

# Characterization of graft-type polymer electrolyte membranes at low grafting degrees for fuel cells

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## ABSTRACT

**Introduction:** Proton exchange membrane (or polymer electrolyte membrane) fuel cells (PEMFCs) are attracting enormous research activities because they are a new power source for applications in different industrial sectors, such as transportation, stationaries, and portable devices. Nafion is the available commercial material for PEMs, but it has a high production cost, leading to a strong demand for alternative membranes. Polystyrene sulfonic acid (PSSA)-grafted poly(ethylene-co-tetrafluoroethylene) (ETFE) polymer electrolyte membranes (ETFE-PEMs) have been investigated extensively as alternative membranes for PEM fuel cells, but the results are mainly reported at grafting degrees (GDs) higher than 19%. Therefore, this study reports the results of thermal stability, mechanical strength, and proton conductivity for the ETFE-PEM with a low GD of 10%. **Methods:** ETFE-PEM was prepared by radiation-induced grafting and subsequent sulfonation. The performance characteristics of ETFE-PEM related to fuel cells are investigated using thermal gravimetric analysis (TGA), mechanical testing, and electrochemical impedance spectroscopy. **Result:** The ETFE-PEM shows higher or comparable mechanical strength and thermal stability to those of Nafion. In addition, ETFE-PEM can exhibit a conductance of  $6.10^{-4}$ – $21.10^{-4}$  S/cm with a relative humidity (RH) of 40–60%, even at a very low GD of 10%. **Conclusion:** ETFE-PEM shows better mechanical and thermal properties than Nafion and exhibits a rapid increase in conductance with RH of 40–60%, providing a potential application in PEM fuel cells for small devices such as motorcycles, mobile phones, or portable electronics.

**Key words:** Polymer electrolyte membrane, thermal stability, relative humidity, mechanical property, graft polymerization

## INTRODUCTION

A proton exchange membrane (PEM) is an important fuel cell component because it acts as an electrolyte to transport proton particles from an anode to a cathode and as a separator to prevent gas crossover and electron conductance through the membrane<sup>1,2</sup>. To obtain high fuel cell performance, PEMs should exhibit high ionic conductance, mechanical strength, and thermal and chemical stability. Nafion is presently considered a state-of-the-art PEM material because of its excellent physical-chemical stability and high ionic conductance at moderate operation temperatures<sup>3,4</sup>. However, the Nafion membrane shows some limitations, such as high production cost, low glass transition temperature, low-temperature operation (< 100 °C), and quite high fuel crossover<sup>5-8</sup>. Thus, research and development of alternative membrane materials for PEMs are necessary.

Recently, radiation-induced graft polymerization has been shown to be a cost-effective method to prepare PEMs for fuel cell applications<sup>8</sup>. This method can

flexibly use a variety of substrates, monomers, and conditions of irradiation and grafting to obtain proper final electrochemical properties of PEMs. Using high energy radiation (MeV) of gamma, X-ray or electron, each step of preparation can be conducted at an industrial scale. In particular, the irradiation step can be performed at room temperature to modify a large amount of various matrix polymers at the same time. This is why the method is highly cost-effective compared with other approaches. In this method, styrene and/or its derivatives are usually grafted onto fully or partly fluorinated polymers such as poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(ethylene) (PE), poly(ethylene-co-tetrafluoroethylene) (ETFE), poly(vinylidene fluoride) (PVDF), and poly(tetrafluoroethylene) (PTFE) and subsequently by sulfonation to obtain graft-type PEMs<sup>8</sup>. Among these graft-type PEMs, polystyrene sulfonic acid (PSSA)-grafted poly(ethylene-co-tetrafluoroethylene) (ETFE) polymer electrolyte

