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Preparation of composite polymer electrolytes by electron beam-induced grafting: Proton- and lithium ion-conducting membranes

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Abstract

Two classes of composite polymer electrolyte membranes, one conducting lithium ions (Li^+) and the other conducting protons (H^+) were prepared using simultaneous electron beam-induced grafting. Porous poly(vinylidene fluoride) (PVDF) films were impregnated with styrene and subjected to electron beam (EB) irradiation to obtain polystyrene (PS) filled PVDF precursor films that were subsequently treated with either chlorosulfonic acid/1,1,2,2-tetrachloroethane mixture to obtain H^+-conducting composite membranes or $LiPH_6$/EC/DEC liquid electrolyte to obtain Li^+-conducting composite membranes. The properties of the obtained membranes were evaluated using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and AC impedance measurements. The obtained membranes were found to achieve grafting content up to 46% with superior Li^+-conductivity of 1.91×10^{-3} S/cm and H^+-conductivity of 5.95×10^{-2} S/cm. The results of this work show that simultaneous radiation-induced grafting with EB is a promising method to prepare high quality ion-conducting membranes for possible use in fuel cells and lithium batteries.

Keywords: Composite polymer electrolyte; Radiation-induced grafting; Electron beam; Lithium batteries; Fuel cells

1. Introduction

Ion-conducting membranes are a class of materials that has been receiving an increasing attention due to their applicability to a wide number of solid state devices and chemical processes. The continuous pursuing of these membranes is substantial to promote the development of new generations of modular, safer, cheaper and robust electrochemical devices. Lithium ion (Li^+) polymer batteries and polymer electrolyte membrane (PEM) fuel cells are among the most investigated power generating devices due to their high power density, modularity and suitability for mobile and portable applications [1]. Nevertheless, commercialization of PEM fuel cells and Li^+ polymer batteries is challenged by the high cost of commercial proton (H^+) conducting membranes such as Nafion and the low Li^+ conductivity of the developing electrolytes membranes [2,3]. Motivated by this situation, many research groups have attempted various polymerization techniques to develop alternative cost effective and highly conductive H^+- and Li^+-conducting membranes [4]. Radiation-induced grafting, which is known for its simplicity, yield composition controllability and absence of film processibility, has been found to be an appealing method to develop a variety of ion-conducting membranes for various electrochemical applications [5,6]. Very recently, we applied simultaneous electron irradiation to prepare H^+-conducting membranes suitable for use in direct methanol fuel cell (DMFC) by grafting of styrene into the porous structure of PVDF films followed by sulfonation reaction [7]. The use of this method was found to greatly reduce the monomer consumption, shorten the reaction time and improve the economy of the membranes compared to pre-irradiation method. In this article, we investigate the use of simultaneous grafting with electron beam (EB) as a single root for preparation of two types of

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composite membranes conducting H^+ and Li^+. Some properties of the two electrolyte membranes are evaluated in correlation with the preparation procedures (grafting and sulfonation) and the content of polystyrene grafted in the porous structure of PVDF films.

