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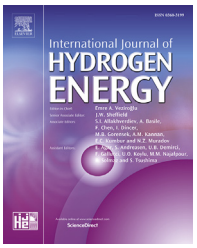

Exploring the role of reinforcement in controlling fatigue crack propagation behavior of perfluorosulfonic-acid membranes

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ABSTRACT

Reinforced composite membranes in polymer-electrolyte fuel cells (PEFCs) are attracting more and more attention due to their simultaneously superior durability and high performance. Despite its improved durability during accelerated stress testing, the underlying mechanism of reinforcement in improving mechanical durability, particularly the crack propagation resistance, has not well been investigated. In this paper, we report the fatigue crack propagation behaviors of reinforced Nafion XL membrane and unreinforced Nafion 212 membrane. It is found that the fatigue crack growth rate of Nafion 212 membrane depends on stress ratios, and that of Nafion XL membrane depends on initial crack length and membrane orientation. In addition, the microstructure changes of reinforced Nafion XL membrane are examined through microscopy studies where two distinct features are observed: crack propagation in outer ionomer layers and interfacial delamination. These two features well explain the distinct fatigue crack propagation behavior of Nafion XL membrane, such as slow and almost constant fatigue crack propagation rate. The findings reported here are not only beneficial for understanding fatigue crack propagation mechanism of reinforced composite membrane but also helpful for designing and optimizing composite ion-conductive membranes.

Introduction

Polymer-electrolyte fuel cells (PEFCs) have attracted a great deal of attention as a promising green energy conversion technology used for automotive applications. Significant progress has been made toward the widely commercialization of PEFCs through improvements in performance, durability and cost reduction from both components developments and systems design [1,2]. One component of particular importance is perfluorosulfonic-acid (PFSA) ionomer membranes which act as solid electrolyte to separate reactant gases from mixing, i.e. H_2 and O_2, while conduct proton from anode to cathode electrode as well as to support electro-catalysts. Thus, the structural integrity is of vital importance for the performance and durability of PEFCs. During hydrogen fuel cell operation, two mechanisms are thought to affect the durability of PFSA membranes: chemical degradation and mechanical degradation [2–6]. While

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chemical degradation is caused by hydroxide radicals formed during fuel cell electrochemical reactions, mechanical degradation results from swelling-induced cyclic mechanical stress imposed on the membrane during relative humidity (RH) cycling of a constrained membrane [7–10]. These two mechanisms act synergistically to affect the durability of membrane. Chemical degradation attacks the main chain or side-chain of the membrane, leading to membrane decomposition and introducing defects in the membrane [4]. The defects act as stress concentration regions which are enlarged and grow under the cyclic mechanical stress during mechanical degradation, resulting in more gases to crossover which in turn exasperate chemical degradation [11–13].

Thus continuous efforts have been done to address the durability issue of proton exchange membrane. However, a great challenge exists to simultaneously meet the requirements of durability and performance in that methods used to increase membrane conductivity tend to reduce its durability. For instance, to achieve higher durability, thicker membranes are preferred in that the gas crossover resistance is higher in the membrane and thus lower chemical degradation rate [14,15]. However, this is achieved at the expense of higher proton and water transport resistance due to the thickness of the membrane, which will inevitably lower the membrane performance. Another way to increase the durability of PFSA membranes is to use membranes with higher equivalent weight (EW) either through increasing backbone length or side-chain length which possess higher swelling stability and mechanical integrity [1,16–19]. In addition, it is found that higher EW membranes shows higher durability due to the less likely of side chain attack by radicals form during fuel cell operation as less side chains are present in such membrane [20]. However, the acid concentration in these high EW membranes is low, and thus brings about low conductivity. An alternative way to address this issue is to use composite membrane that incorporates a reinforcement layer, such as expanded polytetrafluoroethylene (ePTFE), to increase the dimensional stability during humidity cycling. A particular example is Gore-Select membrane [21] manufactured by W. L. Gore & Associates, Inc. and Nafion XL membrane [22] manufactured by Dupont. Because of the additional mechanical strength and dimensional stability brought about by ePTFE reinforcement layer, thinner membranes and lower EW ionomers could be used that otherwise have insufficient mechanical strength. The overall composite membrane was shown to have almost comparable conductivity with widely used Nafion 212 membrane [23]. During accelerated stress testing (AST), Nafion XL membrane [24] and Gore-Select membrane [25] as well as other reinforced composite membranes [26–29] all show superior durability with longer lifetime. The high strength [30–32], high toughness [33] and better resistance to creep and fatigue [34], to some extent, might explain the higher durability of reinforced composite membranes. Nevertheless, still more efforts are needed to elucidate the mechanical degradation mechanism, especially considering the fact that membranes are failed under cyclic loading instead of static force.

The common failure modes of PFSA membranes induced by mechanical degradation are pinholes or cracks. These defects either originate from chemical decomposition during fuel cell operation or gas diffusion layer fibre penetration during fuel cell assembling [13]. The presences of pinholes or cracks do not lead to overall fuel cell failure immediately. Instead, the pinholes or cracks will propagate under cyclic mechanical stress until reaching a certain size. The crack sizes after fuel cell failure are found within tens to several hundred microns, and even larger than 1 mm [35–40]. During practical operation, the fuel cell was found to run for additional 300 h (total life of 650 h) after the diagnostic of pinhole formation, accounting for about 50% of the whole fuel cell lifetime. This demonstrates that the crack propagation stage of PFSA membranes accounts a significant fraction of fuel cell lifetime, and this period can never be overlooked. The normal operation of fuel cell at the presence of pinholes is attributed to the generation of water during fuel cell operation, which covers the surface of pinholes or cracks, preventing reactant gases from further crossover [37,41,42]. The fatigue life of PFSA membrane consists of two stages: crack initiation and crack propagation. While fatigue initiation has been well understood [43–48], the crack propagation behavior is not well investigated. Recently, numerous attempts have been made to understand the crack propagation behavior of PFSA membranes, despite the fact that most studies are done using modelling and simulation methods. Kusoglu and Weber [49] developed a mechanistic approach to model pinhole growth in PEFC membranes and found that increase in pinhole radius strongly depended on tensile stresses and plastic strain increment. For macro cracks, Ding et al. [50] numerically simulated fatigue crack propagation of PFSA membranes by adopting a crack propagation criterion based on plastically dissipated energy and obtained crack growth rate directly from finite element simulations. Nevertheless, almost no paper in the literature measured fatigue crack propagation rate experimentally. Until very recently, Singh et al. [51] measured the crack growth rate of Naifon 211 membrane over a range of stresses, temperatures and relative humidities, and stated that temperature imposed stronger impact on the crack propagation rate than relative humidity. For the more durable reinforced composite membrane where fatigue crack propagation accounts for a much larger proportion of the whole fatigue life than unreinforced Nafion 212 membrane, fatigue crack propagation could not be neglected. Regardless of the importance of fatigue crack propagation in reinforced composite PFSA membranes, it has never been measured experimentally. In particular, the role of reinforcement layer during fatigue crack propagation has never been elucidated.

The objective of the present work is to quantitatively characterize the crack propagation of PFSA membranes through fatigue crack propagation experiments, including reinforced Nafion XL membrane and unreinforced Nafion 212 membrane. In addition, the mechanism of reinforcement layer in improving the fatigue crack propagation resistance will be clarified, and the role of reinforcement will be well explored. This work is expected to provide insight into the understanding of fatigue crack propagation behavior of reinforced PFSA composite membrane and designing of new composite membranes.

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