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membranes (ETFE-PEMs) have been investigated extensively as alternative membranes for PEMs<sup>8-16</sup>. The membrane exhibits good proton conductivity, mechanical integrity, and thermal stability compared to Nafion at a similar water uptake (40%). Moreover, ETFE-PEM shows the unique higher-order structures of lamellar, lamellar grains, and crystallite network structures, which are quite stable under immersed conditions<sup>9,13,17-22</sup>. These hierarchical microstructural features strongly relate to the mechanical integrity of the membranes under severe operation conditions (high temperature and high relative humidity) of fuel cells<sup>14</sup>. However, previous reports mainly represented the results of ETFE-PEMs having a grafting degree (GD) higher than 19%<sup>14-18,20-31</sup>. The higher the GD is, the higher the conductance, but the lower the mechanical integrity and the higher the swelling<sup>7-9,11,17,25,29</sup>. For example, ETFE-PEMs with a GD of 34–128% exhibit a high conductance of 0.104–0.233 S/cm but also high water uptake (41–168%). This large water content reduces the tensile strength from 25 to 7.5 MPa<sup>26</sup>. A membrane showing a good balance between electrochemical properties and mechanical strength is better for fuel cell performance. Therefore, it is necessary to find graft-type membranes with a moderate GD for fuel cells. In this report, the properties of ETFE-PEM with a low GD of 10% are investigated by thermal gravimetric analysis (TGA), mechanical testing, and electrochemical impedance spectroscopy for PEM fuel cell applications.

## EXPERIMENTAL

### Materials

The 50-mm-thick ETFE film was purchased from Asahi Glass Co. Ltd., Japan. Other chemicals, such as styrene, 1,2-dichloroethane, sodium chloride, and sodium hydroxide, were provided by Wako Pure Chemical Industries, Ltd., Japan.

### ETFE-PEM preparation

The preparation procedure and chemical structure of the original ETFE, polystyrene (PS)-grafted ETFE (grafted-ETFE), and ETFE-PEM are depicted in Scheme 1. Sample preparation procedures were similar to those of previous reports<sup>8,17,25,28</sup>. Briefly, all the pristine ETFE films were cut into square pieces with dimensions of 6x6 cm<sup>2</sup> and then irradiated by  $\gamma$ -rays emitted from a <sup>60</sup>Co source under argon conditions. Samples were irradiated with doses of 15 kGy/h and 15 kGy, respectively. After irradiation, the samples were immersed in a

styrene/toluene mixture with different concentrations at 60 °C for graft polymerization to obtain the grafted ETFE films. The grafted films were then soaked in a 0.2 M chlorosulfonic acid solution in 1,2-dichloroethane at 50 °C (approximately 6 hours) for sulfonation. The membranes were finally hydrolyzed by pure water at 50 °C for 24 hours to obtain the ETFE-PEMs. Note that in our previous works, the grafting was already confirmed using Fourier transform infrared spectroscopy (FT-IR)<sup>12,29</sup> and X-ray photoelectron spectroscopy (XPS)<sup>30</sup>. Moreover, the presence of polystyrene grafts in the grafted-ETFE films and final membranes (ETFE-PEMs) was also affirmed using ultrasmall and small-angle X-ray scattering (USAXS/SAXS)<sup>14,21,25,27,28</sup> and positron annihilation lifetime spectroscopy (PALS)<sup>24,27</sup>.

### Characterization

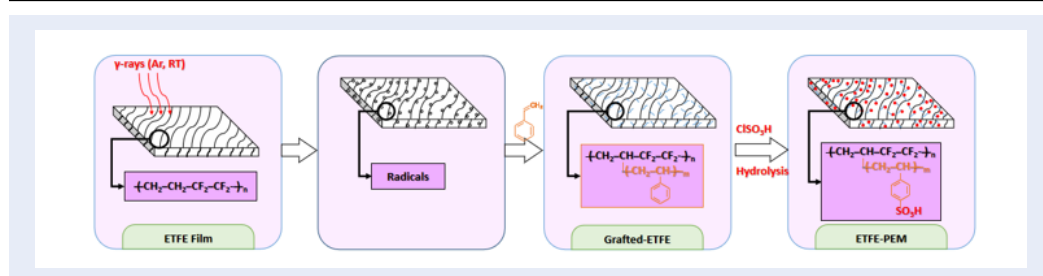
The grafting degree (GD) of grafted-ETFE and ETFE-PEM is determined based on the formula:

$$GD(\%) = \frac{100(w_g - w_0)}{w_0} \quad (1)$$

where  $w_g$  and  $w_0$  are the mass of the sample before and after the grafting process, respectively.

