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Numerical modeling of visco-elasto-plastic hygro-thermal stresses and the effects of operating conditions on the mechanical degradation of PEFC membranes

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HIGHLIGHTS

- Local distributions of membrane strains in an operating PEFC are determined.
- Clamping force suppresses the hygroscopic swelling.
- Plastic strain depends predominantly on the hygroscopic swelling.
- Hygral and plastic strains are observed to have the most significant effects.
- Relative humidity and load current can act interchangeably to reduce degradation.

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ABSTRACT

Durability of membranes is one of the concerns for widespread commercialization of polymer electrolyte fuel cells. Effects of membrane swelling on the durability pose important challenges for the fabrication of the catalyst-coated membrane. This study provides insight into vulnerable locations of the membrane under hygro-thermal loading, mechanical loading due to clamping and realistic conditions where a combination of both of these loadings are imposed. With a half rib-channel model, we simulate a polymer electrolyte fuel cell that operates under varying loads and clamping pressure. Model considers anisotropic diffusion in the gas diffusion layer as well as complex interactions of water transport dynamics between gas diffusion layers and the membrane. Mechanical responses of the membrane subject to conjugate hygro-thermo-mechanical loadings during typical scenarios of fuel cell operation reveal the effects of operating parameters as well as individual contributing factors on the development of local stresses in the membrane.

1. Introduction

Development of stable, reliable and durable polymer electrolyte fuel cells (PEFCs) has attracted considerable amount of research effort. As a result, progress in the mechanical durability of membranes has been remarkable, however the durability still remains as an important issue and needs further studies. Performance degradation is unavoidable but its rate can be minimized thorough understanding of the mechanisms leading to failure. Performance of PEFC deteriorates as the major cell components degrade. The electrolyte membrane, as a primary component, undergoes chemical and mechanical degradations that are not easily detectable with the current monitoring techniques. However, the degradations can lead to destructive membrane failures. Chemical degradation is related to the chemical decomposition of the membrane by the radicals, such as hydroxyl, hydroperoxyl and hydrogen peroxide, against the polymer backbone and side chains. Mechanical degradation is attributed to the gradual reduction in toughness and mechanical strength [1–3]. Mechanical stresses in the membrane originate from three mechanisms. The first is the clamping force applied over the plates to prevent leakages and to reduce contact resistances. Clamping force creates inhomogeneous deformations in the gas diffusion layers (GDLs) and membrane, causing an uneven distributions of thermal and electrical resistances. It also creates non-uniform distribution of GDL porosity under the rib and channel areas, changing the transport properties for mass and charge in the GDL. The second mechanism is the swelling and shrinking due to hydration and dehydration as a

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function of water content; and the third is the thermal expansion due to temperature gradients in the membrane.

Load transients in a PEFC effectuate hydration, dry-out and temperature transients in the membrane. Since mechanical properties of the membrane are strongly dependent on temperature and humidity, the membrane is subject to hygro-thermal fatigue loading during these transients [4]. Temperature/hydration cycling can induce expansion and contraction in the membrane. Since the membrane is constrained in the PEFC by GDLs and bipolar plates (BPs), mechanical stresses occur in the form of in-plane compressive and tensile stresses in the membrane. These stresses may exceed the yield strength thus inducing plastic deformation and can lead to formation of pin-holes, cracks and delamination, resulting in reactant cross-over and cell/stack failure subsequently. Therefore, predicting the local distribution of these stresses is of paramount importance to prevent mechanical failure and to increase the endurance of the membrane by adept control strategies.

Mechanical degradations of PEFC components have become a focus of attention for the last decade. Many researchers have examined the mechanical behavior of fuel cell membranes under humidity and temperature cycling conditions with numerical models based on elasticity or elasticity-plasticity assumptions for material behaviors [1–5]. A preliminary theoretical analysis by Weber and Newman [6] demonstrated that mechanical stresses inside the membrane need to be considered in experiments and models as they play an important role in the water balance in the cell. Tang et al. [7] developed a finite element model to study in-situ stresses in polymer membranes subject to hygro-thermal loading. However, the temperature and relative humidity profiles inside the membrane was assumed to be constant. In-plane stresses were shown to be the dominant stresses in the membrane. Kusoglu et al. [8] performed simulations using previous experimental findings of mechanical properties of Perfluorosulfonic Acid Membrane (PFSA) [9], assuming a linear elasto-plastic constitutive behavior for the membrane with isotropic hardening. During hygro-thermal loading, the membrane experienced compressive stresses due to the cell constraints that prevents it from expansion. However, during the dry-out of the membrane, tensile residual stresses developed in the membrane due to redistribution of stresses induced by plastic deformation. In-plane stresses were observed to be the largest stress component compared to the through-plane stresses and shear stresses induced. Stress levels were reported to exceed the yield stress, causing plastic deformation in the polymer membrane. Kusoglu et al. [10] studied the mechanical behavior of Nafion under hydration–dehydration cycles. The membrane was cycled through various uniformly distributed humidity loads. They showed that membrane swelling has a dominant effect on in-plane stresses depending on the membrane thickness or the assembly conditions. They also suggested that the cathode side of the membrane is more prone to mechanical failure. Bograchev et al. [11] studied the evolution of stress and plastic strains during the start-up in both global and local scales. Hygro-thermo-mechanical loads are introduced into the model. The GDL/seal joint interface was shown to be the most sensitive zone in terms of mechanical deformation. They showed that the generated stresses are significant enough to initiate plastic deformation in the membrane. The effect of non-uniform distribution of water in the membrane is studied by Kusoglu et al. [12] with a prescribed water content at the membrane boundaries and the diffusion of water across the membrane. Mechanical constraints were observed to restrict the swelling of the membrane and alter the water distribution in the membrane. Water content was seen to have a greater influence on the mechanical response than temperature.

