

Short Communication

Effects of γ -Ray Irradiation on Electrical and Physico-Chemical Properties of Sulfonated PVDF-HFP/1H-1,2,4-Triazole Proton Conducting Membranes

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A new material for proton conducting electrolyte base on sulfonated poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP)/1H-1,2,4-Triazole (TriA) membrane operating at low relative humidity and has capability to self-humidify were investigated. Different concentrations of TriA and sulfamic or amidosulfonic acid (H_3NSO_3) in PVDF-HFP were prepared. The pores of a porous PVDF-HFP were packed with proton carrier, TriA and sulfamic acid (SFA). The samples were then exposed to γ -rays of up to 50 kGy. The effects of high energy γ -rays irradiation onto these proton conducting membranes have been observed. The surface morphology was analysed by scanning electron microscopy (SEM). The ionic conductivity of the irradiated membrane was determined using impedance spectroscopy (IS) at different temperatures between 30 °C and 100 °C. The results showed that the pores membranes shrinkage after irradiation and proton conductivity of the membrane increased when the absorbed dose up to 30 kGy and after which the proton conductivity decreased with increasing of absorbed dose.

Keywords: Sulfonated PVDF-HFP/1H-1,2,4-Triazole, Proton conducting membrane, Sulfamic acid, Fuel cell

1. INTRODUCTION

Polymer exchange membrane fuel cell (PEMFC) has received intensive study as a promising alternative green power sources in future. Polymer electrolyte membrane (PEM) is usually a polymer

that acts as a proton transfer between a cathode and anode, and prevent fuel crossover between the electrode catalyst composite [1]. Nafion is a commercially thin polymer membrane that has been known and often used in fuel cell, however, it is considered costly and the procedures for sample preparations are difficult and complex [2- 4].

The abovementioned problem can be addressed by two options. The first is by undertaking other alternative cheaper materials such as a semicrystalline porous fluoropolymer namely poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), poly(vinylidene fluoride) (PVF), and poly(tetrafluoroethylene) (PTFE). For example, Kumar et al. [5] found that a porous PVDF-HFP membrane can be prepared using the different non-solvents evaporation technique. They also found that the pores developed through this method are capable of entrapping liquid electrolyte solutions such as *p*-toluene sulfonic /phosphoric/sulfuric acid. More recently, Cui et al. [6] showed that electrolytes can be stored, and electrolyte uptake can be increased in microporous PVDF-HFP membranes. This finding indicates that the content of carrier ions within a porous polymer membrane increases, thereby enhancing ionic conductivity [7]. The second is to simplify sample preparation by using blending techniques in combination with radiation-induced grafting (RiG) [8]. The membrane produced has a special chemical structure composed of the hydrophobic main chain and sulfonated side chain. The former acts a stable backbone, which provides the necessary strength, dimensional stability, and gas barrier, whereas the latter provides the capacity for proton conductivity [9]. The benefits of the RiG method include the lack of the need for a chemical initiator, simple preparation from ready-made preformed films, and easy control of the degree of grafting and sulfonation that contributes to proton conductivity [10].

In this work, a combination of blending and radiation method was used. A polymer, PVDF-HFP, was used as polymer host, whereas sulfamic acid (SFA) was used as salt. The PVDF-HFP and sulfamic acid solution was blended with 1H-1,2,4-Triazole (TriA) to enhance the conductivity of the PEM. This blending is a novel innovation, and the output is called the PVDF-HFP/TriA/SFA membrane. The membrane will undergo irradiation technique using cobalt-60. This membrane is very unique as it has the capability to self-humidify at room temperature without immersion in water.

2. EXPERIMENTAL

2.1. Materials

PVDF-HFP with an average molecular weight of 400,000 (Aldrich, USA), 1,2,4-Triazole (Merck), sulfamic acid (Fluka), and *N,N* – Dimethylformamide (DMF) (Sigma-Aldrich) were used to prepare the samples.

2.2. Preparation of Samples

PVDF-HFP (1.0 g) was dissolved in 15 ml DMF. The solution was stirred for 6 hours at room temperature. Once the polymer was dissolved, sulfamic acid in different concentrations (0 – 50 wt. %)

were added into polymer solution and stirred for 12 hours. 1H-1, 2, 4 –Triazole (10, 20, 30 and 40 wt.%) were then added into solution and again stirred using Sonochemical Equipment (Newpower Guangzhou, China), for 15 minutes. Upon that, it was poured into Teflon plate and dried in vacuum oven (80°C) for 6 hours to form membrane.

