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Short communication

Use of mechanical tests to predict durability of polymer fuel cell membranes under humidity cycling

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ABSTRACT

A mechanical fatigue life analysis of the type used for lifetime predictions in structural materials has been adapted to characterize PEM fuel cell membranes. It is shown that a stress vs. cycles-to-failure (*S–N*) curve analysis is capable of: (1) predicting the mechanical durability of PEM membranes under humidity cycling, and (2) assessing the fraction of membrane life remaining in degraded MEAs. Mechanical fatigue testing was performed in a dynamic mechanical analyzer (DMA) at 60 °C and 90% relative humidity (RH) under different values of stress amplitude, and the results were used to plot the *S–N* curve. The stress amplitude for the *S–N* curve was then mapped to the equivalent change in RH as a methodology for characterizing membrane mechanical resistance to humidity cycling.

1. Introduction

It is known that the durability of PEM fuel cells can be limited by membrane resistance to mechanical failure [1–4], and there have been numerous publications concerning the membrane mechanical characteristics/durability [5–10]. However, these articles focus on the tensile strength and ductility changes in membranes subjected to chemical and mechanical degradation. Such measurements of mechanical response under monotonic uniaxial loading are not representative of the constraints under which the MEAs operate, and thus these observations cannot form the basis for membrane life prediction methodologies.

PEM fuel cell membranes undergo frequent mechanical stress and strain variations due to water content changes resulting from varying load on the cell, particularly in transportation applications. At high relative humidity levels, membrane water content increases and the membrane expands. At lower humidity levels, the opposite occurs and the membrane contracts. Stress arises as a result of this strain because the membrane is constrained by a seal adjacent to the inlet and by the axial loading of the stack. This situation, in which the membrane experiences a cyclic stress, is analogous to the circumstances under which structural materials undergo mechanical fatigue. Fatigue failure can occur in metals and polymers under cyclic stresses at stress levels far below that required to cause failure under monotonic loading; this is due to the accumulation of damage/defects in each cycle, which can lead to failure over large numbers of cycles. Fatigue data are typically represented on *S–N* curves which show the variation in number of cycles to failure, *N*, against stress amplitude, *S* [11]. In this work, it is proposed that internal stresses experienced by the membrane as a result of in-cell humidity cycling can be simulated by ex situ stress cycling, i.e. mechanical fatigue testing. Thus, mechanical fatigue testing can be used to evaluate membrane resistance to mechanical failure caused by humidity cycling. Although there have been recent attempts to address this issue using cyclic pressurized blister testing [12,13], the experimental set-up is relatively involved and the data reduction required is complex [14]. Furthermore, the correlation of such test data with the magnitude of the humidity cycling has not been made directly. Here we report a much simpler approach based upon DMA cycling; this methodology enables the prediction of membrane life in fuel cells operated under cyclic conditions. Moreover, DMA fatigue testing can also be used to evaluate degraded membranes and thus to assess the amount of life remaining.

2. Experimental

Mechanical fatigue testing has been performed to characterize membrane resistance to mechanical failure under cyclic loading. Details regarding the MEAs investigated and the test procedures used in this study are described below.

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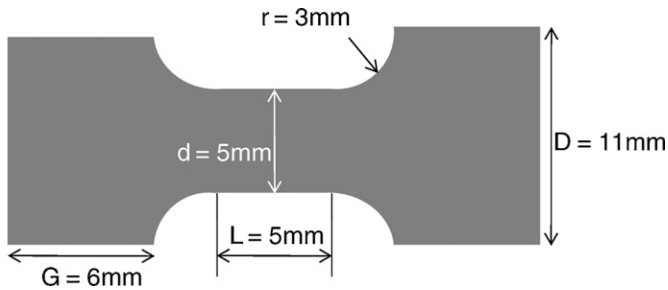

Fig. 1. Schematic diagram of the dog-bone sample geometry used.