The thermal behavior of all samples was investigated by TGA measurements (Labsys Evo TGA 1600 °C) in a nitrogen atmosphere to prevent sample oxidation and any moisture absorption. An aluminum pan was used for each sample, and it was flamed prior to each analysis. The measurements were conducted with temperatures ranging from room temperature to 800 °C at a temperature ramp rate of 10 °C/min. The TGA curves were determined, and the minima and maxima of the derivative curves were selected to determine the decomposition temperature.

Tensile tests were investigated by the stress–strain curves. The instruments of STA-1150 (A&D Co., Ltd., Japan) and Instron-4302 universal testing at a constant crosshead speed of 10 mm/min are utilized. For the grafted-ETFE and ETFE-PEM in testing in the dry state, the samples were placed in a vacuum oven at 60 °C for 24 h. For testing under wet conditions, only ETFE-PEMs were immersed in DI water at 25 °C for 24 hours before surveying. For tensile tests at a relative humidity (RH) of 100% and 80 °C, a temperature-controlled water tank was used to set the desired temperature and relative humidity for testing. For each condition, the sample was cut into five to ten dumb-bell shapes (1x6.3 cm<sup>2</sup> in total and 0.3x2.6 cm<sup>2</sup> in test area) using the ASTM D1882-L instrument, and each specimen was subjected to a tensile test in the machining direction.



Scheme 1: Preparation procedure and chemical structure of the ETFE film, grafted-ETFE film, and ETFE-PEM. The original ETFE film was irradiated by gamma rays to generate free radicals and then grafted immediately with styrene and finally the sulfonation. The membrane was hydrolyzed to obtain the ETFE-PEM.

The proton conductivity is determined based on the formula:

$$\sigma \text{ (S/m}^2\text{)} = \frac{h}{RA} \quad (2)$$

where  $h$  (cm),  $R$  ( $\Omega$ ), and  $A$  ( $\text{cm}^2$ ) are the distance between the two electrodes, the membrane resistance, and the area of the membrane, respectively. In this formula, the resistance value ( $R$ ) is measured using the a.c. impedance method consisting of two platinum electrodes for the LCR HiTESTER 3522-50 over a frequency range of  $10^{-1}$ – $10^{-2}$  kHz and 0.1 V ac amplitude. The membrane was placed in a Teflon cell and located between the two electrodes at a fixed distance (Figure 1).

## RESULTS

The TGA and derivative thermogravimetry (DTG) profiles of the original ETFE, grafted ETFE, and ETFE-PEM are presented in Figure 2. The TGA profile of the original ETFE shows a single-step degradation at 500 °C, ascribed to the decomposition of the polymer main chain<sup>11,22</sup>. However, the DTG curve exhibits an additional thermal decomposition step at 242 °C. The TGA and DTG profiles of the grafted ETFE film show three decomposition temperature steps at 242 °C (Step 1), 413 °C (Step 2), and 507 °C (Step 3) (Table 1). As shown in the DTG curves, the decomposition temperature at 242 °C of the original ETFE and grafted film relates to the intrinsic crystallinity of the ETFE base film<sup>30</sup>. Namely, ETFE possesses a lamellar crystal with a crystallinity of 35%, as determined by small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC)<sup>13,17,20,24–27</sup>. Steps 2 and 3 are attributed to the decomposition of the polystyrene graft and the pristine ETFE backbone, respectively<sup>25</sup>. The TGA and DTG profiles of ETFE-PEM show three decomposition steps at 247 °C (Step 1), 402 °C (Step 2), and