Kusoglu et al. [13] studied the swelling-induced stresses and fatigue behavior utilizing numerical simulations for fuel cell relative humidity cycle tests. They reported that pinholes, cracks and delamination are the most probable failure mechanisms in the low compression region such as under the channel whereas at high humidity levels cavitation that leads to craze formation is less likely to occur in the compressed membrane. Higher humidity cycles lead to larger fatigue stresses and lower number of cycles to failure. Khattra et al. [14] created a viscoelastic-plastic model to capture the transient mechanical response of PFSA membrane. The observed levels of stresses were in direct relationship not only with the humidity and feed rate but also the sorption rate. Uniform humidity ratios in anode and cathode generated larger stresses compared to the non-uniform humidity loading. An elasto-visco-plastic stress model was proposed by Silberstein and Boyce [15] to investigate the effects of uniaxial and biaxial loading on Nafion. The temperature and hydration dependent elastic-plastic stress/strain behavior of Nafion under both monotonic and cyclic loading conditions were characterized. In their subsequent study [16] they performed a bi-material swelling test on the membrane bonded to a GDL material to measure the membrane stresses and deformation magnitudes under hydration and dehydration loading. They incorporated the approach in a simplified fuel cell model to predict the strain evolution and potential failure spots in the membrane and observed negative hydrostatic pressures, which is the onset of cavitation and crazing under the channel.

Fluoride release, membrane crossover and cell resistance as well as decrease in electrochemical surface area (ESA) were correlated to the degradation rate during cell operation by Vengatesan et al. [17]. Using an Infra-Red (IR) camera, they could observe the thermograms for the degraded membrane electrode assemblies (MEAs) with hotspots exhibiting local defects in the membrane. They noticed that the anode inlet is more susceptible to degradation and membrane failures, possibly due to the lower membrane hydration owing to the electro-osmotic drag which carries water from the anode to the cathode. Kreitmeier et al. [18] examined the local mechanical and chemical degradation in PEFC membranes. By analyzing the gas permeation rate through the MEA, the main source of inhomogeneous membrane degradation was identified as the spatial non-uniformities in relative humidity in the membrane and inlet gases.

Numerical models to predict PEFC degradation mechanisms play an important role in improving PEFC technology. In recent years, various cell models were proposed usually focusing on certain aspects while neglecting others to simplify the model. However, these simplifications limit the prediction ability of these models. The degradation mechanisms cannot be considered independently but should be coupled to the detailed cell model to reach the accurate local sources of degradation. There is a limited number of papers discussing membrane stress/strain distribution incorporating the compression effect on all cell components and their physical, electrical and transport properties. Furthermore, most of the existing membrane stress models do not account for transport of water within the membrane to obtain the water distribution across the length and thickness of the membrane for realistic load changes and therefore they use uniform membrane hydration models with the prescribed thermal and hygral boundary conditions. In order to accurately assess the effect of material properties on the cell performance and durability, it is essential to recognize the location and the transport mechanisms of water throughout the cell.

There are some attempts [19–22] to expand the simplified models towards more rigorous multiphysics models incorporating different aspects of an operating fuel cell from electrochemistry and fluid dynamics to solid mechanics for determining the stress distributions. A three-dimensional model of PEFC was developed to investigate the displacement, deformation and stresses inside the cell during its operation by Al-Baghdadi [19]. Non-uniform distribution of hygro-thermal stresses were predicted as an important factor contributing to delamination between the membrane and GDL. A 2D time-dependent model of PEFC incorporating the poroelastic deformation approach along with the water transport in the membrane was proposed by Yesilyurt [20]. The effects of load, inlet relative humidity and clamping force on the water distribution and stress evolution in the membrane were analyzed. Clamping force was seen to squeeze the membrane and flatten water distribution within the membrane. Escalating the inlet relative humidity and the load current led to an increase in the