

Effect of environmental condition on essential work of fracture of proton exchange membranes

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Abstract

The essential work of fracture (EWF) is a key property in understanding the fracture resistance in polymer membranes. As such, it is a promising approach when investigating the fracture resistance of proton exchange membrane in fuel cells. The longevity of these membranes is crucial to the good function of the cell: the membranes have to sustain important variations in the surrounding temperature and humidity, possibly affecting their fracture resistance. This study investigated the essential work of fracture of such proton exchange membranes using a double-edge notch tensile test (DENT test). The tests were performed for different environmental conditions that were relevant to the conditions met by proton exchange membrane fuel cells. The results of the DENT tests strongly depend on the temperature and humidity; in particular the high temperature cases show a large increase of dissipated energy. Based on experimental results, a numerical model was developed and the numerical simulations of DENT tests were performed. The obtained results suggest that the shape factor of plastic zone, β , should be a function of the ligament length and the quadratic regression is appropriate to the calculation of EWFs when the temperature is near the glass transition temperature. The EWFs under ambient temperature (30 °C) conditions were found to be 18.4 kJ/m² for 50 %RH and 21.5 kJ/m² for 100 %RH. Those under high temperature (80 °C) conditions were found to be 48.0 kJ/m² for 50 %RH and 56.4 kJ/m² for 100 %RH.

Key words : Essential work of fracture, Proton exchange membrane fuel cell, Nafion, Double-edge notch tensile test, Temperature, Humidity, Finite element method, Cohesive zone model

1. Introduction

Proton exchange membranes have received a large amount of attention in the recent years from the energy industry, their most notable use being in proton exchange membrane fuel cells (PEMFCs). Their molecular structure allows the chemical reaction to proceed, transporting protons but acting as a barrier to electrons. This way of generating electricity from chemical energy has been considered very promising for a variety of applications, particularly as an alternative to internal combustion engines in cars (United States Department of Energy, 2009). While their high efficiency and absence of greenhouse gases emission earns PEMFCs the interest of automakers, their high initial cost and limited durability still need to be improved in order to be able to be competitive on the market. As such, efforts have been directed to gain a better understanding of the failure mechanisms of the core components of fuel cells.

Specifically, degradation tests show that the failure of the proton exchange membrane is the leading cause of the failure of the whole cell by one order of magnitude (Placca and Kouta, 2011). The cyclic nature of the function of a fuel cell (start up/shut down) is a common cause for its failure (Oyarce et al., 2014; Pestrak et al., 2010; Huang et al., 2006; Yu et al., 2012), resulting in a sharp drop of performance of the fuel cell. In practice, mechanical stresses are due to hygrothermal cycling. When in an idle state, the fuel cell rests at ambient conditions of temperature and humidity. In order to react hydrogen with oxygen at an acceptable rate, temperature needs to be kept high, around 80 °C for PEMFCs. By combining the two reactants, water is created as a by-product, and is either evacuated or absorbed. Both

of these factors, temperature and humidity, cause the proton exchange membrane to swell when increasing, and to shrink again when shutting off the cell. Since the membrane is constrained inside the cell, this results in compressive stresses, eventually leading to pinhole formation and crack initiation (Huang et al., 2006; Kai et al., 2014; Tang et al., 2007).

Given the importance of preventing the degradation of the membrane, it is crucial to have reliable data on its fracture resistance and behavior of its components. By knowing how environmental conditions affect the fracture resistance, it becomes possible to better estimate the lifetime of the membrane. This is important both from the point of view of cost (scheduled maintenance) and safety. Moreover, since failure of the proton exchange membrane is a common cause of the loss of performance of fuel cells, the fracture resistance of the membrane is indicative of the reliability of the fuel cell as a whole.

In this study, the essential work of fracture (EWF) of the proton exchange membrane is calculated for different temperatures and humidities. The EWF is the minimum amount of energy required in order to create a fracture surface in a given material. This property is commonly used for polymer sheets or thin films, as plane stress fracture toughness. The EWF is equivalent to the critical J -integral and easier to be measured by experiments (Bárány et al., 2010). In this paper, the Double Edge Notched Tensile (DENT) tests were carried out in order to extract the EWF. Also, the numerical simulations of DENT tests for proton exchange membranes were developed and the effect of plastic dissipation on the EWFs were discussed.