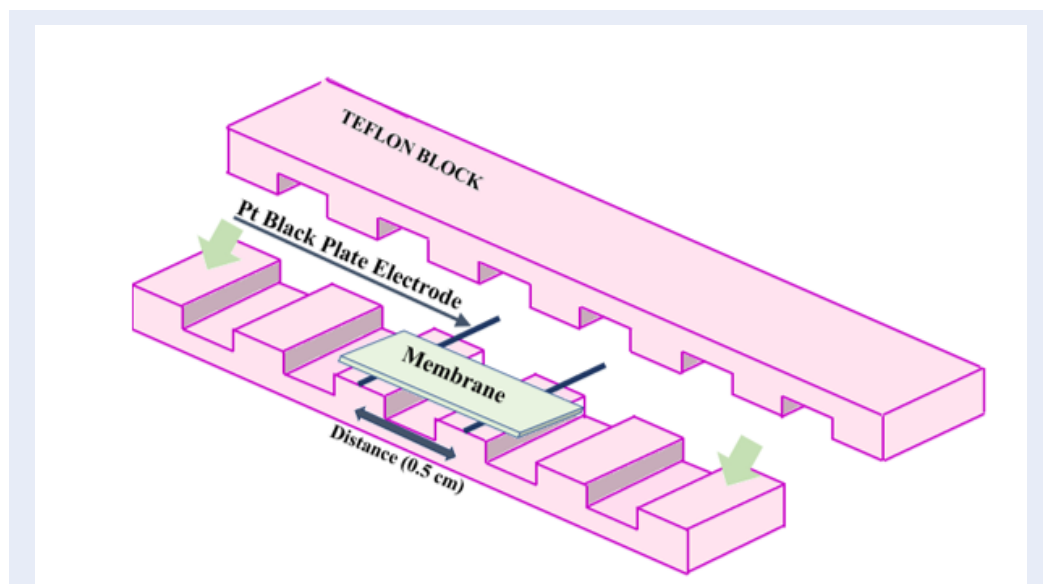
514 °C (Step 3), which correspond to the decomposition of the sulfonic acid group, polystyrene graft, and ETFE backbone, respectively<sup>25</sup>.

Figure 3 shows the stress–strain curves of ETFE-PEM under dry, wet, and humidified (80 °C with 100% RH) conditions. The measurement conditions result in a change in the shapes of the stress–strain curves and their characteristic values (strength and elongation at break). Typical stress–strain curves of the ETFE-PEM are bilinear, i.e., consist of a linear elastic region and a linear plastic region, which are interconnected by a yielding region. Specific results are presented in Table 2. The strengths of ETFE-PEM in dry and wet states are 39 and 30 MPa, respectively. At 80 °C and 100% RH, the strength drops to 20 MPa. The elongation of ETFE-PEM in dry and wet states is 291 and 325%, respectively. At 80 °C and 100% RH, the elongation increases to 500%.

Figure 4a shows the resistance values of ETFE-PEM at an RH of 30% with temperatures ranging from 40–80 °C. The resistance values seem quite stable with time measurement. The proton conductivity is calculated from formula (2) and is presented in Table 3. As shown in Table 3, ETFE-PEM does not show clear proton conductivity with temperature at an RH of 30%. Figure 4b shows the resistance at a temperature of 80 °C with RH ranging from 40–98%, and the corresponding conductance is shown in Table 3. The conductivity doubles from  $6.10 \cdot 10^{-4}$  to  $13.10 \cdot 10^{-4}$  S/cm with increasing RH from 40 to 50% and increase to  $21.10 \cdot 10^{-4}$  S/cm at an RH of 60%. The ETFE-PEM only shows a slight increase in conductance (0.0021–0.0024 S/cm) with an RH of 60–98%.

## DISCUSSION

The TGA and DTG curves of ETFE-PEM at a low GD of 10% are quite similar to those of Nafion<sup>25,31</sup>. The thermal decomposition temperature of ETFE-PEM is



**Figure 1: Schematic of the proton conductivity measurement cell.** The membrane was located between the two platinum electrodes (at a fixed distance of 0.5 cm) in a Teflon cell. The resistance of the membrane is measured using the LCR HiTESTER 3522-50 over a frequency range of  $10^{-1}$ – $10^{-2}$  kHz and 0.1 V ac amplitude.

