Grafting of Vinyl Pyrrolidone/Styrene onto Ethylene/Chlorotrifluoroethylene Membrane for Proton ExchangeMembrane Fuel Cell

E.E. Abdel-Hady[a], M.M. El-Toony[b,*]

[a] Physics department, Faculty of Science, El-Minia University, Atomic energy authority, 3 Ahmad El-Zomor street, P.O. Box 29, Nasr City, Cairo, Egypt
[b] National center for radiation research and technology, Atomic energy authority, 3 Ahmad El-Zomor street, P.O. Box 29- Nasr City, Cairo, Egypt

A B S T R A C T

Simultaneous gamma irradiation was proved to be an effective tool for ethylene/ chlorotrifluoroethylene grafting by styrene and vinyl pyrrolidone with different ratios. It was found that; the optimum grafting yield was 81% by using 40 kGy gamma irradiation dose when the binary monomers ratio was 1:1 (styrene: vinyl pyrrolidone). The grafted membranes were investigated for chemical structure by FT-IR and thermal properties by thermal gravimetric analysis. The mechanical properties were studied by measuring tensile strength while morphological structure was characterized by scanning electron microscope. The membranes' free volume sizes were determined using positron annihilation lifetime spectroscopy (PALS). Ion exchange capacity, water uptake and membranes thickness were investigated and proton conductivity was evaluated. The optimum temperature for attaining the maximum fuel cell performance was at 75 °C while it reduced by decreasing the temperature to 50 °C or increasing it to 85 °C. The fuel cell performance based highest yield of the grafted membrane was more durable than compressed Nr.118 (commercial membranes) up to 450 hours.

© 2015 Published by Elsevier Ltd.

1. Introduction

In the past decades, proton exchange membrane fuel cells (PEMFCs) attracted more attention due to their advantages of high power density, simplicity operation, high-energy conversion efficiency and near zero harmful emissions [1–3]. Three potential applications, such as automotive, stationary and portable power sources, highly motivate PEMFCs current R and D [4].The operation conditions required fuel and oxidant were fed to be applied into the fuel cell. However, the external humidifying equipment made the system more complex and increased its weight, volume and cost, which burdened fuel cell stack design. Obviously, the promoted operation of PEMFCs without external humidifying subsystem seemed to be more attractive and valuable [5].

Many polymer membranes have already been used in PEMFC and their performances in fuel cells were reviewed [6–9]. Radiation grafted membranes have a major advantage of utilizing preformed commercial polymer membranes.A partially fluorinated polymer electrolyte membrane is an interesting candidate for replacing commercial membranes because of low costs along with electrochemical properties [10]. Previous fuel cell membrane research had examined the styrene gamma irradiation-grafting. Furthermore sulphonating partially fluorinated polymers(e.g., PVDF and ECTFE) [11,12] was carried out. Binary monomers were extensively used [13] for grafting to create bi-functional polymers and to increase the grafting yields.

Perfluorosulfonic acid membranes which have high thermal and chemical stability provide high proton conductivity only when they are hydrated. The reason is the mobility of the protons along the water swollen phase which can befeasible up to dew point of water [14]. However atelevated temperatures the conductivity of these hydrated systems changes due to humidity loss [15]. Proton-conducting membranes composed of polystyrene sulfonic acid, (ECTFE), and poly (vinyl pyrrolidone) are novel and promiseable membranes. The possibility of Lewis acid–base pairs between PSSA–ECTFE and ECTFE–PVP played roles also in facilitating proton transport as wellas maintaining the membrane dimensional stability in hydrated state [16].

The PEMFC durability has been recently recognized as one of the most important issues to be addressed before their commercialization [17,18]. It is believed that excessive degradation of stack voltage is the major failure mode for fuel cell systems [19].

* Corresponding author. Tel.: +202 22944718.
E-mail address: Toonyoptrade@yahoo.com (M.M. El-Toony).

In this study, binary monomers grafting (Sty and VP) into ECTFE films with different gamma irradiation doses was performed. The optimum monomers (Sty and VP) ratio used to attain the maximum grafting yields was 1:1. Characterizations of the grafted membranes were carried out using FT-IR, thermal gravimetric analysis (TGA) and scanning electron microscope (SEM). Availability the membranes for PEMFC was studied by measuring ion exchange capacity, water uptake, proton conductivity, free volumes sizes, tensile strength and membranes thickness. At 75 °C the higher values of the fuel cell performance based highest grafted membranes was achieved, while it decreased by reducing temperature to 50 °C or raising them up to 85 °C. The promised prepared grafted membranes proved their applicability into the PEMFC up to 450 hours.

2. Experimental

2.1. Materials

Commercial ECTFE films of 50 μm thickness(supplied by Xylic, USA) were cut into a 5×5 cm^2 size and washed with methanol to remove any impurities cohering the surface. The films were dried under vacuum at room temperature before it was be used for grafting. Irradiation was carried out using Co-60 gamma irradiation source. Ultrapure Sty (molar mass 104.15 g/mol) waspurchased from Merck, Germany while pure VP(97%) andchlorosulfonic acid (99%) were from Aldrich, England. Compressed commercial Nr. 118 membranes with 50 μm thickness was purchased from Optco, Egypt. The 1,1,2,2 tetrachloroethane and different solvents were supplied by El-Nasr Co., Egypt.