2. Experimental

The H^+- and Li^+-conducting membranes were prepared starting with porous PVDF films (70% porosity, 0.22 μm average pore size and 110 μm thickness) supplied by Millipore, in three steps schematized in Fig. 1. In the first step, cleaned PVDF films (10 cm × 10 cm) were impregnated with styrene (⩾99%, Fluka) by rinsing for 24 h in 100 ml of neat styrene prior to irradiation step followed by surface plotting to remove excess monomer adhering to the films surfaces. In the second step, the styrene swollen PVDF films were irradiated with a universal EB accelerator (NHV-Nissin High Voltage, EPS 3000, Cockroft Walton type, Japan) under N_2 atmosphere after being hosted in thin PE plastic bags. The acceleration energy was maintained at 500 kV and the total absorbed dose was 50 kGy at 5 kGy dose per pass. After grafting, the grafted PVDF films were removed and carefully cleaned with warm toluene under ultrasonication overnight. Details of grafting procedures and irradiation parameters can be found elsewhere [7]. The content of polystyrene (PS), grafted into the pores of PVDF films (*G*%) was calculated using this equation: $[G\% = (W_1 - W_0/W_0) \times 100]$, where W_0 and W_1 are the weights of PVDF films before and after filling with PS, respectively. In the third step, the membrane precursor were converted into H^+-conducting membranes by sulfonation with 10% chlorosulfonic acid in 1,1,2,2-tetrachloroethane for 12 h followed by treatment with 0.5 M KOH solution and regeneration into acid form by boiling with 1 M HCl for 2 h. The samples were then washed free of excess HCl with ion free water few times. The grafted PVDF films were converted to Li^+-conducting membranes by impregnation with electrolyte solution composed of 1 M $LiPF_6$ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) for 8 h in a re-circulating Ar glove box (H_2O vapor and O_2 below 1 ppm) at ambient temperature. Physical properties such as water uptake, liquid electrolyte uptake and porosity were determined as reported in [7,8], respectively.

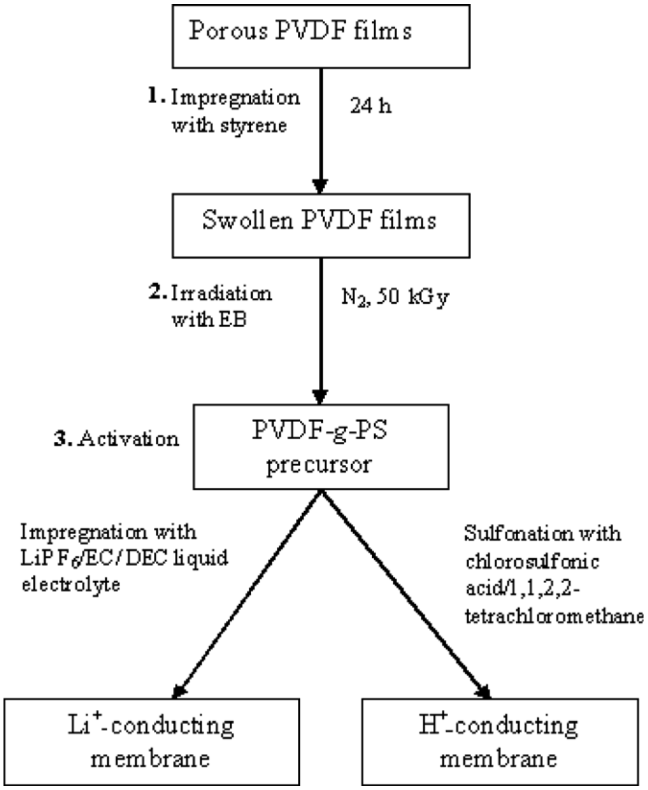

Fig. 1. Schematic representation of preparation procedure for H^+- and Li^+-conducting membranes by simultaneous radiation-induced grafting with EB.

FTIR measurements were carried out using a Nicolet (Magna-IR 560) spectrometer equipped with ATR (Thunder dome-HATR) having Ge spherical crystal. The spectra were measured in transmittance mode at a wave number range of 4000–600 cm^{-1}.

Scanning electron microscope (SEM) investigations were performed by a Philips 505 M microscope. Membrane samples were frozen in liquid nitrogen, fractured to obtain fragments, mounted on disc holder with double sided tape and sputter-coated with thin gold film prior to SEM observation.

Ionic conductivity of fully electrolyte loaded Li^+-conducting membranes and water swollen H^+-conducting membranes (equilibrated in ion free water for 24 h) was measured at room temperature by complex AC impedance spectroscopy. Sample of membrane disc was sandwiched between two stainless steel electrodes and assembled into a tightly sealed test cell. Measurements were performed on Autolab Eco Chemie PGSTAT 30 potentiostat/galvanostat equipped with a frequency response analyzer module at frequency range of 0.01–100 kHz. Ionic conductivity was calculated from the impedance response according to established procedures [7,8].

