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Experimental Investigation on the Mechanical Endurance Limit of Nafion membrane used in Proton Exchange Membrane Fuel Cell

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Abstract: As a solution of high efficiency and clean energy, fuel cell technologies, especially proton exchange membrane fuel cell (PEMFC), have caught extensive attention. However, after decades of development, the performances of PEMFCs are far from achieving the target from the Department of Energy (DOE). So, further understanding of the degradation mechanism is needed to overcome this obstacle. Due to the importance of proton exchange membrane in a PEMFC, the degradation of the membrane, such as hygrothermal aging effect on its properties, are particularly necessary. In this work, a thick membrane (Nafion N117) which is always used as an ionic polymer for the PEMFCs has been analyzed. Experimental investigation is performed for understanding the mechanical endurance of the bare membranes under different loading conditions. Tensile tests are conducted to compare the mechanical property evolution of two kinds of bare-membrane specimens including the dog-bone and the deeply double edge notched (DDEN) types. Both dog-bone and DDEN specimens were subjected to a series of degradation tests with different cycling times and wide humidity ranges. The tensile tests are repeated for both kinds of specimens to assess the strain-stress relations. Furthermore, the yielding stresses were obtained, as well as the work of fracture.

Keywords: PEMFC; Nafion; fracture test; hygrothermal aging; Mechanical Endurance.

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1. Introduction

PEM fuel cell has very high performance in a wide working range with good dynamic characteristics and it works at low temperature. PEM fuel cell also has showed high efficiency of electrical conversion and the total efficiency can be even higher by making full use of the heat generated during the operation . It generates electricity without any emissions and most of the materials employed can be reused or recycled [1]. It was reported in 2010 that PEM fuel cell can reach ~60% electricity conversion efficiency and 80% energy co-generation (electrical and thermal) efficiency with more than 90% reduction of carbon and pollution emissions .

But before that, the low durability of PEM fuel cell is the primary problems that need to be solved. The DOE (department of energy) target for the life time of fuel cell is more than 5000 hours for transportation applications by 2015 and 40000 hours for stationary applications by 2011. According to this target, now the performance of PEM fuel cell is far from achieving the target [2]. So further understanding of the degradation mechanism and development of durability analysis methods are needed to overcome this obstacle.

Within an operating circle of the PEM fuel cell, the diffusion of reactants, the oxidation and reduction of reactants and the conduction of protons, they all take place in the membrane electrode assembly (MEA) where the temperature, humidity and external compressive load have very high variation. The MEA bears the temperature over 80 ℃ and the humidity from RH 30% to RH 90% [3]. During the operating very complex phenomenon are involved in the thin MEA, including heat transfer, multiphase flows, electrochemical reactions, charge transport, mechanical interactions. That's why premature failures in MEA are always observed in forms of throughout crack and delamination [4]. If it is observed in single layer, the failure turns to be cracks, tears, punctures and pinholes though the membrane and cracks and flaking of CL (the electrode) [5]. The mechanical causes of these premature failures include orientation of material on CL (the electrode) [6], the creep of membrane material and damage accumulation . During multiple cycles operation, with the change of temperature and humidity, the swelling of the membrane is the primary drive force and the main factor which affects the stress distribution through MEA [7]. The alternation between wet-up and dry-out can cause significant stresses in membrane [8].Besides, freeze and thaw cycles also induce physical damages to the MEA [9].

To make a progress in accurate modeling as well as the potential failure analysis, the mechanical properties of nafion membrane, which is the most widely used ionic polymer of PEMFC, should be obtained as a database in order to make a contribution to PEMFC degradation modeling and simulation. In this paper, two kinds of tests were conducted including the dog-bone tensile test and deeply double edge notched test (DDENT). The mechanical properties were obtained in terms of Young's modulus, yielding strain, specific essential work of fracture and so on. What is more, the temperature and humidity aging effect are also discussed in both kinds of tests.

