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Time-dependent mechanical behavior of proton exchange membrane fuel cell electrodes

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HIGHLIGHTS

- Time-dependent mechanical behavior of proton exchange membrane fuel cell electrodes.
- Experimental-numerical hybrid technique used to determine properties.
- Mechanical damage mechanisms investigated as function of temperature, humidity and strain rate.

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ABSTRACT

The electrodes used for Proton Exchange Membrane Fuel Cells (PEMFCs) are typically painted or sprayed onto the membrane during manufacturing, making it difficult to directly characterize their mechanical behavior as a stand-alone material. An experimental-numerical hybrid technique is devised to extract the electrode properties from the experimentally measured properties of Nafion® 211 membrane[1] and a membrane electrode assembly (MEA) based on Nafion® 211 membrane at various temperatures, humidities, and strain rates. Within the linear regime, the rule-of-mixtures assuming an iso-strain condition is used to calculate the rate-dependent Young's modulus of the electrodes. Beyond the linear regime, reverse analysis is conducted using finite element models of the MEA to determine the non-linear behavior of the electrodes. The mechanical damage mechanisms that occur in the MEA during tensile loading are also investigated through interrupted tension tests and then incorporated into the finite element models for determining the electrode behavior. The results suggest that the electrodes have similar behavior to Nafion® 211 membrane as functions of strain rate, temperature and humidity, but with lower Young's modulus and proportional limit.

1. Introduction

Numerous studies have been devoted to understanding the durability of proton exchange membrane fuel cells (PEMFCs) motivated by the desire to improve the lifetime of PEMFCs without unduly increasing cost or compromising performance [1–14]. Studies have shown that, although the electro-chemical interactions, transport losses and lack of ideal water management affect the durability of PEMFCs, chemical degradation and mechanical damage in the membrane electrode assembly (MEA) are major sources of failure [1–7]. Degradation and/or material loss in the MEA is commonly attributed to chemical attacks, but can also be significantly governed by the mechanical damage in the MEA [6]. Several forms of mechanical damage have been commonly observed in the MEA, such as through-the-thickness tears, pinholes in the membrane and delaminations between the membrane and electrodes [3–10]. It is commonly believed that the mechanical stresses, due to hygro-thermal changes in the MEA, are primarily responsible for the mechanical damage [9–14]. Therefore, investigating the hygro-thermal mechanical behavior of the MEA, which consists of the membrane and electrodes, is an important step toward understanding the fuel cell failure mechanisms and providing a science base for increasing the durability of PEMFCs.

In our previous experimental work, we have investigated the time-dependent mechanical behavior of a perfluorosulfonic acid (PFSA) membrane (Nafion® 211 membrane) at selected strain rates for a range of temperatures and humidities [15]. The results showed that Young's modulus and the proportional limit stress increase as the strain rate increases, and decrease as the temperature or humidity increases. The results also showed that the mechanical response of Nafion® 211 membrane is more sensitive to typical changes in strain rate or temperature than to typical changes in

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[1] Nafion is a registered trademark of E.I. DuPont De Nemours & Co.

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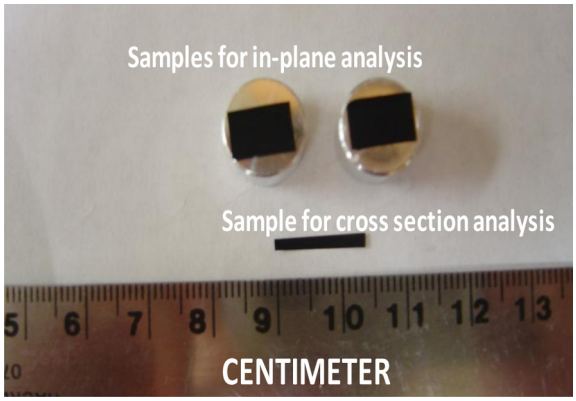

Fig. 1. Aluminum stubs and samples used for SEM characterization.

humidity. Some other articles regarding testing and modeling of the mechanical behavior of fuel cell membranes are also available in the literature [11,12,16–25].

However, little work has been published regarding the mechanical behavior of the electrodes. This is due to the fact that the electrodes are typically painted or sprayed onto the membrane during manufacturing and therefore do not exist as independent solid materials. Consequently, it is difficult to directly characterize the mechanical behavior of the electrodes. In this work, we devised an experimental-numerical hybrid technique to determine the mechanical behavior of the electrodes. Tensile and relaxation tests have been conducted to characterize the time-dependent mechanical behavior of both Nafion® 211 membranes and GORE™ PRIMEA® MEAs[2] based on Nafion® 211 membranes at various temperatures, humidities, and strain rates. Within the linear regime, the rule-of-mixtures assuming an iso-strain condition can be used to calculate the rate-dependent Young's modulus of the electrodes. Beyond the linear regime, however, the problem becomes highly non-linear with the onset of plasticity, strain hardening, and mechanical damage. Therefore, we used finite element models, created in the commercial software ABAQUS 6.9 [26], to conduct reverse analyses for determining the electrode mechanical behavior at moderate to large strain.