3. Results and discussion

In this study precursors for H^+- and Li^+-conducting membranes (PS grafted PVDF films) were prepared by simultaneous irradiation with EB under controlled conditions. Samples with *G*% in the range of 8–46% were obtained by varying the irradiation dose in the range of 5–50 kGy at 5 kGy/pass as depicted from Fig. 2. The increase in *G*% with the rise in the absorbed irradiation dose is attributed to the increase in the number of created radicals which further take part in the grafting reaction.

Fig. 3 shows typical FTIR-ATR spectra of H^+- and Li^+-conducting membranes having *G* of 46%. The corresponding PS grafted PVDF precursor and the pristine porous PVDF film were included as references. Grafting of PS into

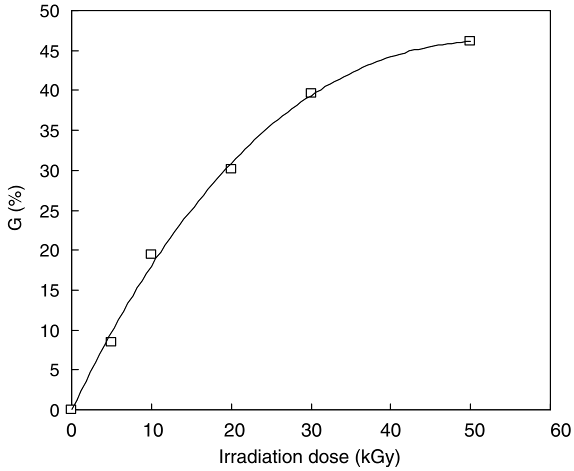

Fig. 2. Variation of the content of polystyrene with the irradiation dose.

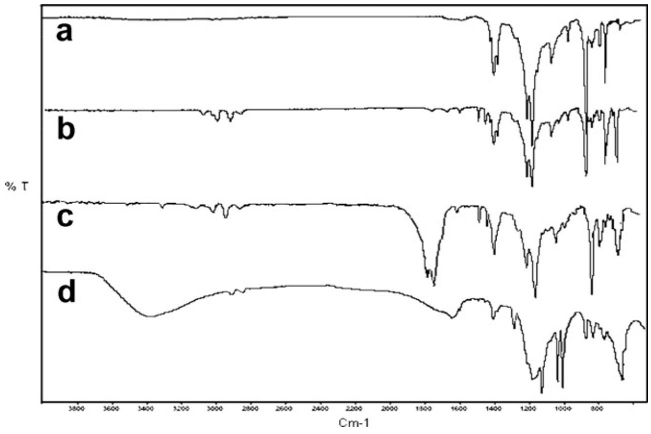

Fig. 3. Typical FTIR spectra of: (a) original PVDF film, (b) PVDF-g-PS film ($G = 46\%$), and corresponding (c) Li^+-conducting membrane and (d) H^+-conducting membrane.

pristine PVDF have produced additional characteristic peaks of benzene rings features at 3080 and 3015 cm^{-1} representing C–H aromatic symmetric stretching vibrations and at 1493 and 1602 cm^{-1} for in plate-stretching vibrations of skeletal C=C, respectively. The spectrum of H^+-conducting membrane reveals SO_3^- groups representing bands at 1123 and 1003 cm^{-1} with addition two sharp peaks detected at 1300 and 1160 cm^{-1} assigned for to S=O. The broad band at 3100–3700 cm^{-1} is due to the OH groups of water molecules strongly bound to SO_3^- groups by hydrogen bonding. The spectrum of Li^+-conducting membrane shows characteristic bands of C=O groups attributed to the fragmented and polymerized solvents (EC and DEC) at 1750–1800 cm^{-1}. The weak band at 3320 cm^{-1} is assigned to $LiPF_6$ [8]. These results confirm the successful grafting of PS into the porous structure of PVDF films and the subsequent two post grafting activation treatments.