2.1. MEA samples

Commercially available PRIMEA® MEAs have been used for the current study. Fig. 1 shows the dog-bone geometry of the samples extracted from the MEAs for the cyclic fatigue testing. The samples had a gauge length of 5 mm and a width of 5 mm. It is noted that this sample geometry does not follow the ~5:1 length:width ratio required for ASTM standards. This non-standard geometry was adopted both to accommodate the very limited extension that can be achieved with the DMA instrument used in this study and to facilitate the extraction of specific/localized areas in post-mortem cells. For this study, samples were extracted from as-received MEAs in two orthogonal directions, which are designated the transverse and longitudinal directions as shown in Fig. 2. The results of the fatigue tests performed on these samples were then used to construct the *S–N* curves for the MEAs. In addition, testing was carried out on degraded MEA samples taken from full size fuel cells that had been operated to failure. Since these latter samples were taken from MEAs in which the membrane had already failed (as revealed by fuel-to-air cross-over), the DMA samples were extracted from the intact regions of the MEA to assess the accumulative damage (or remaining life) of the membrane at these regions.

2.2. Mechanical fatigue testing

Mechanical fatigue testing was performed using a Q800 DMA from Thermal Analysis Instruments. The Q800 DMA is equipped with an environmental chamber that is capable of maintaining a relative humidity (RH) of up to ~93%. For the majority of this study, tests were performed at 60 °C under 90% RH in N_2 using a cycle frequency of 10 Hz. The samples were equilibrated in the unloaded condition for ~100 min prior to cyclic (sinusoidal) stress testing at different stress amplitudes. For each value of the stress amplitude, multiple tests were performed. In all cases, the minimum stress was set at 20% of the maximum stress. Since MEA (as opposed to bare membrane) samples were used in the current study, the actual stress is calculated based on the assumption that the membrane is the only load-bearing component in the MEA, i.e. the catalyst layers do not bear any load. For instance, for a nominal stress of 2.0 MPa, the actual stress is calculated as:

$$\frac{2.0\,\text{MPa} \times 40\,\text{mm}\,(\text{thickness of MEA})}{18\,\text{mm}\,(\text{thickness of membrane})} = 4.44\,\text{MPa}.$$

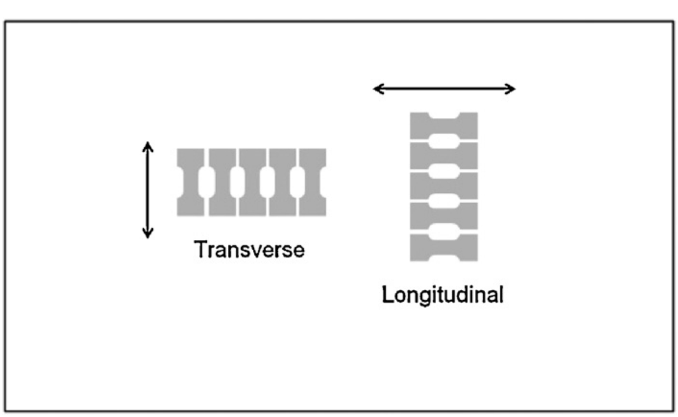

Fig. 2. Schematic diagram showing the orientations of the samples extracted from the as-received MEA.

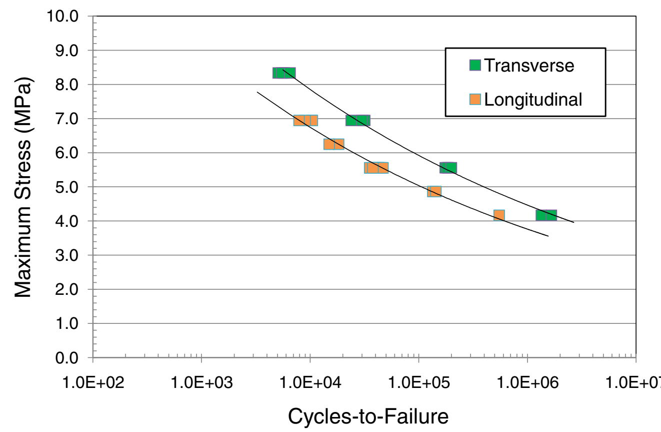

Fig. 3. Mechanical fatigue data for samples extracted from the as-received MEA in the transverse and longitudinal directions (60 °C, 90% RH, 10 Hz in N_2).

