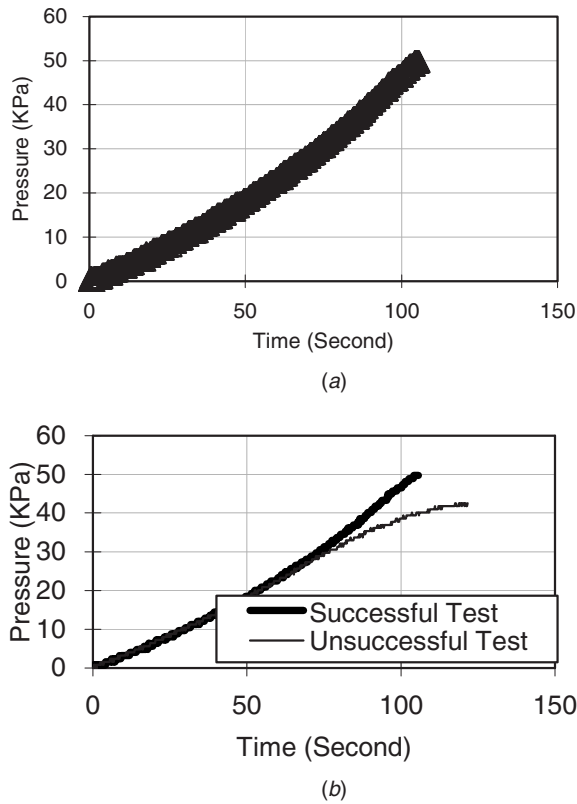

(a)

(b)

Fig. 5 Illustrations of (a) a typical pressure trace of Gore™ Select® series 57 tested at 80°C at an infusion rate of 14 ml/min and (b) a typical pressure traces valid and invalid test results for specimens tested at 80°C with an infusion rate of 14 ml/min

in the results. Figure 5(b) shows the results for a specimen exhibiting a plateau compared to a typical test result, both conducted under similar conditions.

The raw pressure at burst data exhibits significant time dependence, as might be expected for a viscoelastic membrane tested near its glass transition temperature. Because of this systematic variation, results presented herein will be shown as functions of the time to rupture. During a burst test, the syringe pump provides a constant infusion rate but the air is compressed as the specimen in loaded, resulting in a stiffening trend. Converting pressures to stresses using Hencky's analysis and quasielastic estimation, however, results in relatively linear stress traces, as shown in Fig. 6. Thus the resulting loading will be referred to as ramp to rupture.

To determine the robustness of the experimental technique and analysis method, blister specimens made of Gore Select® series 57 membranes of various diameters were tested with the same
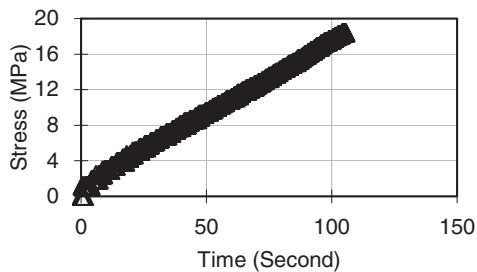

Fig. 6 Illustration of typical pressure trace converted to stress history using Hencky's solution (Gore™ Select® series 57 at 80 °C with an infusion rate of 14 ml/min)
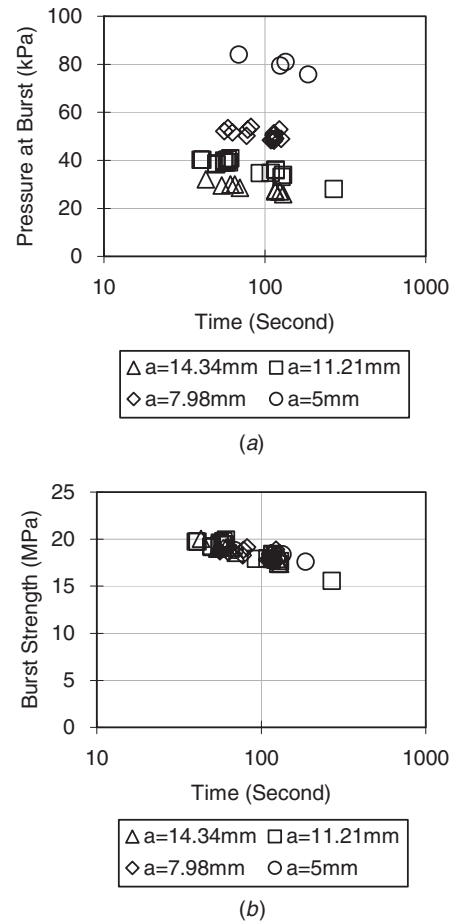

(a)

(b)