To investigate the structural changes caused by grafting and subsequent activation in both membranes, SEM micrographs of the cross sections of pristine PVDF film, grafted PVDF film ($G = 30\%$) and its corresponding H^+- and Li^+-conducting membranes were recorded and presented in Fig. 4. It can be obviously seen that PS grafts overwhelmingly invaded the fibrous microstructure of PVDF film converting it into the granular network with a number of partially opened pores remained scattered in the structure despite being thickened by partial PS filling. The structure of H^+-conducting membrane shows the existence of aggregated ionic clusters having bigger sizes in the granular network coupled with a reduction in numbers and sizes of the remaining pores. No distinction between ionic cluster domains and the PVDF matrix could be observed. The structure of Li^+-conducting membrane reveals the presence of larger granular clusters arranged in gel-like network caused by gelation of the liquid electrolyte trapped inside the membrane. These observations confirm the formation of composite ion-conducting membranes. Furthermore, they shed some light on the possible mechanism by which grafting proceeds in the pores of PVDF matrix where grafting fronts starts at the wall side of the pores and the PS graft growing chains propagation proceeds inward until either the whole pores are blocked or the monomer molecules in the pores are totally consumed leaving them partially blocked.

Fig. 5 shows the variation in the ion exchange capacity and the water uptake of the H^+-conducting membranes with PS content ($G\%$). As can be seen, both the ion exchange capacity and the water uptake increase with the increase in $G\%$. This is due the increase in the number of incorporated sulfonic acid groups caused by the availability

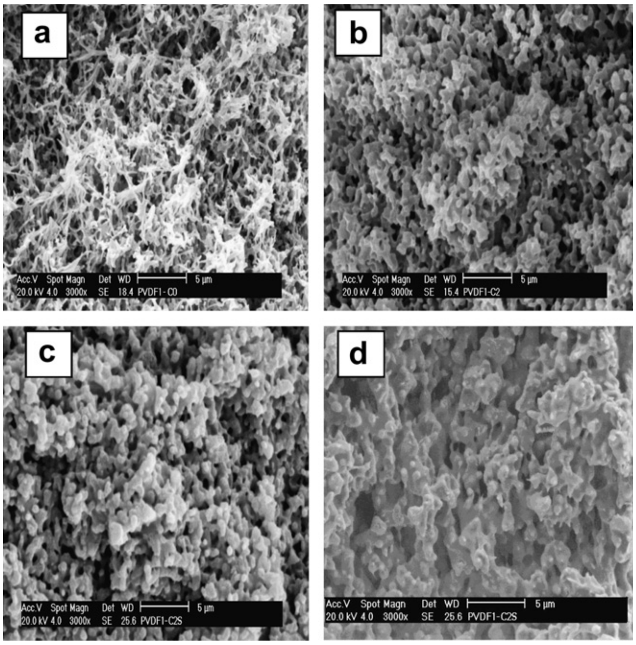

Fig. 4. SEM micrographs of: (a) original PVDF film, (b) PVDF-g-PS film ($G = 30\%$), and corresponding (c) H^+-conducting membrane and (d) Li^+-conducting membrane.