2.3. Fixed strain testing

In addition to the cyclic stress tests described above, static tests were also performed by measuring the stress induced in samples held at a fixed length while changing the relative humidity. Each sample was first equilibrated to 90% RH for ~100 min under zero load. A nominal strain of 0.2% was then applied to straighten the sample before humidity cycling. The RH was then stepped down to 30% or 10% and ramped back up to 90% for multiple times and the DMA response was used to monitor the induced stress. The purpose of these tests was to establish the amplitude of the mechanical stress associated with membrane dry-out as a result of reduced humidity. This enables the fatigue response of the MEAs measured in cyclic stress testing to be related directly to the humidity cycling experienced during operation (i.e. stress ↔ ΔRH).

3. Results

3.1. Mechanical fatigue S–N curve

As-received PRIMEA® MEA samples were subjected to mechanical fatigue testing at various stress amplitudes. On average four samples were tested at each value of the stress amplitude. The results were used to plot *S–N* curves for the MEA as shown in Fig. 3. Since the values obtained from the samples oriented in the transverse and longitudinal directions are different, the data are plotted on two separate *S–N* curves. For the stress amplitudes used in this study (i.e. between 4.17 MPa and 8.33 MPa), the membrane failed after 10^7 to 10^3 cycles. These *S–N* curves show that the membrane exhibits characteristics that are typical for polymeric materials. In addition, it is noted that, at a given stress amplitude, the PRIMEA® MEA exhibits a greater resistance to fatigue failure in the transverse direction than in the longitudinal direction. This is presumably due to structural anisotropy in the plane of the membrane that arises as a result of the manufacturing process used by W.L. Gore & Asso-

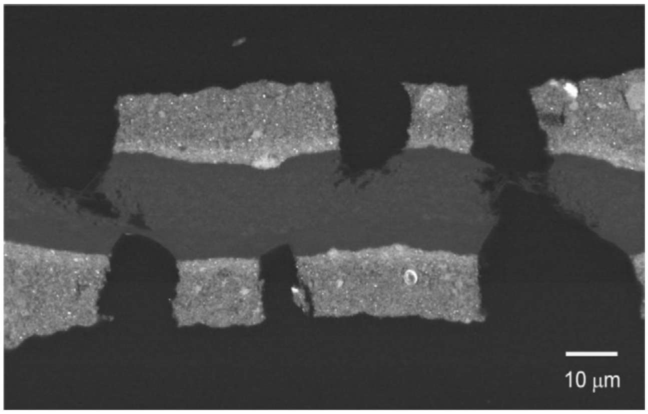

Fig. 4. Backscattered electron SEM image obtained from a cyclic fatigue tested MEA.

ciates (Gore). Fig. 4 is an SEM image obtained from a sample fatigue tested at a stress amplitude of 5.56 MPa. Multiple through-plane cracks can be observed and these appear to have initiated in the catalyst layers.

