Tension-Torsion Fatigue Tests on the proton Exchange membrane Nafion 115, used in fuel cells

Ensayos de fatiga por tensión-torsión en la membrana de intercambio de protones Nafion 115, utilizada en las pilas de combustible

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ABSTRACT

Fatigue tests under tension-torsion have been carried out on the membrane Nafion 115 (Perfluorosulfonic acid, PFSA). This polymeric material is a main component to construct fuel cells, used as proton exchange membrane. These membranes undergo mechanical loading of tension and torsion during its industrial life. A self-designed machine has been constructed to obtain the fatigue endurance on this polymeric material under tension-torsion and the following conditions: one magnitude for the torsion angle, five initial tensile stresses, room temperature, and environmental relative humidity, and frequency of 1.6 Hz. The experimental results show that fatigue endurance decreases with the increase of tensile stress when the torsion angle remains constant, as well as temperature and relative humidity (both taken at environmental conditions). Fracture surfaces were analyzed by SEM, in order to investigate the principal trends of crack initiation and propagation under this modality of fatigue loading.

Keyword: Nafion 115, Fuel cells, Tension-torsion, Fatigue resistance, Fracture surfaces.

RESUMEN

Se han realizado ensayos de fatiga bajo tensión-torsión en la membrana Nafion 115 (ácido perfluorosulfónico, PFSA). Este material polimérico es un componente principal para la construcción de pilas de combustible, utilizado como membrana de intercambio de protones. Estas membranas se someten a cargas mecánicas de tensión y torsión durante su vida industrial. Se ha construido una máquina de diseño propio para obtener la resistencia a la fatiga de este material polimérico bajo tensión-torsión y en las

siguientes condiciones: una magnitud para el ángulo de torsión, cinco tensiones iniciales de tracción, temperatura ambiente y humedad relativa ambiental, y frecuencia de 1,6 Hz. Los resultados experimentales muestran que la resistencia a la fatiga disminuye con el aumento de la tensión de tracción cuando el ángulo de torsión se mantiene constante, así como la temperatura y la humedad relativa (ambas tomadas en condiciones ambientales). Las superficies de fractura fueron analizadas por SEM, con el fin de investigar las principales tendencias de iniciación y propagación de grietas bajo esta modalidad de carga de fatiga.

Palabra clave: Nafion 115, Pilas de combustible, Tensión-torsión, Resistencia a la fatiga, Superficies de fractura.

1 INTRODUCTION

Proton exchange membranes (PEM), destined to fuel cells have been introduced at the end of last century [1-3], as electrolytes of new sources for clean renewable energy and electricity production [4]. Even if the physicochemical properties of these materials have been studied the last 25 years [5, 6], the mechanical properties of PEM have been less analyzed and understood [7, 8].

During use in fuel cells, PEMs may undergo mechanical loading, which include tension and torsion; nevertheless, very limited studies have been conducted in this matter in the knowledge of the authors. The durability is one of main problems for polymers used as PEM; in turn, this is related to thermic, physicochemical and mechanical loading [9,10]. Furthermore, the mechanical behavior of PEM is highly dependent on the loading magnitude and rate, as well as temperature [11,12]. Mechanical loading in PEMs induces damage by sliding, bond rotation and entanglements or cross-links at the scale of polymeric chains [13], and it is well recognized that elastic modulus and yield strength of PEMs decrease notably with temperature and less with humidity [14, 15]. Since the use of Nafion 115 as PEMs is subjected to different loading, including tension and torsion, temperature, humidity and ultraviolet rays, it is of main interest to carry out mechanical testing to assess its behavior in fuel cells.

2 MATERIALS AND METHODS

2.1 MATERIALS

Polymeric material Nafion 115 was obtained from the Fuel Cell Store society, College Station, Texas, USA. Rectangular strips of this polymer were used for experimental tests of tension-torsion; Figure 1 shows the dimensions (mm) of testing strips.

Figure 1. Dimensions (mm) of the experimental Nafion 115 strip and image.

In Table 1 are listed the main physical and mechanical properties of tested Nafion 115.

Table 1: Main physical-mechanical properties of Nafion 115

Specific Gravity	1.98
Basis Weight 250 g/m ²	250 g/m ²
Tensile Modulus (50% RH, 23 °C)	249 MPa
Tensile Strength (50% RH, 23 °C)	43 MPa
Elongation at Break, % (50% RH, 23°C)	225
Tear Resistance – Initial (50% RH, 23°C)	6000 g/mm
Tear Resistance – propagating (50% RH, 23°C)	> 100 g/mm

2.2 EXPERIMENTAL PROCEDURE AND TEST APPARATUS

A new self-designed and constructed device was used to carry out the tension-torsion experimental tests; a general description is as follows:

- 1) An acrylic box (1) with dimensions: 20 x 15 x 15 cm as shown in Figure 2, contains different elements destined to carry out the experimental tests.
- 2) Three motors working under programmed steps are employed to impose longitudinal (2) and torsional (2') movement with the precision of $\pm 4 \mu\text{m}$ in longitudinal motion and ± 0.1 degrees in torsion.
- 3) Three thermocouple heaters (3), are destined to control temperature during experimental tests, inside the acrylic box.
- 4) A Nafion 115 testing specimen (4), is clamped (10 mm of each side) by the two jaws (5), connected to two rotation step motors.
- 5) A load cell (not shown), is destined to measure the applied tensile stress on the Nafion 115 strip.
- 6) A temperature and humidity sensor (6), is used to measure the imposed environmental temperature and humidity.