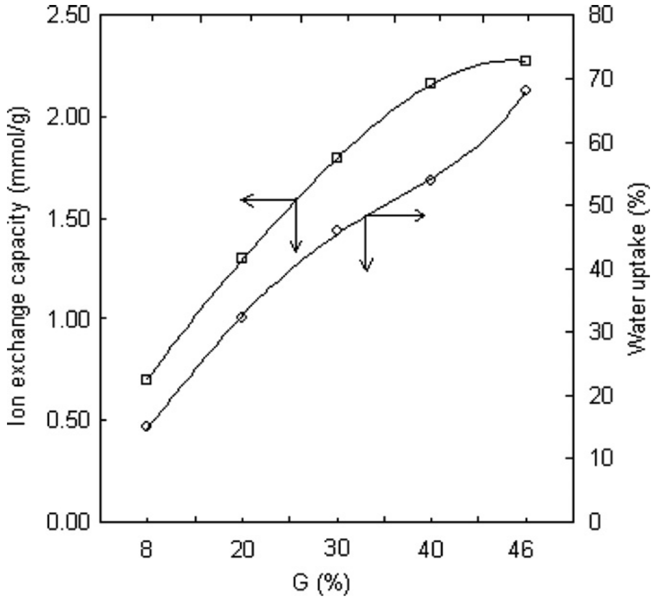

Fig. 5. Variation of the ion exchange capacity and the water uptake in the H^+-conducting membranes with the PS content.

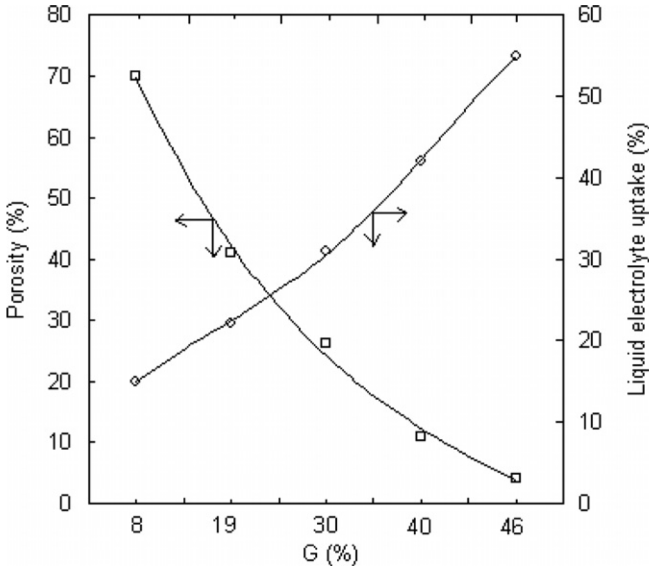

Fig. 7. Variation of the porosity and the liquid electrolyte uptake in the Li^+-conducting membranes with the PS content.

of more sulfonation sites, which imparts more water absorbing capacity to the membranes.

The relationship between the proton conductivity of H^+-conducting membranes and the PS content (*G*%) is shown in Fig. 6. The proton conductivity was found to increase steeply with the increase in *G*% and this can be mainly attributed to the coincided increase in both ion exchange capacity and water uptake with the incorporation of more sulfonated PS in the pores of the membranes. Other structural properties such as crystallinity may also play a role in affecting the conductivity of these membranes but to lesser extent [9]. It is interesting to mention that the membrane with *G* of 46% recorded H^+ conductivity of $\sim 6.0 \times 10^{-2}$ S/cm which is higher than that of Nafion 117 membranes (5.3×10^{-2} S/cm) measured at the same conditions.

Fig. 7 shows the variation in the porosity and the liquid electrolyte uptake of the Li^+-conducting membranes with PS content (*G*%). The porosity of the membranes was found to decrease with the increase in *G*% unlike the liquid electrolyte uptake, which has an increasing trend with *G*%. The former is due to the progressive pore filling with incorporation of more PS whereas the latter is caused by the increase in the amorphous content of the membranes, which entraps more liquid electrolyte with the increase in *G*%.

