Journal of Power Sources 185 (2008) 374–380

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Characterizing the fracture resistance of proton exchange membranes

Yongqiang Li[a,*], Jennifer K. Quincy[a], Scott W. Case[a], Michael W. Ellis[b], David A. Dillard[a], Yeh-Hung Lai[c], Michael K. Budinski[c], Craig S. Gittleman[c]

[a] *Department of Engineering Science and Mechanics, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0219, United States*
[b] *Department of Mechanical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0238, United States*
[c] *Fuel Cell Research Labs, General Motors Corporation, 10 Carriage Street, Honeoye Falls, NY 14472-1039, United States*

ARTICLE INFO

Article history:
Received 11 March 2008
Received in revised form 14 June 2008
Accepted 16 June 2008
Available online 1 July 2008

Keywords:
Proton exchange membrane durability
Essential work of fracture
Trouser tear test
Knife slit test
Intrinsic fracture energy
Pinhole formation

ABSTRACT

Pinhole defects that form in proton exchange membranes (PEMs) due to the cyclic hygrothermal stresses induced during the operation of a fuel cell and cause gas crossover may be interpreted as a result of crack formation and propagation. The goal of this study is to employ a fracture test to approach the intrinsic fracture energy of a perflourosulfonic acid proton exchange membrane. The intrinsic fracture energy has been used to characterize the fracture resistance of polymeric materials with minimal plastic dissipation and the in absence of viscous dissipation, and has been associated with the long-term durability of polymeric materials where subcritical crack growth occurs under slow time-dependent or cyclic loading conditions. Insights into this limiting value of fracture resistance may offer insights into the durability of PEMs, including the formation of pinhole defects. In order to achieve this goal, a knife slit test which significantly reduces the plastic deformation during the test by limiting the plastic zone size with a sharp blade is conducted. Additionally, double edge notched tension tests and trouser tear tests are conducted to obtain the essential work of fracture and tear energy, respectively. It has been found that although the fracture energy obtained with the knife slit test is still several times larger than the intrinsic fracture energy of regular polymer materials, it is several orders of magnitude lower than those obtained with the other two methods, where process-dependent viscous and plastic dissipation dominate over the intrinsic material property.

1. Introduction

Long-term reliability of proton exchange membrane (PEM) fuel cells depends on the long-term electrochemical and mechanical integrity of the PEMs. Over a range of test conditions, small tensile coupons of these membranes often demonstrate considerable ductility, dissipating large amounts of energy and straining to several times their original length [1,2]. Examination of pinhole defects in membranes removed from failed fuel cells often show considerable thinning, presumably resulting from plastic flow of material due to concentrated stresses. In the mean time, these same micrographs reveal cracks that appear to result from relatively brittle crack propagation. Due to the brittle nature of catalyst layers, mud cracks of different depths are typically present in the electrodes. When these cracks reach the electrode–PEM interface, they can cause delamination and/or cracking of the PEM. When the surface cracks in the PEM initiated this way propagate through the thickness, reactant gases can crossover and reduce the efficiency and eventually halt the operation of the fuel cell [3–5].

Concepts of fracture mechanics may be employed to study the formation of mud cracks in membrane electrode assemblies (MEAs) during manufacturing, storage and handling, cracking behavior at the electrode and PEM interface, crack propagation within a PEM, and interactions of cracks propagating from both sides of a PEM. However, direct application of fracture mechanics is not without challenges. The uniaxial stress–strain response of a PEM shows substantial plastic deformation exhibiting over 100% strain at break [1,2] and common fracture mechanics tests give measured fracture energies on the order of $20\,\mathrm{kJ\,m^{-2}}$ or more [6]. Both properties indicate that a typical PEM is highly ductile and the plastic zone ahead of a crack tip is many times larger than the thickness of the membrane. Nevertheless, cracks have been found to propagate into the PEM and cause significant amounts of gas crossover during RH cycling tests with little evidence of macroscopic plastic deformation seen in post-mortem examination. This led us to consider the effect of sustained loading and cyclic fatigue. Refs. [7,8] represent finite element analyses of fatigue stresses in PEMs during RH cycling. Fatigue fracture requires substantially less energy than quasi-static fracture, which

---

[*] Corresponding author. Tel.: +1 585 624 6560; fax: +1 585 624 6680.
E-mail address: li233@vt.edu (Y. Li).

0378-7753/$ – see front matter © 2008 GM Global Technology Inc. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2008.06.056

involves extensive viscous dissipation and plastic deformation. When cracks in the materials propagate at an extremely low rate such that viscous dissipation disappears, the energy cost during the process is called the intrinsic or threshold fracture energy. The existence of the intrinsic fracture energy provides a threshold that governs the fracture of a material under extended static (creep) and/or cyclic fatigue loading. At such energy level, plastic yielding of the material also disappears [9]. To experimentally obtain the intrinsic fracture energy, plastic deformation ahead of the crack tip during a fracture test needs to be minimized. However, reducing plastic deformation is not easy to accomplish during fracture tests of PEMs that are 0.025 mm or thinner, as large scale yielding is often incurred during fracture toughness tests in a plane stress situation [10].

In this study, we evaluated three different testing methods to investigate the fracture response of PEMs: the double edge notched tension (DENT) test for obtaining the essential work of (plane stress) fracture (EWF), the trouser tear test, and a modified knife slit test. Following the experimental details, fracture resistance results obtained from these tests are compared and the advantages of the modified knife slit test over others are discussed. The effect of the cutting angle was studied with the modified knife slit test and a desirable cutting angle associated with minimal frictional effects and plastic dissipation was found.