2. Essential Work of Fracture

2.1. Double-Edge Notched Tensile Test

The Essential Work of Fracture is an important material property to calculate when studying the fracture of polymers, as it gives the minimal amount of energy necessary in order to create a crack surface. The interest of the EWF approach over other methods lies in the relative simplicity of the experimental protocol. The double-edge notch tensile test (DENT) was developed in order to calculate the EWF of thin, ductile membranes. It is performed on a membrane with two symmetrical V-shaped notches, as described in the literature (ESIS TC-4 Group, 1993; Bárány et al., 2010). A tensile load is applied until complete tearing of the specimen. The total work of fracture, W_F , can then be calculated from the load-displacement diagram of the experiment.

2.2. Method of calculating the EWF

The total work of fracture W_F can be separated into essential energy of fracture and other non-essential dissipated energies. This can be written as,

$$W_F = W_E + W_P, \quad (1)$$

where W_E is the fracture energy and W_P is the plastic dissipated energy.

Several assumptions are taken in this experiment: there is supposed to be no out-of-plane stress, no edge effects, and the zone of plastic deformation should be limited in a small region along the ligament. In practice, in order to validate the underlying assumptions of the DENT experiment to obtain accurate measurement of the EWF, it is generally accepted (ESIS TC-4 Group, 1993; Karger-Kocsis, and Czigfany, 1996) that the ligament length should verify

$$5t < l < \frac{W}{3} \quad (2)$$

where t and W are respectively the thickness and width of the specimen, while l is the ligament length. However, these inequations are only estimations; the actual range of valid ligament length is dependent on the material used. As the thickness of the membranes used in this study is very thin (25 μm), the first part of the inequation is easily met. As reported by the ESIS TC-4 Group (1993), ligament sizes greater than $W/3$ are valid as long as the specimen fails in a ductile manner. Ideally, the ligament should be fully yielded before the crack initiation, however it has been shown that this condition is too stringent and not necessary in order to calculate the EWF (Ching et al., 2000; Poon et al., 2001).

The plastic dissipated energy is proportional to the volume of the plastic zone around the ligament, while the EWF is a surface energy proportional to the surface of the created crack. It is therefore possible to rewrite Eq.(1) as

$$w_F l t = w_E l t + \beta w_P l^2 t \Rightarrow w_F = w_E + \beta w_P l, \quad (3)$$

where w_F , w_E and w_P are the specific energies relative to W_F , W_E and W_P respectively, and l and t are the ligament length and thickness of the specimen. β is the shape factor of the plastic zone, and is not directly accessible from the experiment. The simplest method to calculate the EWF from Eq.3 is to perform the DENT with several ligament lengths, then to linearly extrapolate the results to a length of 0 in order to isolate w_E .

3. Experimental details

3.1. Material

The proton exchange membranes in this study are made of DuPont's Nafion® NR211. This perfluorosulfonic acid polymer is commonly used in modern PEMFCs thanks to its high proton conductivity and good chemical stability (Cele and Ray, 2009). From the mechanical point of view, Nafion shows a non-linear visco-plastic behavior, and its properties are sensitive to temperature, humidity and pre-treatment. For these reasons, relatively little data is available on its properties, especially in non-ambient conditions (Kai et al., 2013; Vermot des Roches and Omiya, 2013; Kusoglu et al., 2009). The specimens in this study are all cut to the same dimensions, with a width of 10 mm and a gauge length of 20 mm. The nominal thickness is standard for the NR211 type at 25 μm . No pre-treatment was applied to the specimens before cutting; they were used as received from the distributor.

3.2. Experimental protocol

The tensile testing equipment, purposely built for the needs of the experiment, was composed of two linear stages with stepping motors (SGSP26-100, Sigma Koki Co., Ltd.) controlled by a motor controller (GSC-02, Sigma Koki Co., Ltd.) using LabVIEW (National Instruments Corporation). The displacement resolution is 40 μm . The gripping ends are large enough to grip the entire width of the specimen and are coated in non-slip rubber so as to avoid dislodging. The crosshead speed that was applied to the specimen during tensile loading was 0.04 mm/s.

In order to control for temperature and humidity around the specimen, the setup was placed inside an environmental chamber. Temperature is controlled by heaters around the specimen, specifically a transparent glass heater above (S-101, Blast Co., Ltd.) and a rubber heater below (SCR-SQ, Sakaguchi E.H. Voc Corp.). Transparency of the glass heater was required in order to be able to observe the specimen in situ. Temperature was monitored by a thermocouple. Humidity was controlled using an injection hose connected to a dew-point generator (me-40ADP-SRZ, Micro Equipment Co., Ltd.). This setup allowed to control the environmental conditions with an accuracy of $\pm 1^\circ\text{C}$ and $\pm 5\%\text{RH}$. Experiments were only conducted once equilibrium was reached in the chamber. The experimental setup is shown in Fig. 1.