**Table 1: The results of TGA/DTG measurements of original ETFE, grafted-ETFE, and ETFE-PEM**

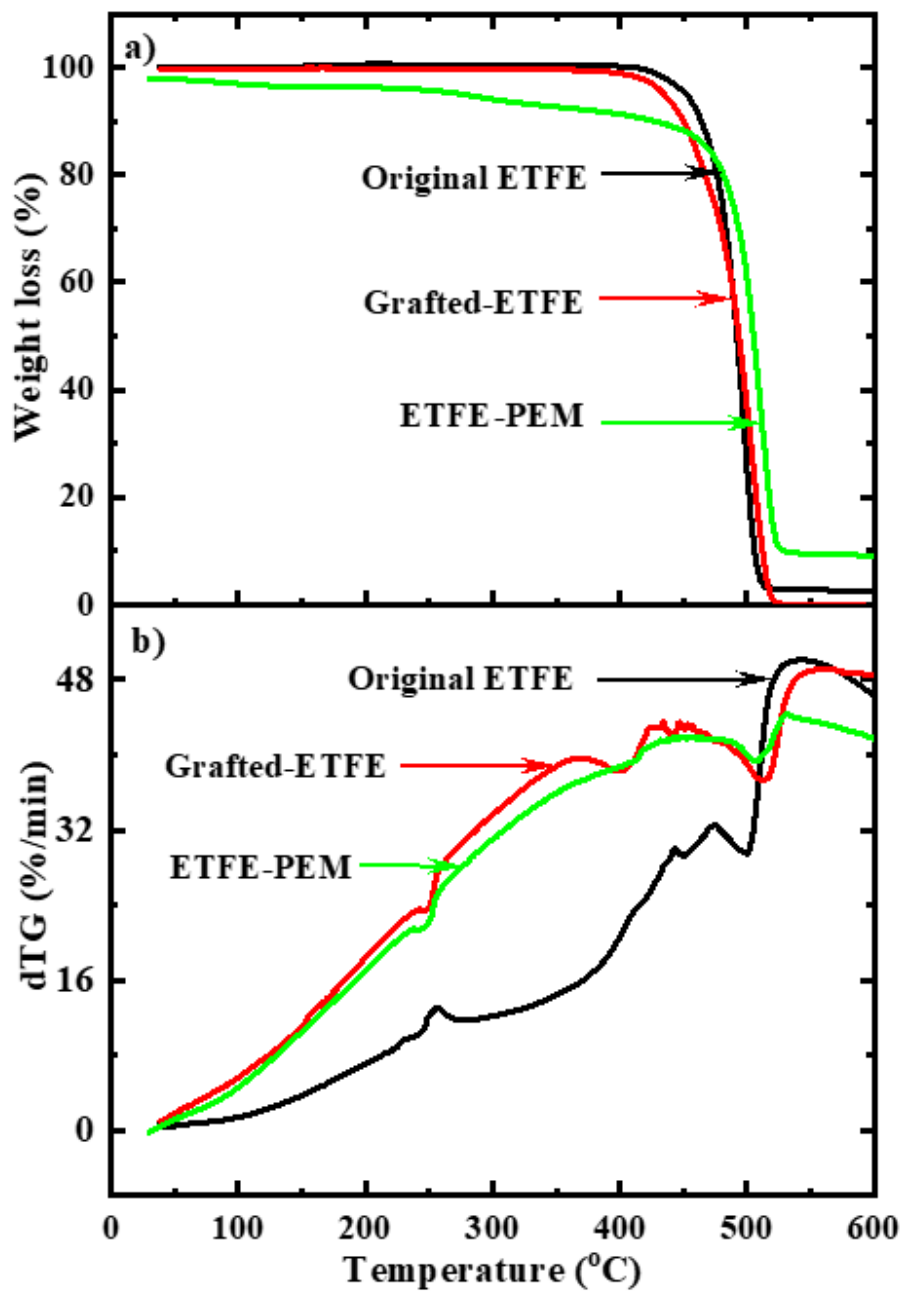
Samples	Step 1 (°C)	Step 2 (°C)	Step 3 (°C)
Original ETFE	242	–	500
Grafted-ETFE	242	413	507
ETFE-PEM	247	402	514

**Table 2: Stress and strain of ETFE-PEM with a GD of 10% under dry, wet, and humidified (80 °C with 100% RH) conditions**