3.2. Fixed strain test

To measure the mechanical stress induced by humidity cycling, samples of as-received Gore PRIMEA® MEA were subjected to a fixed strain experiment whereby the samples were held at a constant length while the relative humidity was changed in fixed increments of 2% (instrument maximum capability). The stress required to maintain the constant sample length was recorded during the experiment. The results for the samples oriented in the longitudinal direction at 60 °C are shown in Fig. 5(a). The stress can also be plotted with respect to ΔRH which is presented in Fig. 5(b). It is concluded that reducing the RH level from 90% to 70%, 50%, 30% and 10% leads to stresses of 2.8, 4.3, 5.3 and 6.3 MPa, respectively. It should be noted that these stress values are likely to be lower than the actual stress that the membrane experiences in fuel cell applications where the humidity cycling is more rapid. In the fixed strain tests reported here, stress relaxation reduced the apparent stress endured by the membrane as the duration of the test was relatively long. Evidence for this stress relaxation process can be observed on the stress curve in Fig. 5(a): there are serrations visible in the magnified inset, and a significant drop in stress following the application of 0.2% initial strain to the MEA prior to humidity cycling.

We note that the stress values associated with reducing RH in the samples oriented in the transverse direction are identical to those in the samples oriented in the longitudinal direction.

3.3. Degraded MEA

Fatigue testing was also performed as a post-mortem evaluation of a degraded MEA. The MEA used was removed from a stack that had been operated to failure. Samples were extracted from portions of the MEA away from the failure site, and these samples were subjected to cyclic stress testing at 60 °C and 90% RH. At a maximum stress value of 5.56 MPa, the samples failed after only 1000–2000 cycles. We note that the number of cycles-to-failure for the as-received samples at this stress amplitude was ∼40,000 (Fig. 3); it is therefore concluded that the remaining life for this region of the degraded MEA is less than 5%.

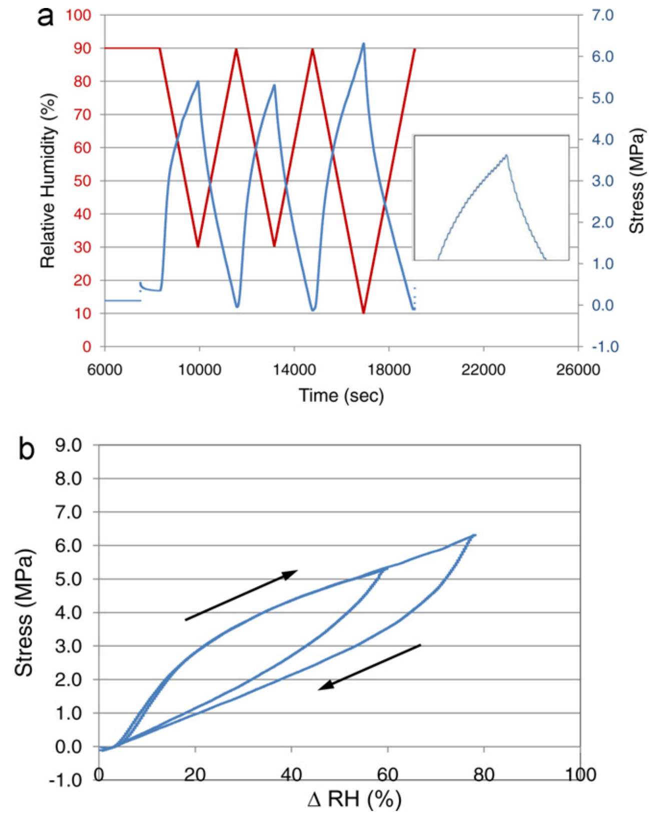

Fig. 5. (a) Effect of RH cycling on stress in as-received MEA samples: the blue trace represents the stress that the membrane experiences, and the RH variation is shown in red. (b) Mechanical stress induced expressed as a function of ΔRH (multiple RH cycles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Discussion