Figure 2: Acrylic box and principal elements to carry out tension-torsion on the Nafion 115 strip

2.3 CALIBRATION OF TENSILE DISPLACEMENTS

To perform a correct calibration between the motor steps and the linear displacement of the membrane, displacement measurements were made using an inductive displacement sensor of the GPX series with a linearity error of $\pm 0.3\%$ F.S. Figure 3 shows the sensor used for the actual measurement of the linear displacements generated by each step of the NEMA 23 motor.

Figure 3. Inductive displacement sensor for calibration of linear displacements of the NEMA 23 motor.

In Figure 4 is shown the arrangement of the sensor (in the membrane fastener) in a place suitable for a correct reading of the displacement. On the opposite side of the sensor, metal elements were placed that serve as a reference to the internal electromagnetic field of the sensor for its operation (for the reading of the displacements).

Figure 4. Placement of the inductive sensor to measure the displacements generated by the NEMA 23 motor.

3 EXPERIMENTAL RESULTS

3.1 TENSILE RESULTS

The first experimental tests were carried out to evaluate the stress-strain curve on this polymeric material at room temperature and 50% of relative humidity. Applied steps motor for tensile displacement was used for this purpose: 10 steps in the motor represented 1500 μm of longitudinal displacement in the Nafion 115 strip, and approximately 11.2 MPa of maximum tensile stress. In Figure 5 is plotted the stress-strain curve obtained from experimental tests for this material. The experimental points plotted in Figure 5 are the average of 5 experimental tests. Linear behavior is observed for an applied tensile load of as high as 20 MPa and deformation of about 8-9 %.

Figure 5. Stress-Strain curve obtained experimentally (points), and projection (dotted line), for Nafion 115.

3.2 FATIGUE ENDURANCE RESULTS

In Figure 6 are plotted the experimental results of tension-torsion on the Nafion 115 strip. The experimental parameters were: constant torsion angle of 50 degrees (25 degrees induced by the first torsion step motor in one direction and 25 degrees in the opposite direction induced by the second torsion step motor), 25° C of room temperature, relative humidity of 50%, frequency of 1.6 Hz and loading rate $R = -1$. The vertical axis of this graph represents the static tensile stress applied to the Nafion 115 strip and the horizontal axis the number of cycles of fatigue life under the described loading conditions. Five tensile loads were used for fatigue tests: 60, 55, 50, 45 and 40 MPa, as shown in Figure 6.

Figure 6. Fatigue endurance results for the Nafion 115 strip, under tension-torsion tests and environmental conditions.

3.3 CRACK INITIATION AND PROPAGATION ON NAFION 115, UNDER THE DESCRIBED LOADING CONDITIONS

Figure 7. Fracture of the Nafion 115 strip under tension-torsion loading

Figure 7 illustrates the fracture trends under this modality of loading on the polymeric strip. Fracture initiation presents two trends: at one corner of the strip where this polymeric material is fastened by the metallic jaws; at this zone is localized the highest stress under tension.

The second site of crack initiation is localized close to the center of the specimen, where the combination of tension and torsion induces stress concentration. Fracture initiation is characterized by a crack path quasi perpendicular to tensile stress, Figure 6a; whereas crack propagates with a bifurcation path when it attains 4.5 mm of propagation approximately, as illustrated in Figure 6b. The last behavior should be associated with torsion loading, which induces a variation on the path propagation when crack attains a specific length: the mode I of crack propagation is modified to mode II. In addition, this indicated that the maximum hoop stress criterion of Erdogan and Sih [16], governed the crack initiation and propagation in these fatigue tensile-torsion tests.

4 DISCUSSION

The static stress-strain curve of Figure 5 presents values higher compared to previous tensile tests carried out on this material [17]. The Nafion strip thickness may related to this discrepancy: 127 μm in the present work, 25 μm in the referred work, leading to a factor of 3 approximately. In addition, density and rigidity of cross-linked polymeric chains may contribute to this behavior [18]. Concerning the fatigue endurance results, tension-torsion results show a decreasing behavior when the static tensile load increases, at constant torsion angle of 50 degrees. Experimental results show that fatigue endurance is close to 200,000 cycles when the tensile load is 60 MPa; this value increases close to 900,000 cycles for tensile load of 40 MPa. A logarithmic regression curve is obtained from the experimental points for the evolution of fatigue endurance under the described loading conditions, which is plotted in Figure 6. Concerning the fracture trends, the tension-torsion loading on this polymer induces a predominant mode I at the crack initiation; nevertheless, this behavior is modified when the mode I and II compete and generates transition when the rate: tensile fracturing stress/shear fracturing stress decreases to a critical value. The bifurcation observed in the crack path of fracture surfaces of this polymer, Figure 7b, is the physical evidence of such transition.

5 Conclusions

The following conclusions may be drawn from this work:

- Fatigue endurance has been obtained for the proton exchange membrane Nafion 115, under tension-torsion loading.

- A new testing machine self-designed and constructed was implemented to obtain experimental fatigue results on the Nafion 115 strip, with control of tension and torsion loads, as well as temperature and humidity.
- The results presented in this study were obtained for a constant torsion angle, room temperature and relative humidity of 50%, varying only the applied tensile stress.
- Logarithmic regression was used to obtain the tendency curve from the fatigue endurance experimental points.
- The dispersion of fatigue endurance results increases as the tensile applied load increases, for the range of applied tensile stress.
- The General trends for the crack initiation and propagation have been observed and described under the mentioned loading conditions.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests in the publication of this paper.

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