2. Experimental section

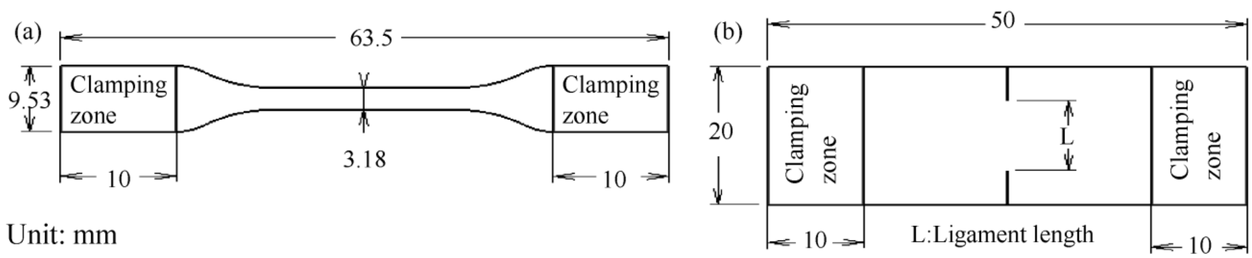
2.1. Materials

Non-reinforced films based on chemically stabilized Perfluorosulfonate acid (PFSA) and Polytetrafluoro-ethylene (PTFE) copolymer in the acid (H+) form, which was obtained from Dupont Company with the commercial name Nafion® N117.

2.2. Specimen

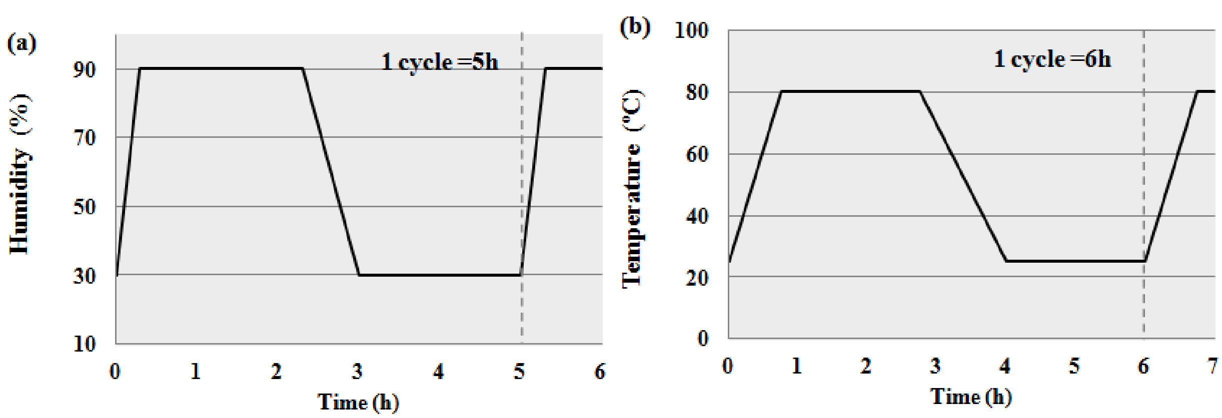
There were two kinds of specimens, the dog-bone ones and the DDEN ones. The dimensions of both specimens are shown in Figure 1, where L equal to 10mm. All the specimens are cut in shape (including the deep notches of DDENT specimens) before cycling.

Figure 1. The dimensions of (**a**) dog-bone specimen [10] and (**b**) DDEN specimen



Both kinds of specimens are divided into three groups, untreated, humidity cycling aged and temperature cycling aged. Both humidity and temperature aged specimens were maintained with no constraint (free to expand) in the temperature & humidity incubator for 12 cycles to analogue the real Fuel cell working condition. The humidity and temperature change is shown in Figure 2. It should be noted that the temperature was maintained constant as room temperature (25 ℃) during humidity cycles and the humidity was also maintained constant at 30% during temperature cycles.

Figure 2. The curves of (**a**) Humidity and (**b**) Temperature cycling with one period.



2.3 Mechanical properties

Mechanical properties of Nafion N117 membrane were measured by tensile tester (BS-205, C&FO, Korea) with a load sensitivity of 0.1N. For the tensile test, the strain rate is the most important factor which should be carefully determined. Normally, if the strain rate is lower than 0.001, the tests would be considered as quasi-static tests which are not suitable for the purpose of our study, and according to the literatures discussing the mechanical response of nafion membranes [11-13], we chose two test strain rates, 0.01 and 0.001. And the tensile tests were conducted at room temperature (25 ℃).

To avoid the influence of temperature and humidity residual, all the aged specimens after 12 cycles was maintained in room conditions (25 ℃ and RH 30%) for 24 hours before testing.

3. Results and Discussion

3.1 Dog-bone tensile test

The response of a typical polymer is shown as Figure 3.

