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# In-plane biaxial cyclic mechanical behavior of proton exchange membranes

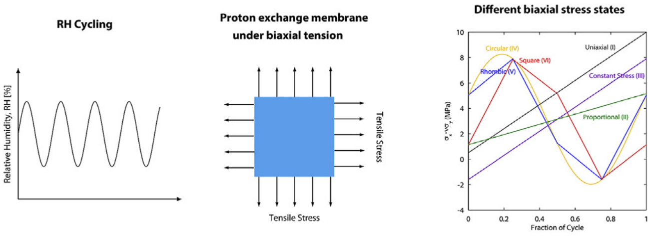
Qiang Lin [a], Shouwen Shi [a, **], Lei Wang [a], Shan Chen [b], Xu Chen [a], Gang Chen [a, *]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin, China
[b] Shanghai Aerospace Control Technology Institute, Shanghai, China

## HIGHLIGHTS

- In-plane biaxial constraint effect on strain evolution is investigated.
- Equibiaxial stress state imposes the largest constraint.
- Large amplitude stress cycle suppresses subsequent strain accumulation.
- Cyclic effect on membrane fatigue behavior is related to membrane stress state.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The durability of a proton exchange membrane is affected by both mechanical degradation and chemical degradation. While fatigue and relative humidity cycling tests have been conducted to address mechanical degradation, the cyclic behavior that bridges the gap between the stress-strain response and fatigue behavior is not well established. The objective of this study is to understand the strain evolution during biaxial cyclic loading that resemble the actual stress state of the membrane. In particular, the effect of loading paths on strain evolution is examined to account for the stress state on strain accumulation. It is found that the constraint effect of stress in one direction on strain evolution in another direction strongly depends on the stress state of the membrane, and the equibiaxial stress state imposes the most significant constraint on strain evolution. Furthermore, the constraint effect induced by biaxial loading is more significant at higher relative humidity values. Moreover, high-stress amplitude cycle acts to retard strain accumulation in the subsequent low-stress amplitude cycle. The findings reported here will provide new evidence for an understanding of the fatigue behavior of a proton exchange membrane as well as durability modeling of proton exchange membrane fuel cells.

## 1. Introduction

As promising candidates to replace internal combustion engines in automotive applications, proton exchange membrane fuel cells (PEMFCs) have attracted significant attention from both industry and academia. One of the technical challenges facing the fuel cell industry is the development of high durable proton exchange membranes that can meet the automotive industry's durability targets [1,2]. In particular, simultaneous requirements of performance and durability, which are meant to reduce the transport resistance without sacrificing the mechanical durability, impose significant challenges on proton exchange membranes [3]. As a result, increasingly thinner composite membranes [1,4] are used to address this issue. However, as the thickness of the membrane

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* Corresponding author.
** Corresponding author.
*E-mail addresses:* swshi@tju.edu.cn (S. Shi), agang@tju.edu.cn (G. Chen).

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decreases, the challenges imposed by chemical and mechanical stress tensors increase. Two factors are thought to significantly affect the durability of proton exchange membranes: mechanical degradation and chemical degradation, which act synergistically during practical operation condition [5]. Mechanical degradation mainly arises from relative humidity cycling that induces compressive stress during membrane sorption and residual tensile stress during desorption [6,7]. The cyclic stress, therefore, serves as the driving force for pinhole and crack initiation and propagation [8–10], which finally lead to the leakage of reactant gases.

To evaluate the mechanical durability of proton exchange membranes, different accelerated stress testing (AST) procedures have been proposed as screening methods, including open circuit voltage (OCV) and relative humidity cycling [2,11–18]. However, owing to the diffusion kinetics of water in the membrane, cycling between dry and saturated conditions usually takes several minutes. Besides, the stress induced by the relative humidity is not very large, which increases the time required to test until failure, and this is especially true when considering the reinforcement composite materials that are mechanically more durable [4]. Therefore, ex-situ test methods [19–21] have been proposed to address this issue and, at the same time, to represent the actual relevant condition of the membrane. As proton exchange membranes are sandwiched between gas diffusion layers that keep the membrane in a nearly in-plane strain state, the resulting stresses are basically biaxial in nature owing to the planar constraint. Hence, the pressurized blister method that produces an equibiaxial stress state in the center of the blister has been adopted by many researchers [20–24]. The strength [21,23], fatigue, and creep [20,22] behaviors of different types of proton exchange membranes, as well as the time-dependent mechanical properties of membrane electrode assembly (MEA) [24], have been measured and characterized with this method. However, the pressure-loaded blister test also comes with its shortcomings, in that the calculation of stress in the pressure-loaded blister test would require air pressure history, geometric parameters, and constitutive properties of the membrane. This is also complicated by the continuous changes in the membrane properties due to its viscoelastic nature [25–28], and the anisotropic behaviors of some membranes, which involve additional analyses. Therefore, it is difficult to directly and accurately obtain the stress-strain responses with this method.

