

# 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 ( $\text{Li}^+$ ) and the other conducting protons ( $\text{H}^+$ ) 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  $\text{H}^+$ -conducting composite membranes or  $\text{LiPH}_6/\text{EC}/\text{DEC}$  liquid electrolyte to obtain  $\text{Li}^+$ -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  $\text{Li}^+$ -conductivity of  $1.91 \times 10^{-3}$  S/cm and  $\text{H}^+$ -conductivity of  $5.95 \times 10^{-2}$  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.

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**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 ( $\text{Li}^+$ ) 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  $\text{Li}^+$  polymer batteries is challenged by the high cost of commercial proton ( $\text{H}^+$ ) conducting membranes such as Nafion and the low  $\text{Li}^+$  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  $\text{H}^+$ - and  $\text{Li}^+$ -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  $\text{H}^+$ -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  $\mu m$  average pore size and 110  $\mu m$  thickness) supplied by Millipore, in three steps schematized in Fig. 1. In the first step, cleaned PVDF films (10 cm  $\times$  10 cm) were impregnated with styrene ( $\geq 99\%$ , 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.

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

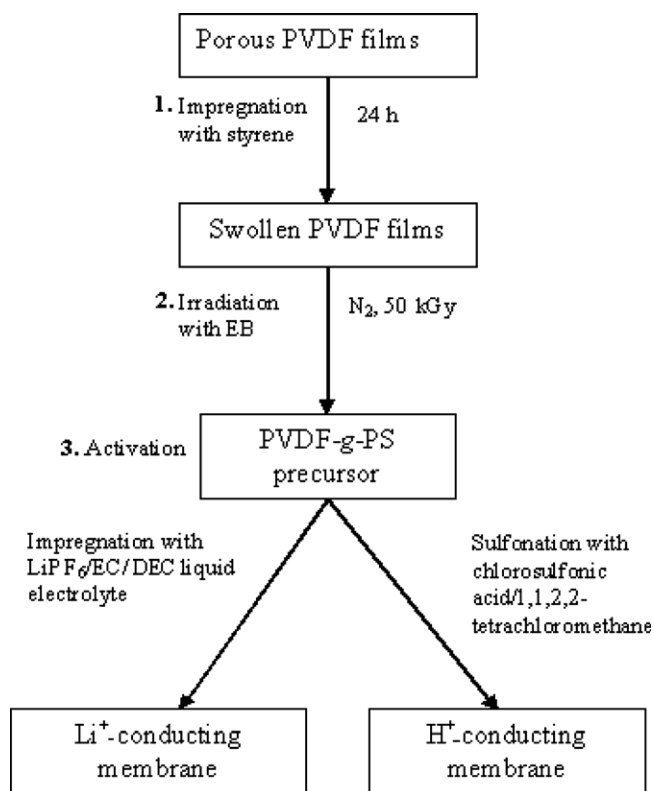


Fig. 1. Schematic representation of preparation procedure for  $H^+$ - and  $Li^+$ -conducting membranes by simultaneous radiation-induced grafting with EB.

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