For the purpose of obtaining enough data to calculate the EWF, specimens were prepared with ligament lengths of 2, 4, 6 and 8mm. For each ligament length, experiments were repeated four times on different specimens. Four environmental conditions were considered; ambient conditions (30 $^\circ\text{C}$, 50 %RH), high humidity (30 $^\circ\text{C}$, 100 %RH), high temperature (80 $^\circ\text{C}$, 50 %RH) and high humidity and temperature (80 $^\circ\text{C}$, 100 %RH). These conditions mimic those met by fuel cells during normal function, as they commonly operate at 80 $^\circ\text{C}$ in order for the chemical reaction to be sustained at a satisfying rate, while humidity naturally increases as water gets created by the oxidation of hydrogen.

A load cell (LUX-B-100N-ID, Kyowa Electronic Instruments Co., Ltd.) situated on one of the stages monitors the load applied to the specimen during the experiment. Combined with the displacement of two linear stages, the load-displacement curves of DENT tests were obtained. Then, the total work of fracture, W_F , was calculated from the load-displacement curve.

3.3. Experimental results

Figure 2(a) (cross symbols) shows the results of the DENT tests performed in ambient conditions (30 $^\circ\text{C}$, 50 %RH). As expected from Eq.(3), the measured dissipated energy increases with the ligament length in a linear fashion. The linear regression shows a value at the origin of 18.4 kJ/m² (the EWF) and a slope of 13.6 kJ/m³ (the increase rate of plastic dissipated energy). The only value found in the literature for the EWF of a Nafion membrane with the DENT test is 20.5 kJ/m² in ambient conditions (Li et al., 2008). This value is somewhat higher than the one found here, however the authors note that considerable viscous and plastic deformations dominated the fracture

process. The difference of crosshead speed during the experiment might also be one factor explaining the discrepancy.

The same set of data was gathered for high humidity conditions (30 °C, 100 %RH). The results are also shown in Fig. 2(a) (round symbols). Compared to the previous case, the data is less scattered, with results clustering more closely along the trend line. The EWF obtained by the experiments is 21.5 kJ/m², which is close to the EWF calculated for ambient temperatures, though a bit higher. In contrast, the slope of the linear regression is lower for high humidity than for ambient conditions, indicating a lower amount of plastic dissipated energy. This is linked to the change of mechanical properties of Nafion in humidified states.

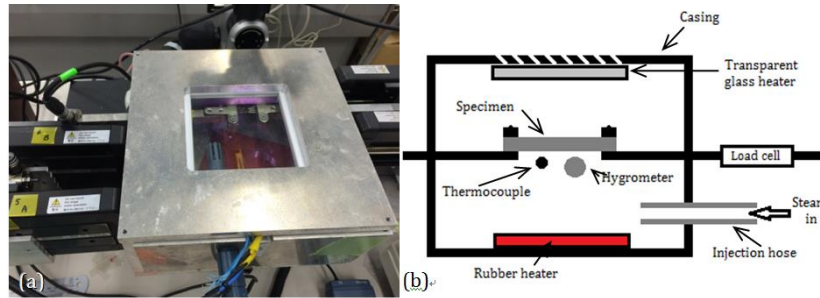


Fig. 1 Experimental apparatus: (a) Experimental Setup; (b) Schematic

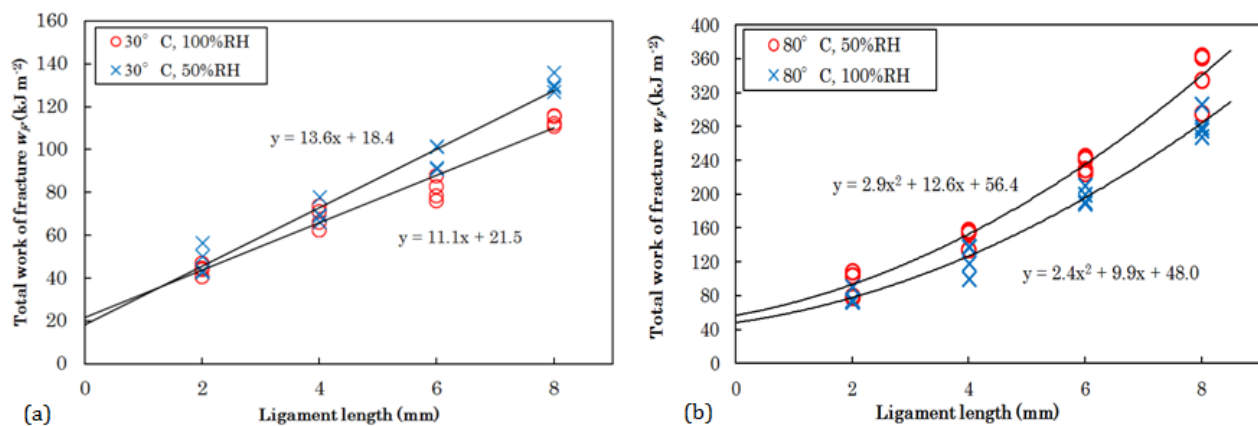


Fig. 2 Total Work of Fracture calculated for different ligament lengths: (a) ambient temperature (30°C); (b) high temperature (80°C).