Furthermore, mechanical damage mechanisms such as cracks and delaminations play a role in the mechanical behavior of the MEA. However, once a material has completely failed, it is generally difficult to identify the failure evolution. By performing interrupted tests at selected strain levels under uniaxial tension, we were able to characterize how the mechanical damage develops as the strain increases. This information was then incorporated into the finite element models to simulate the stress–strain response of the MEA up to strains of 0.4.

In the following, we will briefly review the experimental procedure to determine the mechanical behavior of the membranes and MEAs, followed by the numerical work and reverse analysis used to determine the electrode properties.

2. Experimental procedure

Details pertaining to the experimental procedure for determining the mechanical properties of Nafion® 211 membranes are discussed in our previous work [15]. A similar experimental procedure was employed to characterize the MEAs, and will be briefly reviewed here for clarity. The interrupted tension tests will also be discussed. The MEAs used in this study were manufactured at W.L. Gore & Associates Inc., using Nafion® 211 membrane material, nominally 24 μ thick, affixed with GORE™ PRIMEA® electrodes, by way of their proprietary

[2] GORE PRIMEA is a registered trademark of W.L. Gore & Associates, Inc.

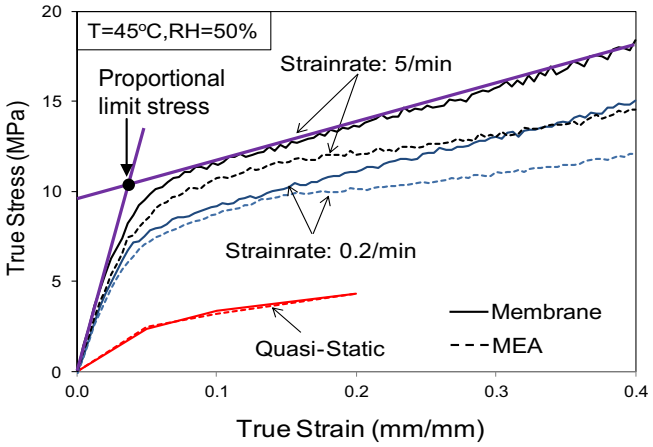

Fig. 2. True stress as a function of true strain for Nafion® 211 membrane [15] and the MEA at selected strain rates with $T = 45$ °C, RH = 50% (the quasi-static results are derived from relaxation tests).

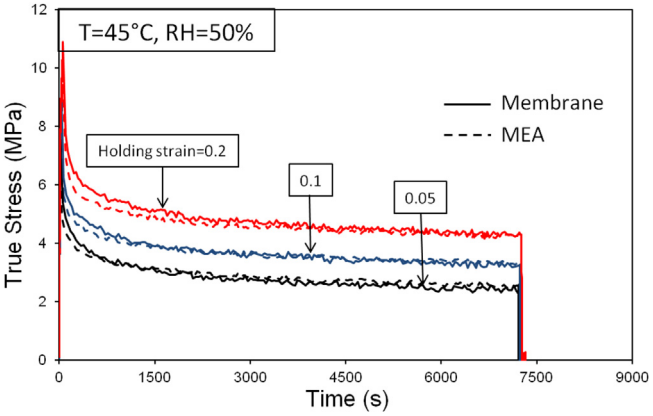

Fig. 3. True stress as a function of time for relaxation tests of Nafion® 211 membrane and MEA at selected holding strains for $T = 45$ °C, RH = 50%.

electrode deposition process. The cathode was nominally 12 μ thick and made from GORE™ PRIMEA® 580.3, with platinum loading of 0.3 mg cm^2 and the anode is nominally 6 μ thick and made from GORE™ PRIMEA® 584.1, with platinum loading of 0.1 mg cm^2.

2.1. Tensile and relaxation tests

We measured the time-dependent mechanical properties of Nafion® 211 membranes and MEAs based on Nafion® 211 membranes at three strain rates (5.0, 0.2, 0 mm mm^{-1} per minute[3]) (in the following, the notation/min will be used for simplicity) for sixteen temperature and relative humidity combinations, i.e. four selected temperatures (25, 45, 65, 80 °C) and four selected relative humidities (30, 50, 70, 90%).

The tests were conducted using an MTS Alliance™ RT/5 material testing system fitted with an ESPEC custom-designed environmental chamber [15]. The environmental chamber was used to set the desired temperature and relative humidity for testing. We conducted two sets of experiments at each environmental condition: tensile tests and relaxation tests. The tensile tests were conducted at two selected strain rates (5 min^{-1} and 0.2 min^{-1}) and the relaxation tests, at three selected holding strains (0.05, 0.1 and 0.2) [15].

[3] We also conducted a limited set of tensile tests at higher strain rates (up to 12 min^{-1}) and found very similar stress-strain response to the response seen at the strain rate of 5 min^{-1}.