2.3. Irradiation method

The PVDF-HFP/SFA/TriA membranes were irradiated using simultaneous method with Co-60 γ -rays up to 50 kGy. The irradiation was carried out using MINTec-Sinagama at Malaysian Nuclear Agency. The dose rate used was 2.033 kGy/h.

2.4. Impedance Spectroscopy (IS)

IS was carried out to measure the conductivity of the sample. The conductivity was determined using WEIS510 Multichannel EIS System in the frequency range 10 Hz to 1 MHz in the temperature range between 298 K and 373 K inside a Humidity & Temperature Chamber (ESPEC-SH 221) at relative humidity (RH) 60%. The membranes were cut into suitable size and sandwiched between two stainless steel electrodes. The conductivity was evaluated using the equation:

$$\sigma(S.cm^{-1}) = \frac{t}{R_b A} \quad (1)$$

Where t is the thickness of the membrane; A is the area of surface between electrode and membrane; R_b is the bulk resistance of the membrane obtained from cole-cole plot.

2.5. Surface Morphology

Scanning electron microscope (SEM) investigations were carried out on a Supra 40VP, Zeiss, Gemini. The samples were vacuum-dried, sliced with microtome, and coated with thin film for SEM observation.

2.6. Water Sorption

Water sorption experiment was carried out by hanging a membrane in the Humidity & Temperature Chamber (ESPEC-SH 221). Prior to water sorption is carried out; the membrane was dried in the chamber at 80°C for two hours. Then, the dry PVDF-HFP/TriA/SFA membranes were measured using weighing balance immediately. Next, set a relative humidity (RH) at 80% RH at fixed temperature (50 °C) to let the polymer membrane absorption vaporized water. The measurements of water sorption were calculated using equation (1), where W_w and W_d are the weight of wet and dried membranes, respectively.

$$\text{Water Sorption (wt.\%)} = \frac{w_w - w_d}{w_d} \times 100\% \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Conductivity Study

It can be observed that the ionic conductivity at room temperature (27°C) and room RH (68%) of the membranes increased with increasing SFA concentration up to 35 wt. %, after which the conductivity decreased (Table 1). The variation in polymer conductivity is due to ion association and dissociation [11]. The decrease in conductivity at higher concentrations is probably caused by the formation of ion aggregates, which decrease the number of free mobile ions available to take part in the conduction process. The samples PF6 was then chosen for further step (blend with TriA) due to the best composition of PVDF-HFP/SFA ratio that has produced the highest conductivity.

Table 1. The composition of PVDF-HFP doped with sulfamic acid (SFA) and 1H-1,2,4-Triazole

Samples	PVDF-HFP	SFA (g)	SFA (wt.%)	Conductivity (S/cm)
PF1	1.0g	0.111	10	5.85 x 10 ⁻⁶
PF2	1.0 g	0.177	15	9.44 x 10 ⁻⁶
PF3	1.0 g	0.250	20	1.08 x 10 ⁻⁵
PF4	1.0 g	0.333	25	2.10 x 10 ⁻⁴
PF5	1.0 g	0.429	30	2.67 x 10 ⁻⁴
PF6	1.0 g	0.539	35	4.84 x 10 ⁻⁴
PF7	1.0 g	0.667	40	3.68 x 10 ⁻⁴
PF8	1.0 g	0.818	45	2.67 x 10 ⁻⁴
PF9	1.0 g	1.000	50	2.67 x 10 ⁻⁴

The conductivity values of the γ -rays irradiated (10-50 kGy) PVDF-HFP/TriA/SFA membrane are influence on the different concentration wt.% of TriA (Figure 1). As can be observed, the conductivity increases at absorbed dose 10-20 kGy. Then, significant radiation effect on the conductivity of the irradiated PVDF-HFP/SFA/TriA membrane is achieved at 30 kGy. Afterwhich, the conductivity of the irradiated PVDF-HFP/TriA/SFA membrane decline at absorbed dose higher than 30 kGy. This could best to explain that the possibility of irradiation effect which can damage the atoms or molecules in the PVDF-HFP/TriA/SFA membrane it passes through [12-13]. This will distort the ion pathway and hence reduces the ionic conductivity of the samples.