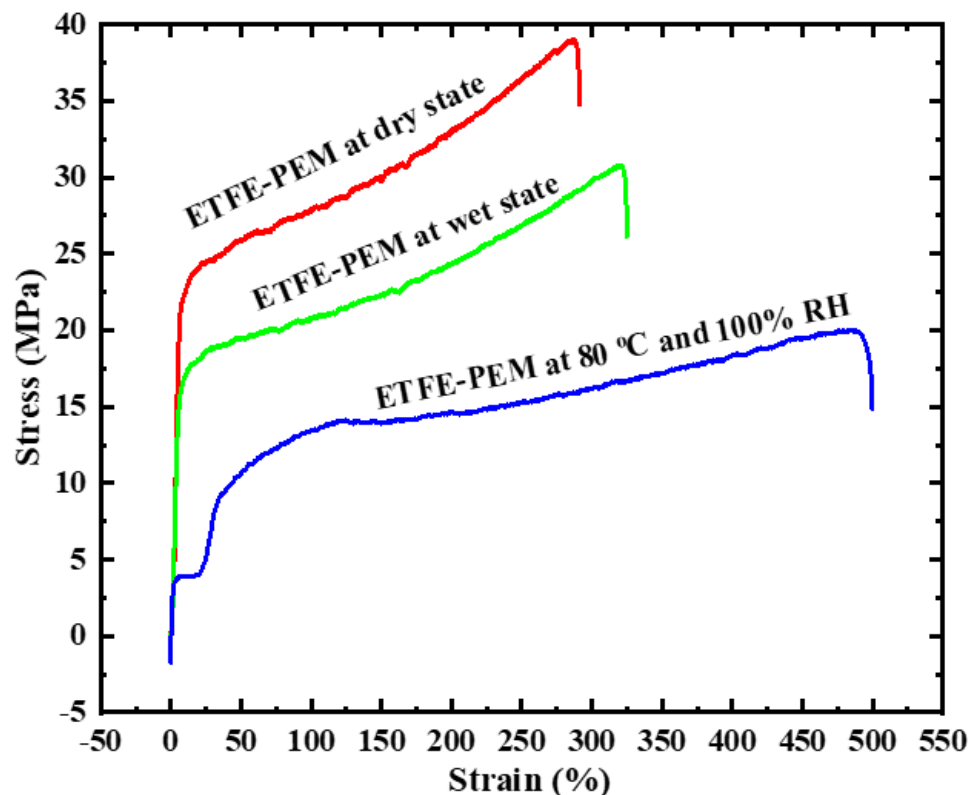
Conditions	Stress (MPa)	Strain (%)
ETFE-PEM at dry state	39 ± 0.7	291 ± 9
ETFE-PEM at wet state	30 ± 0.5	325 ± 12
ETFE-PEM at 80 °C and 100% RH	20 ± 1.1	500 ± 17

**Table 3: Proton conductivity of ETFE-PEM (GD = 10%) at RH = 30% with T = 40–80 °C and at T = 80 °C with RH = 40–98%**

Conditions	$\sigma$ (S/cm)	Conditions	$\sigma$ (S/cm)
T = 40 °C, RH = 30%	0.0003	T = 80 °C, RH = 40%	0.0006
T = 50 °C, RH = 30%	0.0002	T = 80 °C, RH = 50%	0.0013
T = 60 °C, RH = 30%	0.0002	T = 80 °C, RH = 60%	0.0021
T = 70 °C, RH = 30%	0.0002	T = 80 °C, RH = 80%	0.0022
T = 80 °C, RH = 30%	0.0004	T = 80 °C, RH = 98%	0.0024



**Figure 2:** TGA (a) and DTG (b) profiles of the original ETFE, grafted-ETFE, and ETFE-PEM. The grafting polymerization and sulfonation do not alter significantly the decomposition of the polymer main chain. Residual for the original ETFE and grafted-ETFE films is almost zero while that for the ETFE-PEM is approximately 10%.

