



Polyethylene-based radiation grafted anion-exchange membranes for alkaline fuel cells



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ABSTRACT

Vinyl benzyl chloride was grafted onto ultra-high molecular weight polyethylene powder (UHMWPE) by radiation grafting. The grafted powder was subsequently fabricated into membrane by melt pressing. The effect of absorbed radiation dose on the degree of grafting (DG) is discussed. The melt-flow properties of PVBC grafted PE with low degree of grafting was conducive to forming homogeneous pore-free membranes, which was confirmed by scanning electron microscopic analysis. The grafted polyethylene membranes were post functionalized with trimethylamine, followed by alkalization to obtain anion-exchange membranes (AEMs). The structures of the resulting AEMs were characterized by Fourier transform infrared spectroscopy, which showed that the grafted membranes were successfully functionalized. The properties of the AEMs, including ion exchange capacity, water uptake, in-plane swelling, methanol uptake, methanol permeability and hydroxide ion conductivity were investigated. The AEMs showed reasonably good chemical stability, as evidenced by the ion exchange capacity being maintained for a long duration, even in highly alkaline conditions. The membranes exhibited a maximum ionic conductivity of 47.5 mS cm^{-1} at 90°C (30 mS cm^{-1} at 60°C). Methanol permeability was found to be in the order of $10^{-8} \text{ cm}^2 \text{ s}^{-1}$, which is considerably lower than that of Nafion[®]. The membranes have useful properties consistent with anion exchange membranes suitable for alkaline fuel cells.

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1. Introduction

Fuel cells have been recognized as alternative energy devices for the future in both, mobile and stationary uses [1,2]. Among the different types of fuel cells, the majority of efforts have been directed towards the development of polymer electrolyte membranes fuel cells (PEMFCs) using proton exchange membranes (PEMs), because of their convenient features such as low-temperature operation, rapid start-up, high power density, which make them particularly suitable for vehicle and other mobile applications [3]. Although promising, PEMFCs still face some persistent obstacles to widespread adoption, of which the high cost of commercially available PEMs (typically Nafion[®]) and the dependence on expensive noble metal catalysts

(typically platinum) are major contributors [4]. In recent years, the development of anion exchange membranes (AEMs) for anion exchange membrane fuel cells (AEMFCs) has gained rapidly increasing interest, because of their advantage over alkaline fuel cells (AFCs). This is due to the replacement of liquid electrolyte with solid electrolyte membrane, which reduces the adverse effect of CO_2 . AEMFC also have a cost advantage over PEMFCs because significantly less noble metal catalyst or non-noble metals can be utilized in the electrodes [5,6]. Since catalysts are generally more stable in basic media, non-precious metals such as nickel and silver [7] can be used as cathode catalysts, which have the potential to greatly reduce the cost of the fuel cells. In AEMFCs, the AEM separates the reactant gases and conducts the hydroxide ions from the cathode to the anode.

Considerable efforts have been focused on the preparation of AEMs through chloromethylation of polymers, followed by quaternization and alkalization steps [8–11]. However, chloromethylation reactions require chloromethyl ether, which is a potent carcinogen, harmful to human health [12]. The synthesis of AEMs through radiation grafting of vinylbenzyl chloride (VBC) onto polymer matrices has been shown to be an effective way of avoiding the use of chloromethyl ether [13–15]. Moreover,

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electrolyte membranes containing grafted units, due to their comb-shaped nanoscale structural organization, exhibit high ionic conductivity over a wide range of humidity [16]. Radiation grafting, employing ionizing radiation such as γ -rays and electron beams, is an advantageous grafting technique because (1) reactions can be easily controlled by adjusting the experimental parameters; (2) there is a relatively uniform formation of radicals with a thickness of the order of mm; (3) the process is free from contamination because it does not need initiator for radical formation, so that the purity of the processed products may be maintained [17,18].

Many commercially available fluorinated polymers, such as PVDF [19,20], poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) copolymer [13,19–21], ETFE [22], PTFE–FEP [23], etc., have been the subject of radiation-induced grafting with vinylbenzyl chloride followed by quaternization and alkalization for AEMs. However, in the context of radiation grafting, the main disadvantage associated with PTFE is that it exclusively undergoes main-chain scission due to the relatively stronger C–F bond as compared with the C–C bond, and a relatively low irradiation dose can effectively reduce the molecular weight of the PTFE [24,25]. Moreover, some of the fluorinated polymers are easily degraded in basic media [19,26]. Thus, fluorinated polymers may be less suitable polymer substrates for radiation-induced grafting and also for AEMFC application. Recently, LDPE and HDPE films were also used to prepare AEMs by radiation grafting [27]. However, the ionic conductivity of the resulting AEMs studied so far is considerably lower compared with Nafion® membranes, thus needing further improvement.