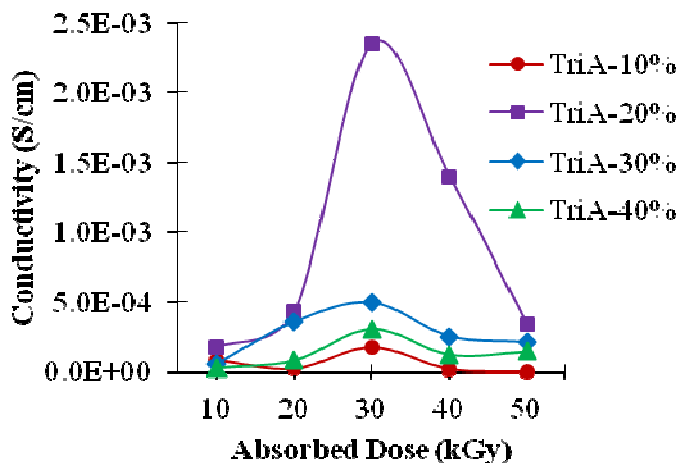


Figure 1. Plot of conductivity versus different triazole concentration and irradiated of PVDF-HFP/SFA/TriA membrane at room temperature.

Figure 2 depicts the conductivity-temperature dependence of conductivity for the sample containing 35 wt.% of sulfamic acid with 10, 20, 30, 40 wt.% 1H-1,2,4-Triazole respectively for irradiated membrane in temperature range of 298 to 373 K at RH 60%. The plot shows that conductivity for these membranes is thermally assisted. A linear relationship was observed, confirming that the behavior of ionic conductivity followed the Arrhenius rule. The membrane containing 20 wt.% of triazole shows the highest proton conductivity (1.50×10^{-3} S/cm at 373 K) when the temperature increased.

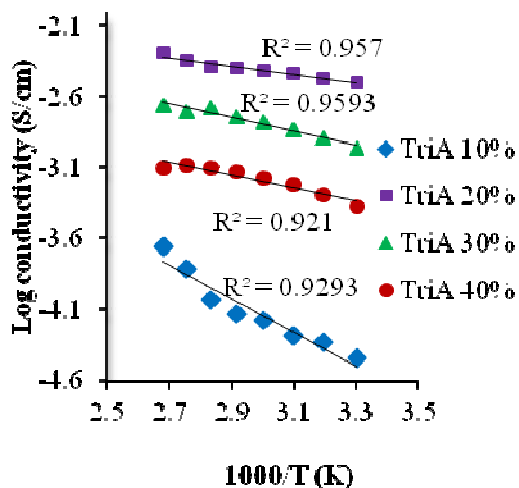


Figure 2. Variation of ionic conductivity with temperature for irradiated membrane PVDF-HFP/SFA/TriA at 60% RH for different TriA concentrations at absorbed dose 30 kGy.

The increase in conductivity with temperature is governed by the hopping mechanism between coordinating sites, local structural relaxations, and segmental motions of the polymer host [14]. SFA consists of a sulfonic acid group for ion (proton) exchange and provides a site or base for proton conducting. On the other hand, TriA provides proton transport facilitators. Both SFA and TriA play major roles in conducting protons in membranes, indicating the strong possibility for the sulfonic acid of SFA hopping or conducting upon TriA. Thus, this proton conduction can be best explained as intermolecular mechanism [15-16].

3.2. Surface analyses

Figure 3 shows the comparison between the non-irradiated PVDF-HFP/SFA/TriA and the irradiated membrane. The size of the pores were around 2 -6 μm and it can be considered as a micropores PVDF-HFP/SFA/TriA membrane. Pore size diameter were around 1.0 to 7.0 μm measured capillary flow porometer (CFP-1500-A) from Porous Materials, Inc. (PMI). The non-irradiated membrane exhibited large pores which were reduced after irradiation. The shrinking of the pores can be achieved using the triazole grafted onto the PVDF-HFP membranes or the triazole polymerized into the pores of PVDF-HFP. The SEM images indicate that the sizes of the membrane pores can possibly be controlled by the irradiation method.