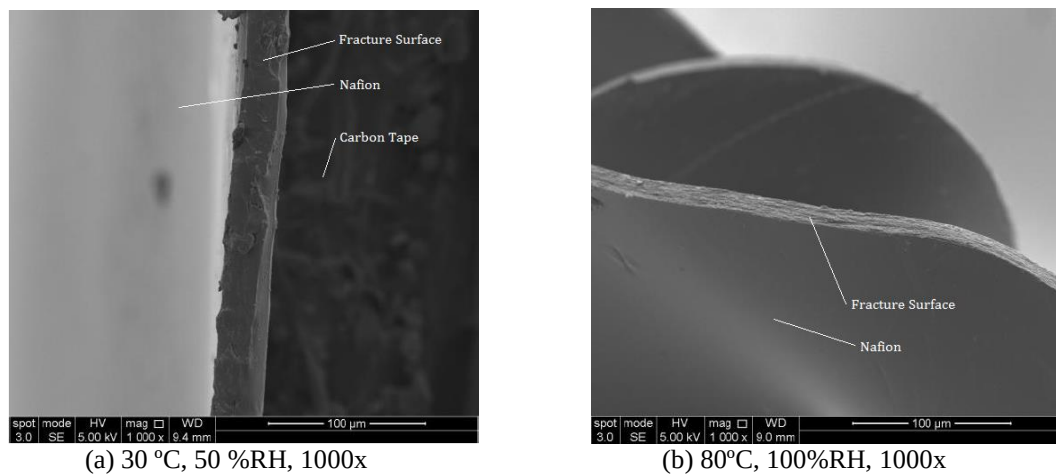


Fig. 3 Scanning electron microscope observation of the fracture surface of 8 mm ligament length specimens.

Figure 2(b) shows the experimental results for high temperature conditions. Different from the previous cases, the total work of fracture does not follow a linear law. Instead, the data seems to follow a square law. Trying to fit the data with a linear regression would lead to a negative value for the EWF, which is obviously incorrect. This suggests that in this case the shape factor of the plastic zone β (see Eq.(3)) becomes geometry-dependant and therefore varies with the ligament length l . The detail discussion of the shape factor will be mentioned later.

The fracture surfaces of the specimen were observed by a scanning electron microscope as shown in Fig.3. There, the effects of tearing can be seen: While the ambient temperature case shows a relatively smooth fracture surface, the high temperature case shows rougher and more damaged fracture surfaces. The local observation of the fractured surfaces supports a qualitative explanation to the differences in the total work of fracture in the different cases.

4. Finite Element Model

4.1. Modeling the mechanical behavior of Nafion

Nafion, the material used in the experiments, exhibits a non-linear visco-plastic behavior, with a strong dependency on both humidity and temperature. Silberstein and Boyce (2010) have proposed the visco-plastic constitutive model for Nafion. It uses a variety of components to account for both intermolecular and network deformation of Nafion, as well as for the back stresses that occur during dynamic loading. In the present study, this constitutive model was used as a constitutive model for Nafion. Silberstein and Boyce (2010) shows very good agreement with experimental data at low to middle strains, however there was some divergence happening at larger strains, where molecular alignment becomes the most important factor of the constitutive model. Since in this study the fracture of Nafion is modeled, it is necessary that the model be valid at larger strain until the maximum stress is reached, therefore some parameters of the initial model were modified in order to match as closely as possible the experimentally observed stress-strain behavior of the membrane.

At high strains, the behavior of Nafion is governed by two independent mechanisms. The first is the decrease of the shear modulus until its saturation value μ_{sat} , which controls the post-yield softening of the material. The second mechanisms is the intermolecular shear resistance s , increasing as the strains in Nafion become larger, accounting for the increasing difficulty of deforming the polymer as the individual molecules start to align with each other. It is calculated as a function of the network stretch with the following equation,

$$s = h(\lambda_{chain}^n - 1), \quad (4)$$

where λ_{chain} is the measure of the network stretch, while h and n are fitting parameters. This leaves three parameters, μ_{sat} , h and n , that need to be adjusted in order to replicate the behavior at high strains.