Figure 3. True stress- true strain curve of a typical polymer and different zones

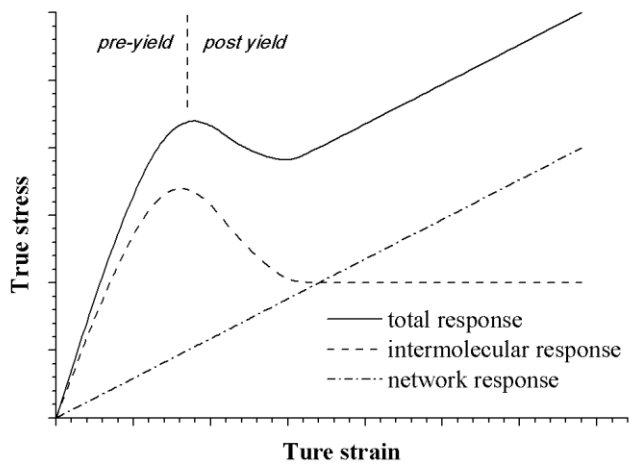
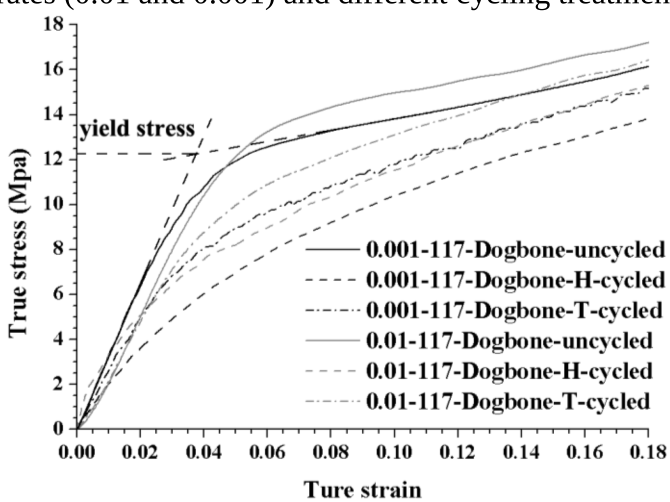


Figure 4. The true stress-true strain curves of N117 dog-bone tensile test under different strain rates (0.01 and 0.001) and different cycling treatments



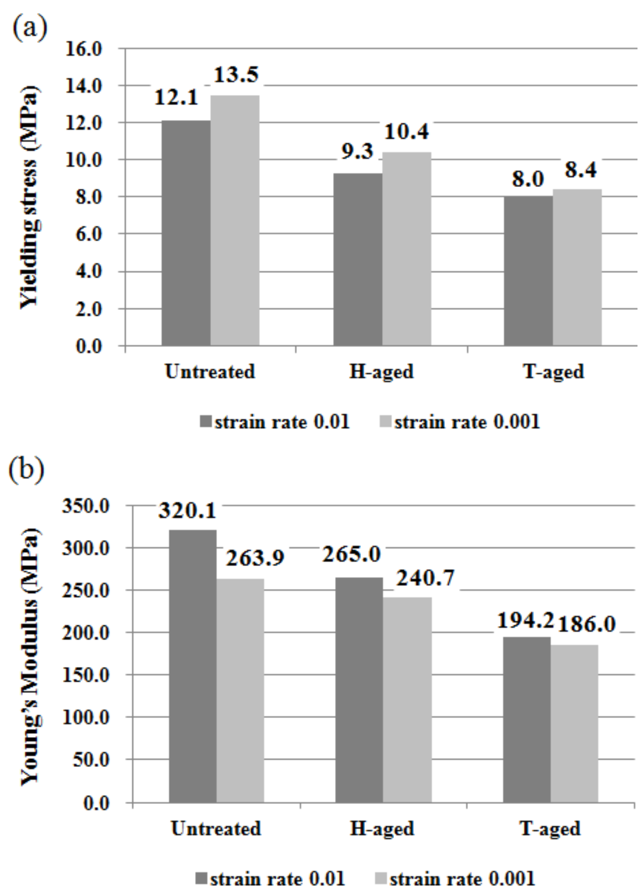
As we know, the response of Nafion membrane includes both intermolecular resistance and network stress [13]. And the total response can be divided into two zones termed as pre-yield and post-yield zones by the potential barrier. After the post yielding, the total response is nearly linear, so we cropped the curves with the true strain range from 0 to 0.18 in order to have a clearer scope of yielding behavior. The curves of true stress-true strain of Nafion N117 dog-bone specimens are shown in Figure 4.