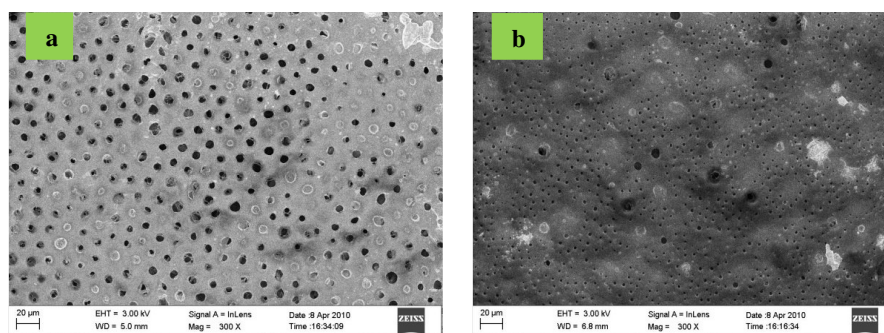


Figure 3. SEM images of PVDF-HFP/SFA(35 wt.)/TriA (20 wt.) for (a) non-irradiated and (b) irradiated membranes at an absorbed dose of 30 kGy

3.3. Water Sorption

Water uptake and transport of water in polymer membranes plays an essential role in the operation of polymer electrolyte membrane fuel cell (PEMFC) and it could determine the proton conductivity of the membrane. Figure 4 depicts water sorption of PVDF-HFP/SFA/TriA (20 wt.%) membranes versus time at 80 % relative humidity. Radiation effect (30kGy) on PVDF-HFP/SFA/TriA membrane show that water sorption increased with increasing amount TriA. As a result, polymerization of triazole can gain the mass of the membrane onto the pores of PVDF-HFP membrane. It can be inferred that the polymerized of triazole onto PVDF-HFP membrane increased the mass of the membrane upon irradiated to γ -rays. The increase of the membrane mass due to

polymerization of triazole onto the PVDF-HFP/SFA/TriA membrane could more provide its ability to absorb or diffuse more water. Thus, it can be concluded that water sorption of the PVDF-HFP membrane can be enhanced by using irradiation technique.

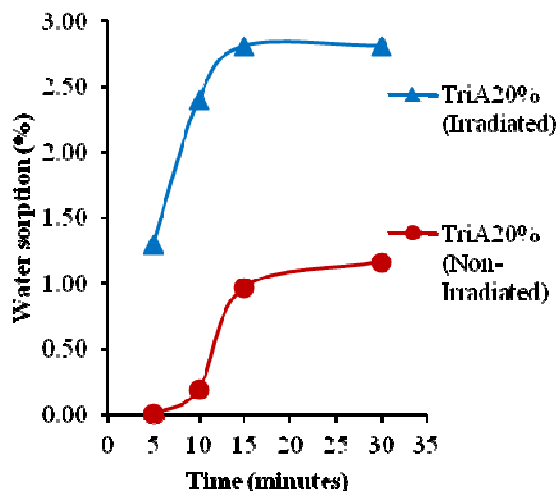


Figure 4. Comparison of water sorption of the PVDF-HFP/TriA/SFA membrane from water vapor (50°C) at different relative humidity.

4. CONCLUSION

The radiation effect on the proton exchange membrane based on composited PVDF-HFP with TriA and SFA exhibited excellent proton conductivity at room temperature up to intermediate temperature. The highest conductivity obtained was $1.50 \times 10^{-3} \text{ Scm}^{-1}$ for 35 wt.% of SFA and 20 wt.% of TriA. The proton conductivity depended on the concentration ratio of TriA and SFA onto microporous PVDF-HFP membrane. Surface images showed that the PVDF-HFP/SFA/TriA membrane had micropores. These micropores were filled with electrolytes and underwent shrinking after radiation by γ -rays. The shrinking of the pores can be observed through the triazole grafted onto the PVDF-HFP membranes or the triazole polymerized into the pores of PVDF-HFP. Results also showed that water sorption of the PVDF-HFP/SFA/TriA membrane increased upon being exposed to γ -rays. This study on the PVDF-HFP/TriA/SFA membrane indicated that it can be affected significantly by γ -rays, which can make this material a potential candidate as a membrane in proton exchange membrane fuel cells. Overall, this finding is promising, and future work will focus on the further enhancement of membrane durability.

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