The relationship between the ionic conductivity and the PS content (*G*%) of Li^+-conducting membranes is shown in Fig. 8. The ionic conductivity was found to increase gradually with the increase in *G*%. This behavior is caused by the parallel increase in the uptake of liquid electrolyte (swelling)

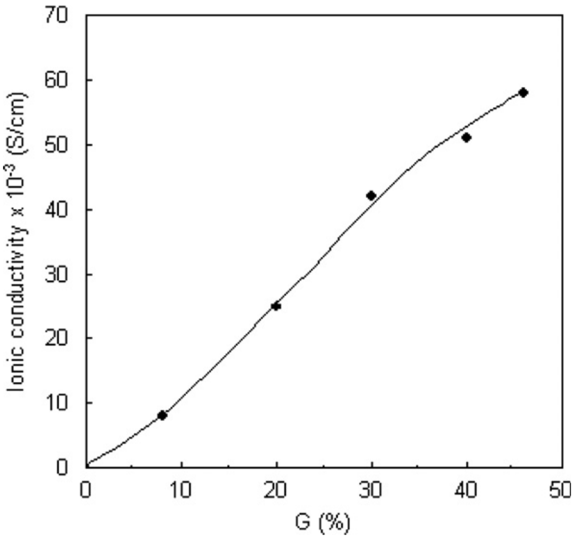

Fig. 6. The relationship between the proton conductivity and the PS content in the H^+-conducting membranes.

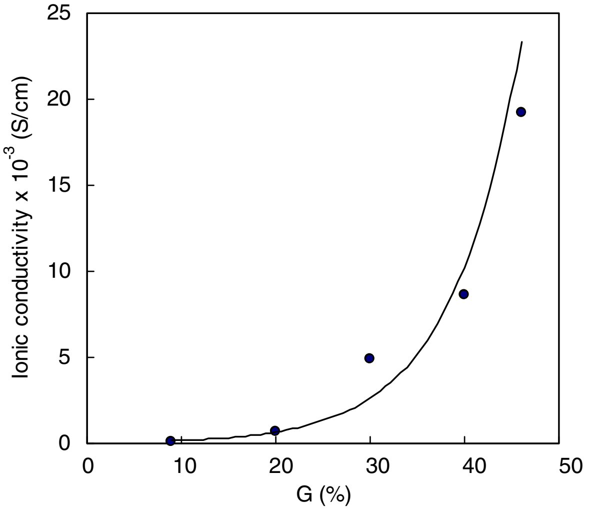

Fig. 8. The relationship between the ionic conductivity and the PS content in the Li^+-conducting membranes.

and the reduction in porosity, which permits the complexation of the occluded amorphous PS with $LiPF_6$. Interestingly, the membrane with *G* of 46% recoded a superior conductivity of a value of 1.91×10^{-3} S/cm which is substantially higher than that of the PVDF-HFP and PVDF-HFP/PS based polymer electrolytes, which equal 0.2×10^{-3} and 0.162×10^{-3} S/cm, respectively [10,11]. Crystallinity reduction that is mostly caused by the incorporation of amorphous of PS is also expected to contribute to the conductivity rise in these membranes by enhancing the polymer/liquid electrolyte complex formation [12].

4. Summary

Simultaneous grafting of styrene into the porous structure of PVDF films with EB irradiation was used as a single method to prepare membrane precursors that can be converted to both H^+- and Li^+-conducting composite membranes by selected chemical activation. The content of PS (*G*%), which was controlled by variation of the irradiation dose, plays a vital role in the affecting the properties of the obtained membranes. Particularly, the ionic conductivity was found to increase with the increase in *G*% in both types of membranes. This behavior is attributed to the cumulative effects of the increase in both ion exchange capacity and water uptake together with the possible reduction in the crytallinity in PVDF matrix caused by preparation procedure of H^+-conducting membranes. Whereas, in Li^+-conducting membranes, it is due to the collective effects arising from the reduction in the porosity, the increase in the liquid electrolyte uptake most likely caused by the reduction in the crystallinity of PVDF matrix. Finally, it can be suggested that simultaneous irradiation with EB used in this study is a promising method for preparation of high quality conducting composite membranes for possible use in fuel cells and lithium batteries.

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