The present study focuses on the grafting of poly(vinylbenzyl chloride) onto ultra-high molecular weight polyethylene (UHMWPE) powder (hereafter represented by PE) by gamma (^{60}Co) irradiation. The purpose of grafting vinylbenzyl chloride groups is that they are readily amenable to quaternization, ultimately providing inexpensive polyelectrolyte membrane materials. The main advantages of using UHMWPE are that (1) it is inexpensive in comparison with fluoropolymers; (2) polyolefin copolymers generally have excellent bulk physical/chemical properties; (3) it has a tendency for crosslinking upon exposure to gamma irradiation; (4) it is relatively stable towards alkaline conditions. Ultra-high molecular weight polyethylene grafted poly(vinylbenzyl chloride) (PE-g-PVBC) powder was then fabricated into membrane by compression moulding followed by quaternized with TMA and subsequently alkalized to form the AEMs. The morphology of the grafted membranes was analyzed by SEM, while Fourier transform infrared (FTIR) spectroscopy was utilized to characterize of structure and functionality of the AEMs. The ion exchange capacity (IEC), water uptake (WU), in-plane swelling, methanol uptake (MU) was investigated. Furthermore, thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), methanol permeabilities and hydroxyl ion conductivities are also included.

2. Experimental

2.1. Materials

UHMWPE ($MW=300,000\text{--}600,000$) powder, vinylbenzyl chloride (mixture of 3- and 4-isomers, 97%), trimethylamine (TMA) solution ~45 wt% in H_2O were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Other chemicals, including, methanol, toluene, sodium hydroxide and hydrochloric acid were analytical grade and were also purchased from Sigma-Aldrich and used as received. Water obtained through a Millipore water purification system was used throughout this study.

2.2. Membrane preparation

2.2.1. Polymer irradiation and grafting

A measured amount of PE powder was washed in methanol and then dried. The PE powder was placed in screw-cap air-tight glass vials sealed with rubber septa. The irradiation of the polymer was conducted in an inert atmosphere, by purging the glass vials with N_2 gas, then filling them with N_2 using a syringe. The samples were inserted into the irradiation chamber, and exposed to ^{60}Co γ -rays for absorbed doses ranging from 3 kGy to 25 kGy at a calibrated dose rate of 1 kGy h^{-1} . Monomer concentration in methanol as solvent was also optimized to obtain maximum grafting yield. The pre-irradiation grafting method was adopted, whereby the monomer (vinylbenzyl chloride diluted in methanol) was added to the irradiated PE powder, immediately after the samples were removed from the irradiation chamber. After the mixture was stirred for 8 h at 60°C , the resulting PVBC-grafted PE (PE-g-PVBC) was washed with toluene several times to remove any trapped monomer or homopolymer (PVBC), and then dried in a vacuum oven at 60°C to a constant weight. The percentage degree of grafting (%DG) was determined by the weight increase of the samples as given by:

$$\% DG = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_o is the measured weight of the original substrate polymer powder and W_g is the measured weight of the grafted powder at a given condition, respectively.

2.2.2. Membrane formation

The PE-g-PVBC powders with different degrees of grafting were melt pressed into membranes before quaternization, to convert them into AEM materials. Melt pressing was conducted at 10,000 psi at a set plate temperature of 220°C for 15 min, providing films with an average thickness in the range of 85–95 μm .

2.2.3. Quaternization and alkalization

PE-g-PVBC membranes in vials were stirred in about 30 mL of 50% aqueous solution of TMA at about $35\text{--}40^\circ\text{C}$ for 36 h. After completion of the reactions, the membranes were washed with DI water to remove excess TMA and then dried at 60°C overnight, followed by vacuum at 70°C for 8 h. The membranes reacted with TMA were treated with 1 M NaOH at room temperature for 48 h to exchange the chloride ions for hydroxide ions. The membranes were washed thoroughly to remove residual NaOH and stored in DI water prior to analysis. PE-g-PVBC membranes quaternized with TMA and reacted with NaOH are denoted as PE-g-PVBC-TOH.

A general representation of the grafting and quaternization is shown in Scheme 1.

2.3. Membrane characterization

The ATR-FTIR analyses of control PE, PE-g-PVBC, PE-g-PVBC-TOH membranes were performed on a FTLA2000 Series FTIR spectrometer. A scanning electron microscope (SEM, LEO 440, UK, magnification $5\times$ to $300,000\times$, resolution of 3.5 nm) was used for the morphological analysis of the pristine and grafted samples to ensure uniform grafting. For SEM analyses, the gold-coated membrane samples were placed in the SEM sample chamber and analyzed at a magnification of $50,000\times$ for surface and $750\times$ for cross-sectional views. The detector used was a secondary electron (SE) detector. The thermal stability of the membranes was investigated by thermogravimetric analysis using a TA Instruments thermogravimetric analyzer (TGA) instrument Model Q 500. Preheating of the polymer samples was performed at 100°C for 40 min under nitrogen atmosphere to remove

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