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Understanding the formation of pinholes in PFSA membranes with the essential work of fracture (EWF)

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ABSTRACT

One of the most harmful degradation process in PEM fuel cell is the development of pinholes in the membrane. There is therefore a need for an effective experimental characterization to allow *ab initio* membrane comparison. In this paper, the mechanical fracture resistance of various PFSA membranes was studied using the essential work of fracture (EWF) and tensile tests. PTFE reinforced membrane better resists pinholes formation due to its high resistance to crack initiation and propagation. Additionally, energy partitioning showed that the necking and tearing stage of the layered structure membrane accounts for the main part of the total fracture energy due to enhanced plastic deformation of PTFE. Moreover, cracks were found to initiate and propagate easily in the direction parallel to the polymer chains which suggest that the fracture control could be optimized by pointing the direction of the gas channel perpendicularly to the orientation of the polymer chains, *i.e.* to rolling process during manufacturing. Finally, EWF technique was found to be more relevant for assessing the differences in the mechanical behaviour of the membranes compared to standard tensile tests.

1. Introduction

To secure long-term durability and efficiency of proton exchange membrane (PEM) for fuel cells, perfluorosulfonic acid (PFSA) based membrane must demonstrate long-term electrochemical and mechanical integrities [1–4]. One of the failure modes that limits the lifetime of the fuel cell involves the fracture of the membranes. The mechanisms of pinhole formation and subsequent crack growth and propagation are complex and not fully understood. Nonetheless, those defects are likely to result from the combination of chemical and mechanical effects. Variations in the temperature and humidity during operation cause hydrothermal stresses in constrained membranes and MEA [5–8]. A considerable thinning of the membrane was reported under fuel cell operation or OCV due to massive ionomer loss throughout the active area caused by radical attacks [9,10]. Mud cracks of different depths, typically present in the electrodes can cause delamination and/or cracking of the PEM membranes [11]. In a recent work, SEM photomicrographs around the detected flaws revealed linear cracks in the membrane essentially oriented in the direction of the gas path which points out the sharp edges of the gas channels [12]. Platinum catalyst dissolution and recrystallization, cationic contaminants are also believed to contribute to the embrittlement of polymer electrolyte membranes [10]. Consequently, this can lead to reactant gases crossover, localized heating and ultimately the failure of the membrane and thereby

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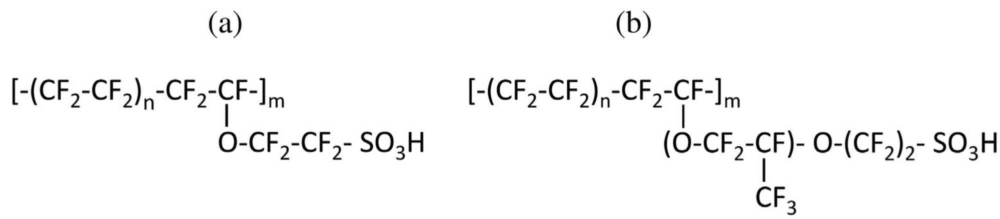

Fig. 1 – Chemical structures of PFSA membrane – (a) Short Side Chain (SSC) type membrane, (b) Long Side Chain (LSC) type membrane.

of the entire system. One of the possible ways to prevent pinhole formation and extend the lifetime of PEM fuel cells relies on the use of reinforced membranes. Mechanical reinforcement with expanded PTFE sheets combined usually with thinner membranes provided high membrane conductance, improved water distribution in the operating fuel cell, less dimensional variation and improved performance without scarifying durability [13]. In reinforced membrane, H_2 crossover rate increased gradually while non reinforced membrane displayed a sudden and drastic jump [14]. While mechanical reinforcement can extend the lifetime, there is no clear understanding of the mechanisms that govern the mechanical behaviour of the reinforced material compared to non reinforced ones.

Mechanical properties of PFSA membranes are usually characterized using tensile tests [9], however few works dealt with the essential work of fracture (EWF) tests, a method widely used to characterize fracture of polymers, related blends and composites [4,15–19]. Does the better mechanical durability of reinforced membrane result from better tensile properties or fracture toughness? Is it the young modulus or the tear resistance that controls the mechanical behaviour of PEM during fuel cell operation?

2. Experimental

2.1. Membranes

Membranes used in this study were provided by Solvay Speciality Polymers and Ion power Inc. All samples were pretreated in an aqueous 10 wt.% in HNO_3 solution for at least 3 h at 80 °C followed by a treatment for 1 h in UHQ water at 80 °C. Three types of PFSA membranes can be distinguished: (i) homogeneous LSC membrane, (ii) homogeneous SSC membrane, (iii) PFSA/PTFE composite membrane. The chemical structures of SSC and LSC membranes are shown in Fig. 1. XL100 composite consists of microporous PTFE impregnated on both sides with an LSC type PFSA solution with an equivalent weight of 900 g/mol. The thickness of the different layers is 9/12/9 μm [20]. The ion exchange capacity of the different layers was estimated by different techniques [20] however in this paper, only the overall equivalent weight was mentioned in Table 1.

Table 1 – Property of commercially available membranes.

Commercial reference	Supplier	EW ($g\ eq^{-1}$)	Type	Acronyms
Aquivion® E110	Solvay Speciality Polymers	1100 ± 20	SSC	SSC-110
Nafion® 111	Ion Power	1100 ± 30	LSC	LSC-110
Nafion® XL100		1100 [17]	LSC/PTFE	XL-100

2.2. Double edge notched tensile test (DENT)

The concept of EWF tests was well described by Cotterell and Reddel [21]. Based on Broberg [22–24], the non-elastic crack tip can be divided into two parts:

- An inner "fracture zone", where the tearing process occurs.
- An outer "plastic zone", where the plastic deformation and dissipative process occurs.

During the crack propagation, a significant amount of energy dissipated in the plastic zone is not directly associated with the fracture process. The total fracture energy can be divided into two components. One component $\overline{We}$ corresponds to the term that characterizes the process zone and the other $\overline{Wp}$, the plastic zone as described in Eq. (1)

$$\overline{Wf} = \overline{We} + \overline{Wp} \tag{1}$$

where $\overline{Wf}$ is the total fracture energy, $\overline{We}$ is the essential work of fracture used in the process zone and $\overline{Wp}$ is the non-essential work of fracture dissipated in the outer plastic zone.

The EWF test should preferably be applied to films, which can be assumed to be in plane stress conditions. $\overline{We}$ is then proportional to the ligament length, L, while $\overline{Wp}$ is proportional to the square of the ligament length, L^2 as described in Eq. (2)

$$\overline{Wf} = w_e L t + \beta w_p L^2 t \tag{2}$$

where w_e is the specific essential work of fracture (work per unit area), w_p is the non-essential work of fracture (plastic work density), L is the ligament length of the specimen Fig. 2a, t is the thickness of the specimen, and β is the shape factor that is related to the formation of the plastic zone. The specific work of fracture, $w_f = \overline{Wf}/Lt$ is given by Eq (3):