The least square method is applied in order to find the best fitting combination of these three parameters. The objective is to match the stress-strain relationship of the finite element simulation and of the experiment as closely as possible by minimizing the function

$$f(\mu_{sat}, h, n) = \sum_{\varepsilon=0}^{\varepsilon_{max}} (\sigma_{exp} - \sigma_{FEM})^2. \quad (5)$$

Since the constitutive model is non-linear, there is no close-form solution to this least square problem. Some initial values for the three parameters need to be chosen; this is done through trial-and-error method. The initial values are decided as such: $\mu_{sat} = 3.5 \times 10^7$ Pa; $h = 2.3 \times 10^6$; $n = 10$.

In order to simplify the problem, it is worth noticing that since μ_{sat} is the only one of the three parameters to control the immediate post-yield behavior of the material before molecular alignment starts to play a dominant role, it is possible to first find the best value for μ_{sat} alone by minimizing the function,

$$g(\mu_{sat}) = \sum_{\varepsilon=0}^{0.4} (\sigma_{exp} - \sigma_{FEM})^2 \quad (6)$$

Experimentally, a true strain value of 0.4 corresponds to the transition between the dominant mechanisms governing the behavior of the material (see Fig.5). Before it, μ_{sat} is the dominant parameter, while h and n control the subsequent behavior. Keeping the initial values for h and n , the function g is depicted in Fig.4(a). It displays a W-pattern with two local minima at 3.4×10^7 Pa and 3.6×10^7 Pa. Even though the former value minimizes the g function, the latter was found to give a better overall fitting when considering the full range of strains, while not

significantly decreasing the accuracy at middle strains. Finally, the f function in the neighborhood of the initial values of the parameters was drawn, with the results shown in Fig. 4(b). The best combination was found to be $\mu_{sat} = 3.6 \times 10^7$ Pa; $h = 2.2 \times 10^6$; $n = 10$. The resulting constitutive model after the least squares optimization is shown in Fig. 5. Other parameters used in the constitutive model can be found in Silberstein and Boyce (2010).

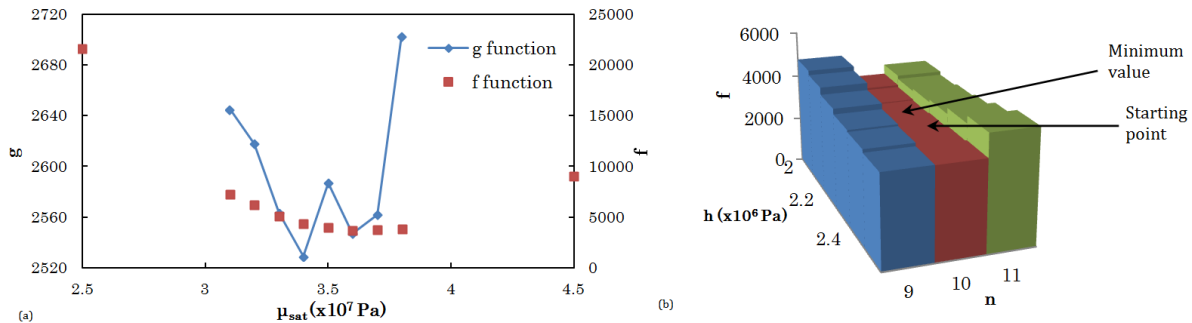


Fig. 4 (a) f and g functions for different values of μ_{sat} ; (b) f function for μ_{sat} fixed at 3.6×10^7 Pa

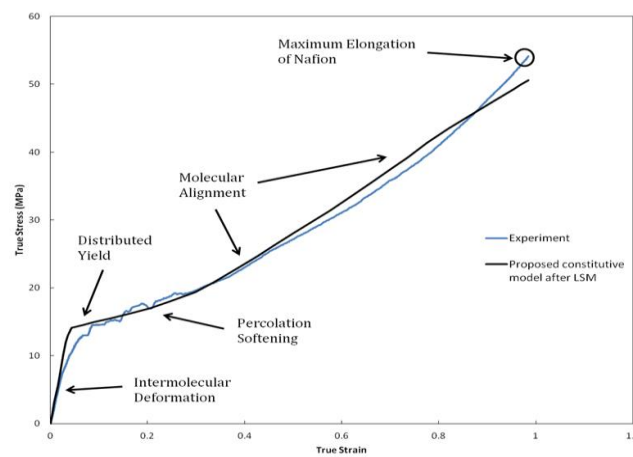


Fig. 5 Comparison of numerical result with experimental result.