The stress at the intersection of linear fits to the pre-yield zone slope and the immediate post-yield zone slope is named the yield stress. The yield stress usually referred that can be affected by both deformation rate and temperature. In Figure 4 we can tell it is also affected by aging treatment.

Besides, the yielding behaviors are also changed largely after the aging treatment applied. In the total response the network stress is linear [14], that is to say the stress produced by the network is in proportion to the true strain, according to Figure 4 the curves are nearly parallel to each other when strain is larger than 0.14, that means the network response was hardly affected by the aging treatments. But the potential barrier had decreased after cycling, so it can be asserted that the aging affect the interaction of molecular chains in membrane structure.

The yielding stresses abstracted form Figure 4 are shown as follow:

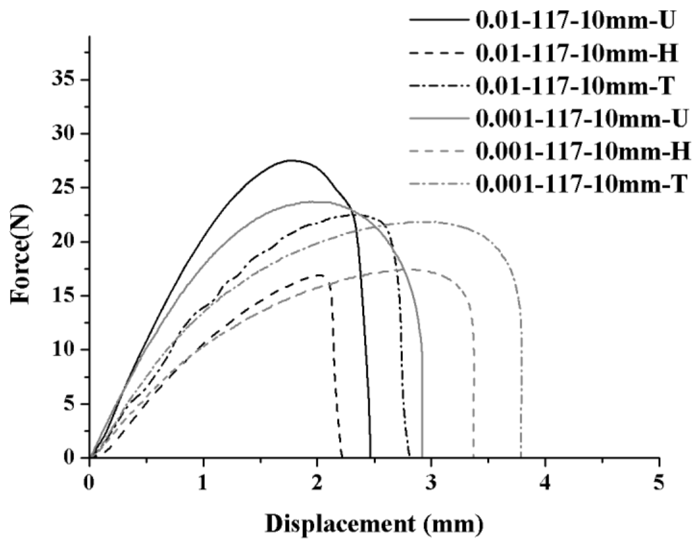
Figure 5. The (**a**) yielding stress and (**b**) Young's modulus of N117 dog-bone tensile test under different strain rates (0.01 and 0.001) and different cycling treatments



3.2 Deeply double edge notched test

Because of the fracture generation, the section area of specimen is changing with time. It is impossible to get the true stress, so the results of DDENT should be presented by force-displacement curves.

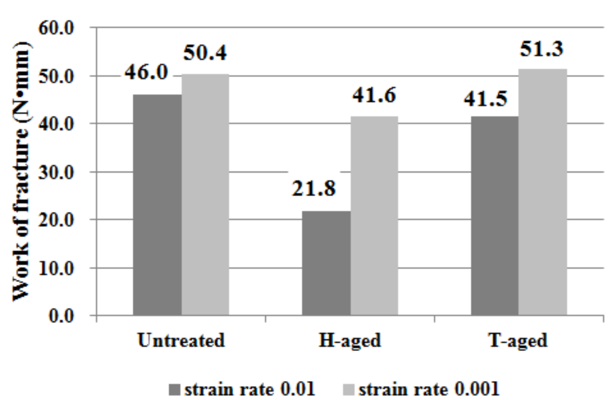
Figure 6 The force-displacement curves of N117 DDENT with L=10mm under different strain rates (0.01 and 0.001) and different cycling treatments



As shown in Figure 6, all the factors, such as tensile speed, humidity aging and temperature aging, have a obvious influence on the total work of fracture (the area bounded by the force-displacement and x axle).With higher strain rate, the maximum force to start facture is larger, but this kind of influence is not obvious in the aged specimens.

Both humidity and temperature aged specimens showed a resistance with larger extension when the loads were applied at a lower strain rate.

Figure 7. The work of fracture of N117 DDENT with L=10mm under different strain rates (0.01 and 0.001) and different cycling treatments



The work of facture calculated from the force-displacement curves showed that after the temperature aging the energy needed to break the sample didn't change much. However, after the humidity aging, the work needed decreased largely and this effect enlarged by higher strain rate.

4. Conclusions

The strength of Nafion membranes as well as the work of fracture was affected largely by the aging treatment. Young's modulus and yielding stress decreased after the aging treatment. And the humidity aging has the greater impact. And the work of fracture showed a similar phenomenon.

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Conflicts of Interest

The authors declare no conflict of interest.

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