4.1. Membrane mechanical durability under humidity cycling

Currently there is no validated ex situ methodology that can be used to characterize membrane durability under humidity cycling conditions (different ranges of RH cycling). It is proposed that the stress applied in DMA tests can be translated to the amplitude of relative humidity cycling that the membrane experiences in the fuel cell. Therefore, the durability of a PEM fuel cell can be estimated. Based on the results obtained from the fixed strain tests (Fig. 5), the magnitude of the stress induced by a change in relative humidity (ΔRH) can be established. The *S–N* curves measured from cyclic stress testing (Fig. 3) can then be converted to ΔRH vs. cycles-to-failure (i.e. ΔRH–*N*) curves. Fig. 6 shows the relationship between ΔRH and cycles-to-failure for as-received MEAs. It is envisaged that such plots can be used to guide PEM fuel cell design; for a given durability requirement (i.e. number of cycles), the maximum ΔRH that the membrane can withstand may be predicted. For instance, for a durability requirement of 10^6 cycles, the maximum ΔRH to which the membrane could be subjected is ∼30%. It should be noted that although the membrane's mechanical durability is different in the two orthogonal directions investigated, under humidity cycling the stress experienced by the membrane in the two directions will be identical. Thus, the overall durability of the MEA will be limited by the weaker orientation, i.e. the longitudinal direction for the MEA studied here.

The SEM image shown in Fig. 4 indicates that cracks initiated in the catalyst layers can propagate into the membrane and potentially lead to the on-set of membrane failure. Therefore the fatigue

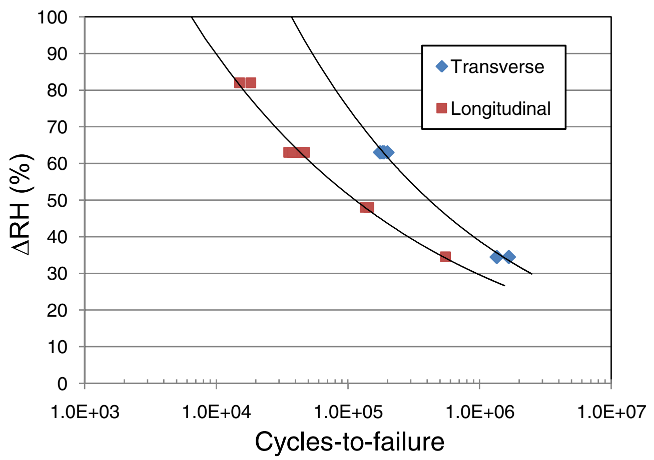

Fig. 6. Membrane failure resistance (ΔRH–*N*) curves obtained by converting the stress amplitude in the *S*–*N* curves shown in Fig. 3 to an equivalent change in RH.

data obtained here may have been affected by the weaker catalyst layers. We postulate that the durability of bare membranes, i.e. those not bonded to catalyst layers, could be higher than those reported in the current study. Further experimental work would be required to confirm this hypothesis.

4.2. Remaining life of degraded MEA

Similarly, there is currently no well-established methodology in the open literature for evaluation of life remaining in degraded membranes. Post-mortem analyses of cells that have not failed often consist of measurements of membrane thickness or uni-axial tensile testing of the membranes. Neither of these methods provides a quantitative estimate of remaining life. In this study, it is suggested that fatigue testing of degraded samples can form the basis of a methodology for quantitative predictions of remaining life. Thus, by comparing the fatigue data from the degraded samples with baseline *S*–*N* data obtained from virgin membranes, the remaining life of a non-failed cell can be estimated. For instance, consider the degraded MEA samples taken from a failed stack and subjected to DMA testing at 5.56 MPa that failed after ∼1500 cycles (Section 3.3). It can be estimated that the remaining life of this degraded sample is <5% (∼1500/∼40,000). Such tests could be applied both to in situ (e.g. accelerated stress testing) and to ex situ (e.g. Fenton testing) degraded membranes.

5. Conclusion

A methodology for the characterization of mechanical durability in PEMFC membranes under humidity cycling has been presented. It has been shown that the stress state that the membrane experiences during the humidity cycling, which arises as a result of load cycling in a fuel cell environment, can be simulated using *ex situ* mechanical fatigue testing. Thus, such testing can be used to evaluate membrane failure resistance under relative humidity cycling. In addition, fatigue testing can be used in post-mortem analyses to assess the remaining life of degraded membranes.

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