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Biaxial fatigue crack propagation behavior of perfluorosulfonic-acid membranes

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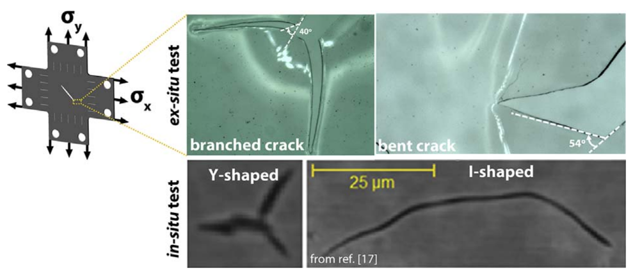
HIGHLIGHTS

- In-plane biaxial effect on fatigue crack propagation behavior is investigated.
- The introduction of transverse stress retards fatigue crack growth.
- Branched and curved cracks are observed under biaxial loading condition.
- Fatigue crack growth paths are discussed from a mechanical perspective.
- Crack after *ex-situ* fatigue test is similar in geometry to that after *in-situ* test.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluorosulfonic-acid membranes have long been used as the typical electrolyte for polymer-electrolyte fuel cells, which not only transport proton and water but also serve as barriers to prevent reactants mixing. However, too often the structural integrity of perfluorosulfonic-acid membranes is impaired by membrane thinning or cracks/pinholes formation induced by mechanical and chemical degradations. Despite the increasing number of studies that report crack formation, such as crack size and shape, the underlying mechanism and driving forces have not been well explored. In this paper, the fatigue crack propagation behaviors of Nafion membranes subjected to biaxial loading conditions have been investigated. In particular, the fatigue crack growth rates of flat cracks in responses to different loading conditions are compared, and the impact of transverse stress on fatigue crack growth rate is clarified. In addition, the crack paths for slant cracks under both uniaxial and biaxial loading conditions are discussed, which are similar in geometry to those found after accelerated stress testing of fuel cells. The directions of initial crack propagation are calculated theoretically and compared with experimental observations, which are in good agreement. The findings reported here lays the foundation for understanding of mechanical failure of membranes.

1. Introduction

Perfluorosulfonic-acid (PFSA) membranes are the most widely used ion-conductive membranes in polymer electrolyte fuel cells (PEFCs) for their superior mechanical and electrochemical properties [1,2]. In PEFCs, electrodes are separated by the membrane that is used as a solid-state electrolyte for proton transport and an electrical insulator for electron insulation. In addition, the membrane also functions as a separator to prevent reactants mixing and a structural framework to support catalysts [3]. Therefore, the structural integrity of the membrane is of vital importance for maintaining high performance and durability of PEFCs. During fuel cell practical operation, the structural

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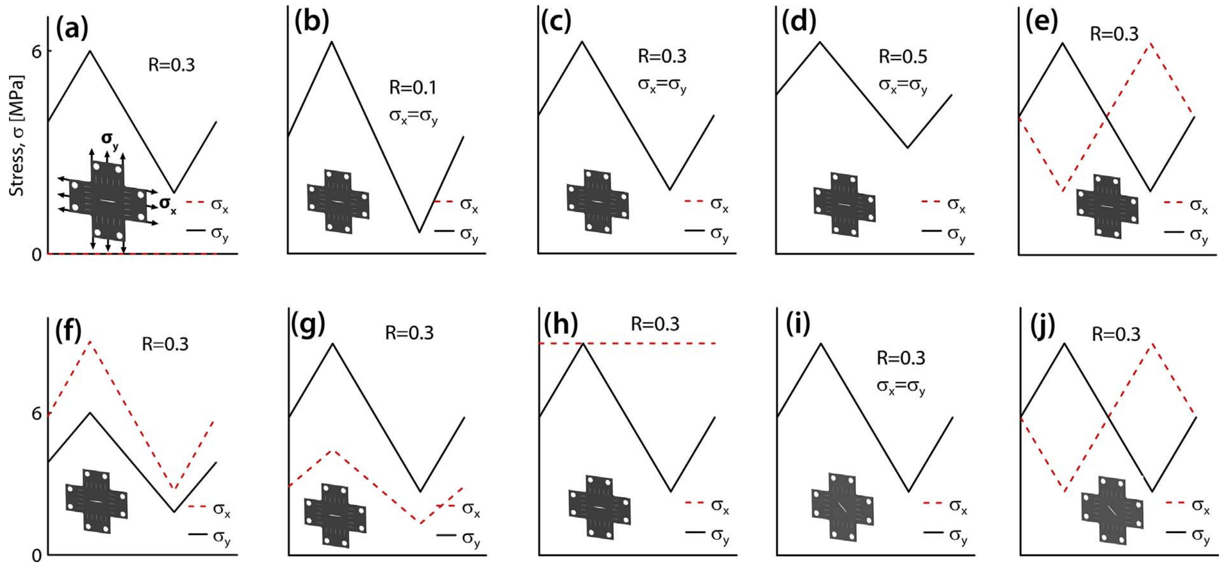

