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Correlations to Predict In-situ Durability of Polymer Electrolyte Membranes in Fuel Cells

G. DiLeo, R. Yadav, N. Dale, K. Adjemian

Nissan Technical Center North America
39001 Sunrise Drive, Farmington Hills, MI-48331, USA

The durability of polymer electrolyte membranes (PEM) must be understood and improved for successful commercialization of PEMFC vehicles. In this work, empirical correlations - "chemical stability factor (CSF)" and "mechanical stability factor (MSF)" - based on ex-situ tests have been defined and developed to predict in-situ chemical and mechanical durability of PEMs in order to save in-situ testing time and resources.

PEM chemical degradation occurs through a mechanism in which free-radicals ($OH^{\cdot}$, $OOH^{\cdot}$) chemically attack the weak end (R_f-COOH) and side (R_f-SO_3H) groups in the PEM leading to a loss of HF, CO_2 and $-SO_3H$ (1). This degradation causes PEM materials loss, gas crossover increase and performance loss. From this mechanism, it is evident that fluoride emission (HF formation), O_2 crossover (free-radical formation) and EW (concentration of functional groups) are important parameters in measuring PEM chemical degradation. PEM mechanical degradation occurs primarily as a result of cycling between dry and wet conditions. Dry-wet cycling causes stress, fatigue and creep leading to PEM degradation, material loss, gas crossover increase, delamination, and performance loss. The membrane's tensile properties, EW, swelling, and gas crossover are important parameters in determining its mechanical durability. The above-mentioned properties for chemical and mechanical degradation measured in ex-situ tests are related to develop the CSF and MSF to predict in-situ chemical and mechanical durability of PEMs, respectively.

The optimized CSF can predict the relative in-situ chemical durability behavior of a variety of membranes in an accelerated stress test (AST). During the AST for in-situ chemical durability, MEAs are tested at 90°C and 30% RH under OCV hold conditions and voltage loss is monitored. These irreversible losses are due to PEM degradation, show linear voltage decay, and are a measure of in-situ chemical durability. CSF as shown in Eqn. [1] is derived from membrane properties measured ex-situ, and correlated to the in-situ voltage degradation rate. Preliminary results using preliminary correlation are shown in Fig. 1. The use of CSF to screen and select the most durable PEMs can save significant in-situ testing time and resources.

$$CSF = f(EW, FER, OCR, \ldots) \qquad [1]$$

The MSF can predict the relative in-situ mechanical durability of a variety of membranes during an AST. For the in-situ mechanical durability AST, MEAs are tested at 80°C under dry-wet cycling in which the MEAs are exposed to dry, wet, and OCV hold condition in one cycle. The OCV of the MEA is monitored and used to determine membrane failure. PEM properties measured ex-situ are related to develop MSF as shown in Eqn. [2], and it is correlated to the number of cycles to failure in the in-situ AST. Preliminary results using preliminary correlation are shown in Fig. 2. MSF is a modified form of a stability factor reported in the literature (2). MSF can predict the relative trend in in-situ mechanical durability of variety of PEMs, and help save significant in-situ testing time and resources.

$$MSF = f(Strain, Swelling, EW, OCR, \ldots) \qquad [2]$$

A variety of PFSA-type (reinforced and non-reinforced) PEMs with different equivalent weights, thicknesses and side-chain lengths is used to develop the Stability Factors to ensure their validity over a wide range of PEMs. The dependence of the CSF and MSF on the appropriate membranes properties is calculated. In this study, the chemical stability factor and the mechanical stability factor will be presented in their optimized form. This study shows the reliability of these factors to predict the lifetime in AST for a variety of PEMs.

References

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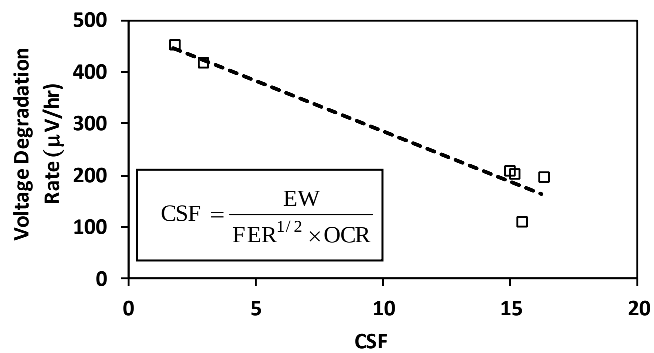

Fig. 1 Preliminary CSF correlation to Voltage Degradation Rate in OCV Hold AST using preliminary CSF correlation as discussed in (3).

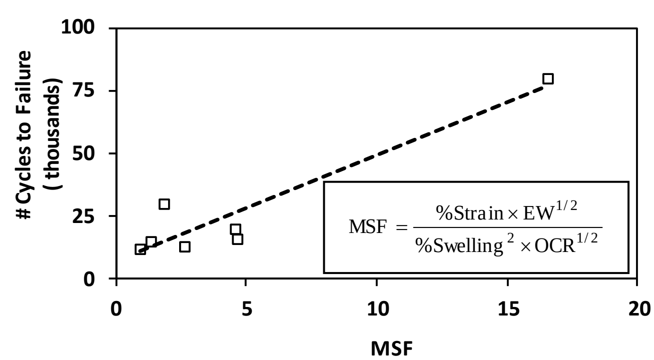

Fig. 2 Preliminary MSF correlation to Cycles to Failure in Dry-Wet Cycling AST using preliminary MSF correlation as discussed in (3).