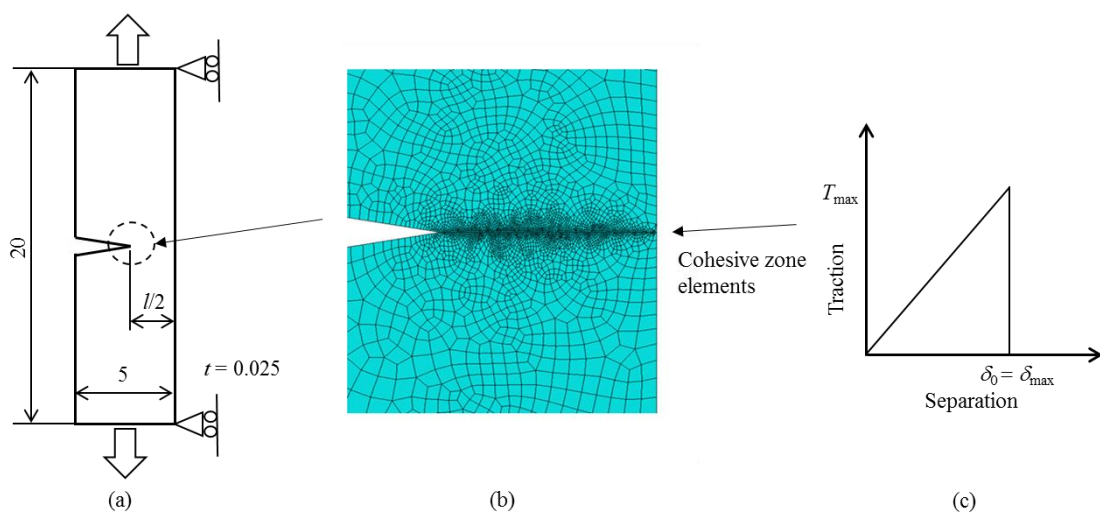


Fig. 6 DENT test specimen: (a) Calculation model with boundary conditions, (b) Detail of mesh around the notch tip, (c) Traction-separation law of cohesive zone model.

The accuracy of the model was deemed to be sufficient for the purpose of this study. It can be noted that since most of the parameters of the constitutive model from Silberstein and Boyce are determined through trial-and error, it could prove valuable to realize an optimization study for the entire set of fitting parameters in order to achieve an even more accurate model. This however is beyond the scope of this study.

4.2. Method of calculating the EWF

Figure 6 shows the numerical model that was used in this study. The analysis was made using the finite element code ABAQUS/Standard. Eight-node brick elements (C3D8) are used in the entire model, and a cohesive zone model is applied to the boundary elements. Because of symmetry, only one half of the model needs to be created. As shown in Fig. 6(a), the upper and lower edges of the specimen were constrained to move in the tensile direction. Since one of the objectives of this model is to be able to reproduce experimental results, several specimens are created with different ligament lengths, allowing calculating the EWF with a linear regression in the same way as the experiment. The mesh is more refined around the notch tip and crack propagation path (see Fig. 6(b)), so the total number of elements will differ depending on the ligament length, in any case the elements along the cohesive zone are 0.01mm in length.

The crack propagation was modeled by using a traction-separation law with a maximum stress criterion. Cohesive elements become separated after the maximum stress has been reached. As there is not currently enough published data on the fracture of Nafion, the failure criterion needs to be first estimated through experiment. Three parameters intervene in the traction-separation law: the crack initiation displacement δ_0 , the maximum stress T_{max} and the displacement at complete failure δ_{max} . T_{max} was assumed to be tensile strength of Nafion. Setting $\delta_{max} = \delta_0$ was found to give satisfying results, and so the cohesive elements are set to become separated as soon as the maximum stress has been reached. The only experimental input that is needed is the crack initiation displacement, which is identified as the displacement at which the maximum stress is reached before cracking.

4.3. Results of the Finite Element Model

Figure 7 shows one result of numerical simulation compared with the experimental result. The simulation results seem to fit the experimental stress-strain curve well. Figure 8(a) shows the total work of fracture calculated by the numerical simulation for ambient conditions, and compares it to experimental results. For all simulations, the calculated total work of fracture was within experimental error. The linear regressions for the experiment and simulation are in agreement with values at the origin (the EWF) of 18.4 kJ/m² and 18.5 kJ/m², respectively. The slopes are very close to each other and the plastic dissipated energy is correctly simulated in the numerical simulation.