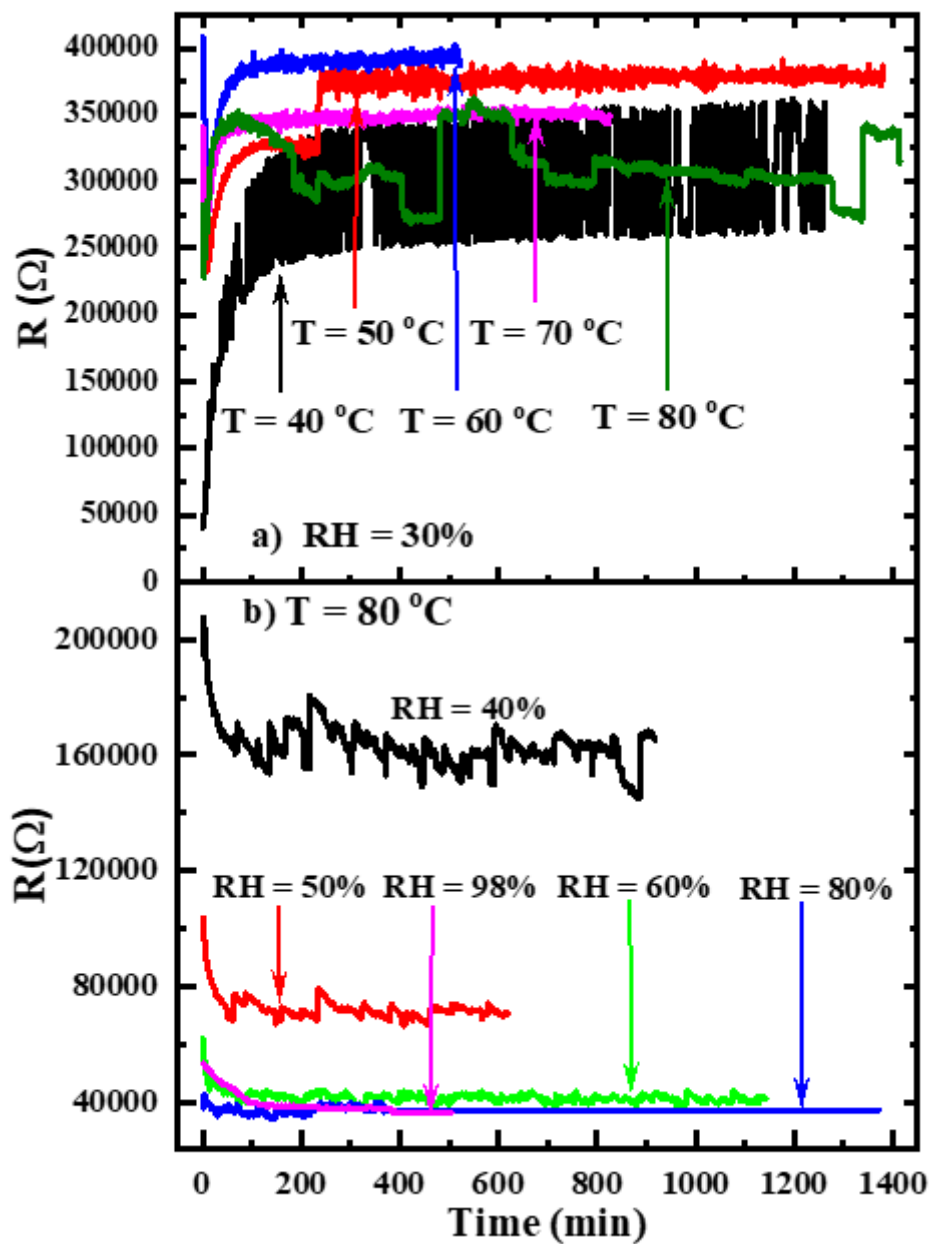


**Figure 3: Stress–strain curves of ETFE-PEM with a GD of 10% under dry, wet, and humidified (80 °C, 100% RH) conditions.** The measurement conditions cause a change in strength and elongation at break. The strength of ETFE-PEM at 80 °C and 100% RH drops to 50% as compared with that at dry condition, indicating the strong effects of high water and high temperature on the membrane even at very low GD of 10%.

above 200 °C, which is suitable for hydrogen fuel cell applications. As reported previously<sup>26</sup>, each step of the thermal decomposition temperature in the ETFE-PEM is hardly influenced by the grafting degree. This can be expected for the side chains but quite interesting for the polymer backbones. The thermal decomposition temperature of the ETFE backbones decreased gradually with a GD of 20–117% only for the grafted ETFE films but was quite small for the ETFE-PEMs<sup>26</sup>. The tensile strength results of ETFE-PEM under dry, wet, and humidified conditions, as represented in Table 2, are believed to be due to the intrinsic water absorption of the membrane because water absorbed by the polymer acts as a plasticizer, which in turn softens the material and reduces the load-carrying capacity<sup>29–33</sup>. An increase in temperature also resulted in a further reduction in the load-carrying capacity of ETFE-PEM. This result can be elucidated using the combined effects of RH and temperature. Upon a sufficient level of hydration (RH =

100%), the increase in temperature from room temperature to 80 °C caused a significant increase in the volume of hydrophilic domains containing the PSSA grafts. This increase is associated with the reduction in tensile strength from 30 to 20 MPa (Table 2). At 80 °C and RH = 100%, the tensile strength dropped dramatically from 20 to 7.5 MPa with GDs of 20–117%, as reported previously<sup>26</sup>. In other works, the tensile strength at a GD of 10% is higher than that with higher GDs.