Fig. 1. Different biaxial loading paths: (a) represents uniaxial loading; (b)–(d) represent biaxial loading at different stress ratios where stresses of x and y directions are always the same; (e) represents 180° out-of-phase biaxial loading; (f)–(g) represent biaxial loading at biaxial stress ratios of 1.5 and 0.5, respectively; (h) represents constant stress of x-direction during biaxial loading; (i)–(j) represent in-phase and 180° out-of-phase biaxial loading of slant cracks.

integrity of membrane is frequently impaired by combined chemical and mechanical degradation which manifest themselves as membrane thinning, creep, delamination, cracks, pinhole etc. [4]. Among them, cracks formation and development in the membrane are considered as the lifetime-limiting failure mode for fuel fell applications.

Failure analysis is a common method to explore the possible failure mechanism of fuel cell during fuel cell durability research, where different techniques have been applied before, during and after fuel cell applications. Prior to fuel cell operation, cracks were found on the surfaces of membrane electrode assemblies which were thought to arise from manufacturing process and identified as the potential source for pinhole formation [5]. Defects in fuel cell catalyst layers could be detected during manufacturing process with the assist of infrared thermography as a quality control tool [6]. The same technique could also be applied on membrane defects detection during fuel cell operation [7–14]. During post-mortem analysis of failure membrane after fuel cell operation, scanning electron microscopy (SEM) might be the most widely used technique. Cracks of different lengths were found, ranging from several microns to hundreds of microns and even larger than 1 cm [15–19]. Additionally, cracks of different geometries and features were also found where both throughout and partially throughout cracks were observed in through-plane directions [8,16,20], and both branched and curved cracks were found in in-plane directions [8,17]. Regardless of the increasing number of studies concerning membrane failure modes and features, the underlying driving force and mechanism for pre-exist defect/crack to propagate is still unclear.

During fuel cell operation, the catalyst coated membrane is sandwiched between two gas diffusion layers where the planar constraint keeps the membrane in a nearly in-plane strain state. Upon water sorption or desorption, the constraint prevents membrane from swelling or shrinking, thus generating in-plane biaxial compressive or tensile stresses [21]. Hence, compared to uniaxial loading conditions, the biaxial loading conditions represent more closely to the actual stress state of membrane during fuel cell practical operation. The equibiaxial stress state had been produced by pressurized blister method where the strength, fatigue, creep behaviors of proton exchange membranes [22–24] had been investigated. To bridge the gap between stress-strain responses and fatigue behaviors, the in-plane biaxial cyclic mechanical behavior was also studied using cruciform specimens [25], and an elastic-viscoplastic model was established to describe the biaxial behavior [26]. Such investigations were mainly concerned with the mechanical behaviors under biaxial loading conditions before small cracks or defects were formed, i.e. the crack initiation period. However, such a period could not represent the whole lifetime of the proton exchange membrane in that more time was needed for cracks to propagate till failure. The fuel cells were found to run for additional 50% of the whole lifetime after the diagnostic of pinholes [27]. Such a phenomenon was ascribed to the presence of water that covered the surface of pinhole or cracks, preventing further crossover of reactants [19,27,28]. Till now, only the fatigue crack propagation behaviors of PFSA membrane under uniaxial loading conditions have been experimentally investigated [29]. In most cases, the fatigue crack propagation behaviors were studied through numerical simulations [30,31]. To have a better understanding of the fatigue crack propagation behaviors of PFSA membrane during fuel cell practical operation conditions, it is instructive to study the fatigue crack propagation behaviors under biaxial loading conditions.

Hence, the objective of this paper is to investigate the impact of biaxial stress state on fatigue crack propagation behaviors, with the aim of finding the underlying mechanism of crack growth under practical operation conditions of fuel cells. For this reason, the fatigue crack growth under different biaxial loading conditions will be compared, and the fatigue crack growth paths will be discussed. The findings in this paper are expected to provide insight into the understanding of failure mechanism of fuel cell membranes, which will potentially help optimize and develop ion-conductive membranes of higher mechanical durability.

2. Experiment

2.1. Materials and preparation

In this study, Nafion® 212 membranes in protonated (H^+) form from Dupont were used with the nominal thickness of 50 µm. Specimens were cut into cruciform shape using a sophisticated molding cutting die with the central gauge area dimension of 30 mm × 30 mm. Detailed description of cruciform specimen could be found in our previous work [25]. During biaxial fatigue crack propagation tests, center-cracked tension (CCT) specimens were used. The specimens were made by cutting notches at the middle of cruciform specimens using fresh razor blade to serve as stress concentration sites. Two kinds of notches were made: one is the notch that was either parallel or perpendicular to