2. Experimental details

2.1. Materials

For all experiments, DuPont's Nafion® NRE-211 membrane was tested as a representative PFSA (perflourosulfonic acid) PEM. NRE-211 is a non-reinforced, dispersion-cast Nafion® film with a nominal thickness of 0.025 mm. Using a dynamic mechanical analyzer (DMA) [11], the α-transition temperature of dry Nafion® was found to be around 103 °C, which is slightly higher than the typical operating temperature of PEM fuel cell stacks. In addition, from dry to the fully hydrated state, NRE-211 shows around 60% isotropic hygral expansion in volume and significant stress can develop during RH cycling tests [7,8]. As a result, NRE-211 exhibits relatively poor performance during relative humidity cycling tests [4,5]. This can be interpreted in that NRE-211 is prone to crack formation and propagation during such tests.

2.2. Double edge notched tension test (DENT)

The essential work of fracture (EWF) has been widely used as a measure of the fracture resistance of polymeric films [12,13], due to the inability to conduct plane strain fracture tests on thin membranes. The concept assumes that the total fracture energy during the fracture of a pre-cracked specimen can be separated into geometry-independent (essential) work and geometry-dependent (non-essential) work:

$$W_F = W_E + W_P \tag{1}$$

where W_F is the total work of fracture, W_E is the essential work that is expended to yield and tear the film within the inner fracture process zone, and W_P is the non-essential work to yield the outer plastic zone. In a DENT test, the size of the outer plastic zone is proportional to the uncut ligament length, thus the above equation can be rewritten as

$$w_F l t = w_E l t + \beta w_P l^2 t \Rightarrow w_F = w_E + \beta w_P l \tag{2}$$

where w_E and w_P are specific works corresponding to the terms in Eq. (1), l is the length of the uncut ligament length, t is the thickness of the specimen, and β is the shape factor of the outer plastic zone. Following Eq. (2), w_E can be obtained by conducting DENT tests with specimens of different uncut ligament lengths and extrapolating the w_F vs. l line to zero l. The concept of EWF and the fracturing of a DENT specimen made of a reinforced PFSA membrane (to aid visibility) as an example are illustrated in Fig. 1 [5,6]. The DENT specimens used in the present study had a gage length of 70 mm and were 35 mm wide. The length of the uncut ligament ranged from 5 mm to 30 mm. The pre-cracks were cut to length with a microtome blade. The specimen was loaded on an MTS universal testing machine to complete rupture at a crosshead rate of 0.08 mm s^{-1} while recording force and displacement.

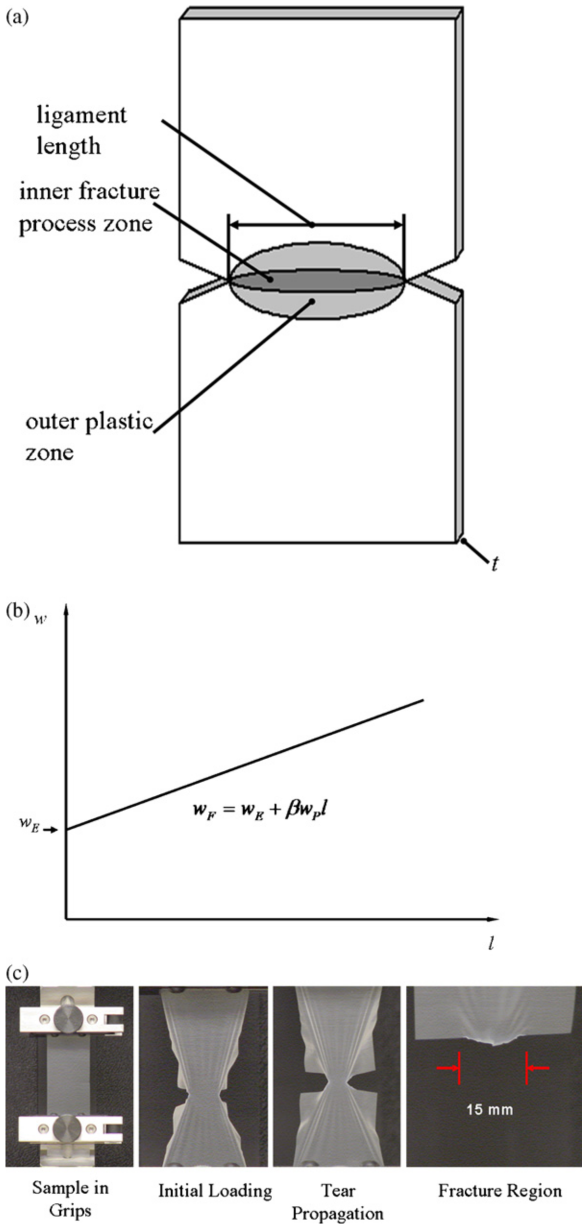

Fig. 1. Essential work of fracture and DENT test images: (a) schematic illustration of the inner fracture process zone and the outer plastic zone in the cracking of an in-plane pre-cracked specimen; (b) the linear relationship between the total specific fracture energy w_F and the uncut ligament length l [12,13]; (c) the cracking of a DENT sample of a reinforced membrane (for ease of photographing).