The proton conductivity of ETFE-PEM shows no clear trend with temperature at an RH of 30%. This result should be related to the very low grafting degree (GD = 10%) and low RH, which result in very low ionic concentration and water uptake for conductance. Thus, an increase in temperature could not clearly accelerate the conductance. However, the conductance of the membrane exhibits a rapid increase with a relative humidity of 40–60% at a temperature of 80 °C. The result can be elucidated from



**Figure 4:** Resistance of ETFE-PEM (GD = 10%) at RH = 30% with T = 40–80 °C and at T = 80 °C with RH = 40–98%. Upon RH = 30%, the change of temperature from 50–70 °C does not cause a change in resistance. In the meantime, at T = 80 °C, the change of RH from 40–98% results in the decrease of resistance, i.e., increase in conductance.

the fact that an increase in relative humidity induces significant phase separation between the hydrophobic polymer backbone and hydrophilic PSSA, which can provide small ionic channels. These ionic channels are assumed to align along the hydrophobicity of the polymer backbone, thus providing conducting layers even at a very low GD. This result can be supported by high-order microstructures consisting of PSSA domains revealed by SAXS as reported previously<sup>13,17,20,24,27</sup>. At GDs of 19–102%, the conductance ( $10^{-3}$ – $10^0$  S/cm) is higher than that at a GD of 10%, as expected<sup>26</sup>. However, this increase is accompanied by a significant reduction in tensile strength and an increase in water uptake, as mentioned above. Thus, conduction at moderate GDs should be considered properly for fuel cell applications.

## CONCLUSION

The thermal stability, mechanical strength, and ionic conductance of ETFE-PEM at a low GD of 10% are investigated for fuel cells. The membrane shows comparable or better mechanical strength (> 20 MPa) and thermal stability (> 240 °C) than Nafion. Resistance measurements demonstrate that ETFE-PEM has stable conductivity over time under varying temperature and humidity conditions. In particular, ETFE-PEM does not show clear conductance with an increase in temperature at an RH of 30% but exhibits a rapid increase in conductance with a relative humidity of 40–60% at a temperature of 80 °C. This result provides a potential application in fuel cells for small devices such as motorcycle motorcycles, mobile phones, or portable electronics. Further investigation of ETFE-PEM at low GD in electrochemical properties and durability is necessary for fuel cell applications.

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## LIST OF ABBREVIATIONS

**DSC:** Differential scanning calorimetry

**DTA:** Differential thermal analysis

**ETFE:** Poly(ethylene-co-tetrafluoroethylene)

**ETFE-PEM:** Polystyrene sulfonic acid (PSSA)-grafted poly(ethylene-co-tetrafluoroethylene) polymer electrolyte membrane

**GD:** Grafting degree

**PEM:** Proton exchange membrane

**PS:** Polystyrene

**PSSA:** Polystyrene sulfonic acid

**RH:** Relative humidity

**SAXS:** Small angle X-ray scattering

**TGA:** Thermal gravimetric analysis

**TS:** Tensile strength

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

## DATA AVAILABILITY STATEMENT

The data sets are not publicly available but are available from the corresponding author upon reasonable request.

## AUTHORS CONTRIBUTION

**Tran Duy Tap:** Conceptualization, Project administration, Funding acquisition, Supervision, Resources, Investigation, Methodology, Data curation, Formal analysis, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. **Vo Thi Kim Yen:** Investigation, Methodology, Data curation, Formal analysis, Validation, Visualization, Writing — original draft, Writing - review & editing. **Dinh Tran Trong Hieu, Lam Hoang Hao, Tran Hoang Long, Nguyen Huynh My Tue, and Nguyen Manh Tuan:** Visualization, Validation, Writing- review & editing. **Nguyen Tien Cuong, Truong Thi Hong Loan, and Tran Van Man:** Visualization, Validation, Data curation.

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