The same set of data was gathered for high humidity conditions (30 °C, 100 %RH). The results are synthesized in Fig. 8(b). The agreement between the experiment and the numerical simulation is good, particularly with the slope of the linear regression, though the simulation data is more scattered than in the previous case. The EWF obtained by the experiments is 21.5 kJ/m², while the numerical simulation gives a value of 16.8 kJ/m². Both of these values are close to the EWF calculated for ambient temperatures. In contrast, the slope of the linear regression is lower for high humidity than for ambient conditions, indicating a lower amount of plastic dissipated energy. This is expected, as Nafion becomes more compliant in humidified states. This implies a lower yield stress in the material, and consequently a lower plastic energy being dissipated.

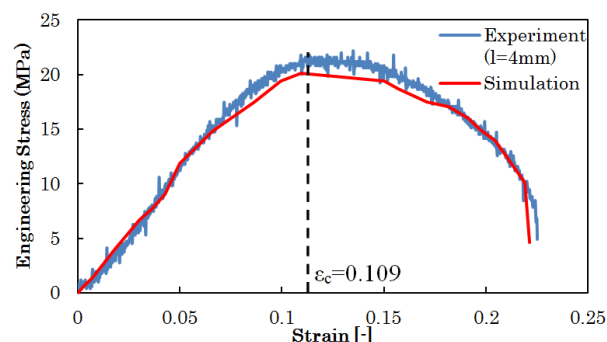


Fig. 7 Stress-Strain curve for Nafion during a DENT test

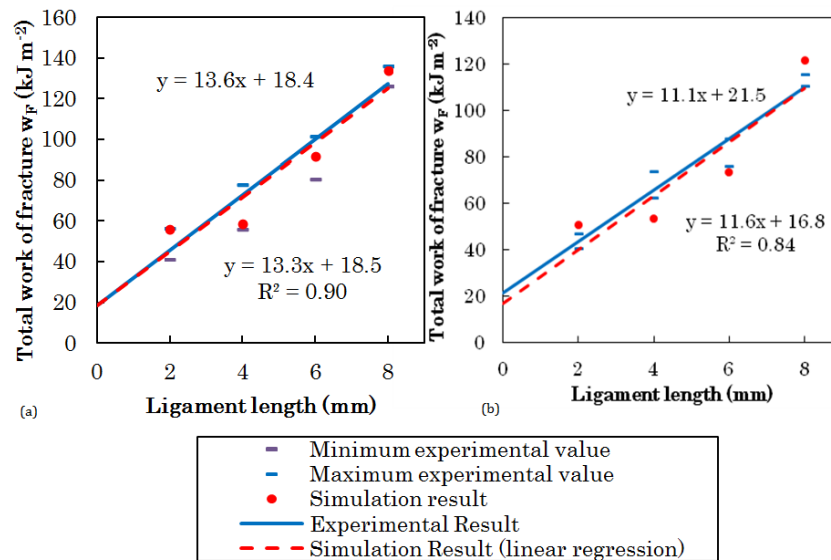


Fig. 8 Total work of fracture calculated for experiments and simulations for different ligament lengths: (a) at ambient conditions (30 °C, 50 %RH); (b) at high humidity (30 °C, 100 %RH)

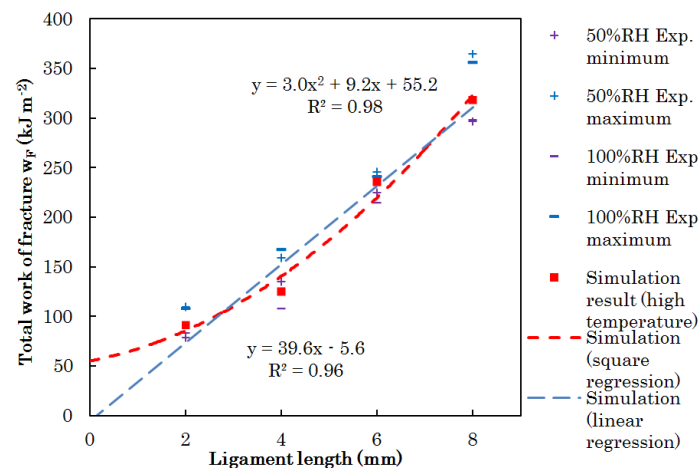


Fig. 9 Total Work of Fracture calculated for experiments and simulations for different ligament lengths at high temperature (80°C)

The experimental results for high temperature conditions (regardless of humidity) differ from the previous cases in that the dissipated energy do not follow a linear law but rather a square law, with values of w_F increasing faster the longer the ligament length. The results from the numerical simulation show the same behavior, as is shown in Fig. 9.