As an alternative way to generate a biaxial stress field, the in-plane biaxial test with material simultaneously stretched in two direction proves to be an effective method. The biaxial elastic-viscoplastic behavior of Nafion membrane was investigated by Silberstein et al. [29] both experimentally and numerically, where the stress-strain responses of Nafion membrane at different stretching ratios were studied. It was found that the initial stiffness, yield stress, and post-yield stress all changed with changes in the stretching ratio. The free selection of the stretching ratio in two mutually orthogonal directions is an advantage of this testing method that could mimic the anisotropic swelling behavior of the proton exchange membrane during relative humidity cycling due to the uneven distribution of water [27,30–32] or the anisotropic nature of the material [4,26]. Relative humidity cycling has been found to have a significant impact on the durability and lifetime of the proton exchange membrane, with the low amplitude humidity cycle showing a longer lifetime [33]. Using the ex-situ test method, the fatigue behavior of the proton exchange membrane has been investigated both under uniaxial [19,34,35] and biaxial [20] loading conditions. However, regardless of the significant impact of cyclic stress on membrane fatigue behavior and durability, the cyclic behaviors of proton exchange membranes that bridge the gap between the stress-strain responses and fatigue behaviors of membrane have not been investigated. Hence, the objective of this study was to experimentally investigate the in-plane biaxial cyclic behaviors of proton exchange membranes that resemble the actual stress state of the membranes in order to provide evidence and help explain the fatigue behavior of the membranes.

In the present work, the in-plane biaxial cyclic behaviors of proton exchange membrane were investigated with an emphasis on the effect of loading paths to account for the possible anisotropic membrane swelling. In particular, the effect of a constraint in one direction on the strain evolution in another direction (orthogonal direction) was qualitatively examined in both air and liquid water environments. In addition, to assess the effect of loading history (the presence of startup/shutdown during practical operation) on subsequent strain evolutions, the strain evolutions of two different loading histories were analyzed.

## 2. Experiments

### 2.1. Materials and specimen design

Commercially available as-received (AsR) Nafion® 212 membrane developed and manufactured by DuPont with the thickness of 50 μm was used in this study. In-plane biaxial tension experiments were performed with the biaxial cyclic testing system (IPBF-300, CARE Measurement & Control Co., Ltd.), a detailed description of which can be found in our previous work [36]. During the experiments, the membrane were cut into cruciform shape using a sophisticated molding cutting die to guarantee accuracy and consistency, as shown in Fig. 1. The specimen consisted of a central square gauge area with dimensions of 30 mm × 30 mm, and four arms that extended from the central gauge area. Several parallel slots were machined into each arm so as to obtain a uniform stress field in the gauge area [37–41]. The narrow strips between slots can only transmit tensile force, which acts to ensure transversal flexibility and eliminate the constraint imposed by the lateral stiffness of the arms [42]. Owing to the absence of shear strain in the gauge area, the stress and strain measured at the central area represented the principal stress and strain. Thus, the stress could be obtained by dividing the applied load by the corresponding cross section.

The strain in the central gauge area was measured using the non-contact displacement detecting system (NDDS), which consists of a monophonic lamp and a charge coupled device (CCD) camera. Two pairs of parallel marker lines were drawn across the specimen's surface with ink-pencil in the central square region, as shown in Fig. 1 (b). The marker positions were tracked optically by NDDS, which recorded the exact displacement between them during the test and converted it to strain. With the NDDS and the measuring method, one can monitor the strain evolution of the membrane in two orthogonal loading directions simultaneously.

### 2.2. Loading path

Two directions named "x-direction" and "y-direction" were defined to distinguish the two orthogonal loading directions. To investigate the extent of the y-direction stress on the stress-strain evolution behavior in the x-direction, several loading paths were designed, including the proportional loading path (II), constant stress loading path (III), circular loading path (IV), rhombic loading path (V), and square loading path (VI), as shown in Fig. 2. The mean stress and loading period for all loading paths were 5.25 MPa and 10 s, respectively. For comparison, a uniaxial tension test was also performed and named the uniaxial stress loading path (I). It had the same parameters as the constant stress loading path (III) but zero stress in the y-direction. To keep the membranes taut, a pre-stress of 0.5 MPa was applied in both directions. All the experiments were performed under ambient conditions (20 °C and 40% RH). Cyclic