Fig. 7 (a) Burst pressures of blisters tested at different rates and with different sizes of ferrules; (b) time-dependent burst strength of Gore™ Select® series 57 at 80°C calculated from peak pressure shown in (a)

procedure. Suspended blister diameters included 9.8 mm, 15.96 mm, 22.42 mm, and 28.68 mm representing standard ferrule sizes in reducing unions of 0.375 in. (9.5 mm), 0.5 in. (12.7 mm), 0.75 in. (19.1 mm), and 1 in. (25.4 mm)−0.25 in. (6.4 mm) o.d. Figure 7(a) presents a summary of the burst pressures obtained for all of the specimens tested at 80°C. To make a meaningful comparison, peak biaxial stresses were calculated as described before and all of the results are presented in Fig. 7(b), which indicates the time dependency of the biaxial strength of Gore™ Select® series 57 membrane. The consistency of the burst strength results obtained with blisters of different sizes is very good, especially considering the limitations inherent in Hencky's solution. Specifically, membrane yielding is known to occur at the pressures required to rupture the membranes. Because Hencky's solution is based on the assumption that the membrane is linear elastic, the stress estimates should be viewed as approximations. Numerical studies have been conducted to evaluate the effect of nonlinear behavior, however, and are not significantly different than Hencky's solution due to yielding of the membrane [19].

Finally, the burst strengths of the three membranes are plotted in Fig. 8. Consistent behavior within the NRE-211 and N111-IP materials is seen as well, and the decreasing trend of the maximum stress versus time to rupture results is reminiscent of delayed failure data obtained by creep rupture tests of viscoelastic materials. The results for the three membranes are quite comparable, although the Ion Power™ Nafion® N111-IP and the Gore™ Se-
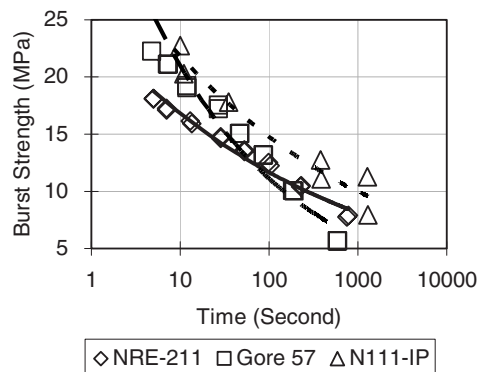
Fig. 8 Burst strengths of Nafion® NRE-211, Gore™ Select® series 57, and Ion Power™ Nafion® N111-IP

lect® series 57 appear to stand out. However, the Nafion® NRE-211 appears to have a slight strength advantage at slower pressurization rates.

The consistent results from these ramp to rupture tests of pressure-loaded blister specimens along with the advantageous attributes discussed in a previous section have led us to utilize this specimen configuration for a range of other test situations. Subsequent papers will report additional results and accomplishments with this test method. A digital image correlation technique is used to characterize the out of plane deformations and in plane strains within the pressurized blister specimens to obtain constitutive properties and determine the effects of inelastic behavior [23]. Special fixtures have been constructed to permit cyclic pressurization of blister specimens to obtain fatigue behavior [24] of proton exchange membranes tested as pressurized blisters. Results obtained from these tests are being used to develop a model for predicting PEM durability and reliability in fuel cell applications [25].

Summary and Conclusions

The use of pressure-loaded blister specimens is proposed for characterizing the strength properties of proton (PEMs) for assessing their durability in fuel cell and other applications. The equal biaxial stress state induced within the central region of the blister is believed to be representative of the hygrothermal stress state induced within a constrained PEM. The lower circumferential stresses that occur near the edge of the blister are believed to reduce the likelihood of failures near the gripped circumference. In addition to measuring biaxial burst strength, characterization of leakage, of particular relevance to fuel cell and desalination membranes, can easily be measured with such specimens, suggesting an important extension beyond the results reported herein.

This paper reports the use of this specimen for measuring the burst strength of Nafion® NRE-211, Gore™ Select® series 57, and Ion Power™ Nafion® N111-IP when the applied pressure is ramped over time. Specimens were fabricated in a very simple fashion by bonding Swagelok ferrules onto membranes supported by a backing layer to provide just taut membranes and prevent wrinkling. These supported membranes were mounted in reducing unions and inserted into a test oven set at 80°C because of the interest in performance at elevated temperatures. Specimens were pressurized with a syringe pump until rupture occurred, accompanied by an audible pop and catastrophic loss of pressure. By using the classic Hencky's solution for linear elastic membranes in conjunction with the quasistatic estimation for viscoelastic materials, stresses within the membranes could be estimated. This allowed comparison of results obtained with several different blister diameters. The size independency gives confidence in the approach and provides flexibility in exploring further applications. Results for all membrane materials showed similar behavior, resulting in lin-

ear plots of burst strength versus time to burst. Such behavior is similar to creep rupture results that have been widely used to study delayed failures of polymers and polymer matrix composites.

In addition to ramp to rupture tests, other loading scenarios, including creep to leakage or rupture and cyclic mechanical fatigue, are also possible. Multiple blisters can be easily fabricated to permit simultaneous testing of numerous specimens under controlled environmental conditions. Other desirable features include the compact size and ability to readily detect damage states (such as leakage) that are not readily measured for uniaxial tensile specimens. The specimen is believed to offer considerable potential for characterizing constitutive properties, bursting behavior, and leakage phenomena in membranes of interest to the fuel cell industry.

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