5. Discussion

In order to clarify the reason why the high temperature case shows such a large difference with the ambient temperature case, the size and shape of the plastic zone were investigated. The calculated length and width of the plastic zone at the onset of failure were retrieved using the results from the finite element analysis. These are shown in Fig. 10 and compared between cases of high temperature and of ambient conditions. Several observations can be made from these measurements. Firstly, the specimens at ambient conditions present plastic zones with almost identical widths and lengths. This means that the plastic zone keeps a symmetrical shape for all ligament lengths. This is congruent to plane stress conditions (Xin et al., 2010), satisfying the plane stress assumption of the DENT test. The second observation is that the plastic zones for all conditions are close for small ligament lengths ($W < 4$ mm) but the difference grows the longer the ligaments. The larger plastic zones are congruent with the larger amounts of dissipated plastic energy.

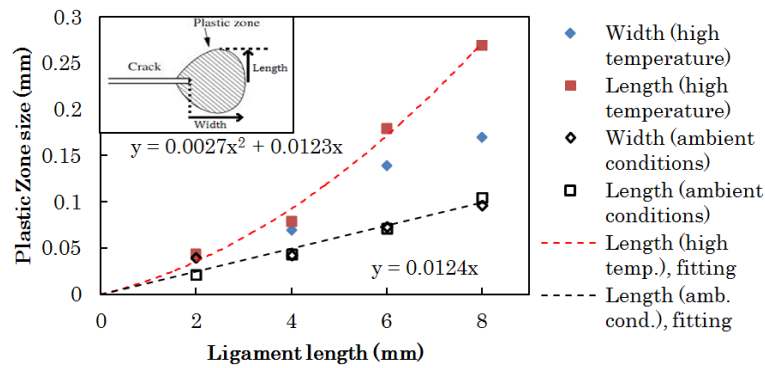


Fig. 10 Dimensions of the plastic zone at the onset of failure at high temperature (filled symbols) and ambient conditions (hollow symbols). Insert: points of reference to calculate width and length of the plastic zone.

In Eq.(3), the volume of the plastic zone was written as $\beta l^2 t$. In this formulation, β is the shape factor of the plastic zone, which verifies

$$\beta \propto \frac{h}{l} \quad (7)$$

where h is the length of the plastic zone, as defined in the insert of Fig.10. In ambient conditions, h is proportional to l , as shown in Fig. 10. This results in β being independent from l , justifying the fact that the w_F term from Eq.(3) is a linear function of l . In the high temperature case, however, h is no longer proportional to l but instead is closer to a quadratic function of it. Thus, β itself becomes a linear function of l . Following Eq.(3), we finally get the result that w_F has become a quadratic function of l , explaining the results from Fig. 9. These changes in the geometry of the plastic zone only affect the plastic dissipated energy. Although it is no longer proportional to the ligament length, it is still possible to calculate the EWF by extrapolating the results to a length of 0, this time using a quadratic regression. Using this different approach, the EWF of Nafion at high temperature can be obtained as 55.2 kJ/m².

Because the glass transition temperature of Nafion is around 100 °C, the glass transition that Nafion undergoes at the high temperature tested affects its higher order structure. This causes ductility to increase, some cross-linking to happen, making the specimen more compliant and therefore harder to fracture.

6. Conclusion

This study focuses on the essential work of fracture (EWF) of Nafion membranes for proton exchange membrane fuel cells (PEMFCs). In order to get insights that are useful for the design of fuel cells, DENT tests were performed under several temperature and humidity conditions. Also, the numerical model was developed to simulate DENT tests and the effects of plastic zone shape around the crack tip on the EWFs were investigated. The obtained conclusions are summarized as the followings.

1. The EWFs of Nafion membranes show a great sensitivity to environmental conditions, especially to increases of temperature. While the EWF in ambient conditions was found to be 18.4 kJ/m², it is more than doubled at high temperature to values of 48.0 kJ/m² (ambient humidity) and 56.4 kJ/m² (high humidity).
2. The proposed numerical model was found to closely reproduce the experimental DENT test results. The EWFs and the plastic dissipation energies obtained by numerical simulations were in agreement with those of experimental results.
3. The formation of plastic zone around the crack tip drastically changed between ambient temperature cases and high temperature cases. This in turn can be attributed to the fact that Nafion undergoes its glass transition at the high temperatures cases.
4. The obtained results suggest that the shape factor of plastic zone, β , should be a function of the ligament length

and the quadratic regression is appropriate to the calculation of EWFs when the temperature is near the glass transition temperature.

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