2.2. Membrane preparation

The simultaneous gamma irradiation grafting was carried out by puttingthe ECTFE films and Sty in 2 cm diameter glass ampoules. A VP with different ratios to styrene were added with their suitable solvents (methanol for Sty and water for VP) to the glass ampoules content. The ampoules were subsequently irradiated for different doses (5, 10, 20, 30 and 40 KGy). After the grafting reaction, the film was taken out, rinsed with benzene and soaked therein over night to remove homopolymer. After drying to a constant weight, the obtained grafting degree was as the following:

$$\text{Grafting Degree} = \frac{W_g - W_o}{W_o} \times 100 \qquad (1)$$

Where W_o and W_g are the weight of ungrafted and grafted membranes, respectively [20].

2.3. Membranes sulfonation

Polystyrene (and poly vinyl pyrrolidone) grafted ECTFE films were initially washed with dichloromethane, soaked therein for 30 minutes, and then removed and dried in a vacuum ovenfor 1 h. Sulphonation was carried out by immersing the films in a 0.2 M chlorosulfonic acid dilutedwith dichloroethane for 5 hs at 50 °C, followed by overnight immersion at room temperature. After sulfonation, the membranes were removed from the sulfonating solution and immersed in fresh dichloromethane for 3 hs, followed by washing with dichloromethane to remove any acid residual. After washing with dichloromethane, the films were thoroughly washed with deionized water. These resulting membranes were then hydrolyzed with 0.5 M KOH solution overnight and regenerated by boiling with 1 M HCl for several hours. The membranes were then washed thoroughly with deionized water in order to ensure complete removal of acid, and finally stored in sealed bottles at ambient temperature [21,22]

2.4. Ion exchange capacity (IEC) and degree of substitution

IEC of the sulfonated polymers (sulfonated ECTFE grafted by Sty and VP) was measured using a typical titration method. The dried membrane in the protonic form was immersed into 25.00 mL of 3 M NaCl solution for 24 hours. A large excess of Na$^+$in the solution ensured nearly ions were completely exchanged. Then, 10.00 mL of the 3 M NaCl solution containing the released H$^+$was titrated against 0.05 M NaOH solution using phenolphthalein as indicator. The IEC was calculated using the following equation:

$$IEC_{exp} = \frac{0.05 \times Vol._{NaOH} \text{x} n}{W_{dry}} (\text{m}_{equiv.}/\text{g}) \qquad (2)$$

where $Vol._{NaOH}$ (mL) is the 0.05 M NaOH solution volume used for titration. n is the factor corresponding to the ratio of the amount of NaCl solution taken to immerse the polymer (25.00 mL) to the amount used for titration (10.00 mL), which is 2.5. W_{dry} (g) is the dry polymer weight of electrolyte membrane in the protonic form [23].

2.5. Water uptake and proton conductivity

The water uptake was measured by immersing the membranes (sulfonated ECTFE grafted by Sty and VP) in deionized water, until no further weight change was observed. The experiment was repeated 3 times at least and the mean value was attained. The equilibrium water uptake weight was determined as the following:

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (3)$$

where W_{wet} and W_{dry} are the membrane weights in the wet and dry states, respectively [24]. Proton conductivity was determined by impedance spectroscopy measurement using a LCR meter, Herioki, Japan by using 20 Hz to 1 MHz frequencies range. A sample with size of 10 mm 10 mm was placed in an open, temperature controlled cell where it was clamped between two blocking gilded stainless steel electrodes. Specimens were soaked in deionized water at 25 °C overnigh prior to the test. The impedance measurements were performed in water with 100% relative humidity (RH) at desired temperature. The high frequency intercept on the real axis of the Nyquist plot was used to calculate the membrane proton conductivity. The ionic conductivity (σ) was calculated according to the following equation:

$$\sigma(\Omega^{-1}\text{cm}^{-1}) = \frac{L}{RA} \times 100 \qquad (4)$$

where L is the membrane sample thickness, A or (πr^2) is the sample surface area and R is the electrical resistance [25].

The free volume sizes are evaluated using positron annihilation lifetime spectroscopy. The positron annihilation lifetime (PAL) spectra of the grafted membranes (sulphonated ECTFE grafted by Sty and PV) were determined by detecting the prompt Y-ray (1.28 MeV) from the nuclear decay that accompanied the emission of a positronfrom the ^{22}Na radioisotope and the subsequent annihilation Y-rays (0.511 MeV). A conventional fast-fast coincidence circuit of PAL spectrometer with a time resolution 240 Ps was used to record all PAL spectra. The PAL spectra containing 1.5×10^6 counts were analyzed into three lifetime components (T_1, T_2 and T_3) and their intensities (I_1, I_2 and I_3) using PALS fit program [26].

2.6. Fuel cell performance

The membrane (sulphonated ECTFE grafted by Sty and PV) electrode assemblies (MEAs) werefabricated by hot-pressing the