



Plasma-grafted anion-exchange membrane preparation and process analysis



Chengxu Zhang^{a,b}, Jue Hu^{b,**}, Wenguang Fan^a, Michael K.H. Leung^{a,*}, Yuedong Meng^b

^a Ability R&D Energy Research Centre, School of Energy and Environment, City University of Hong Kong, China

^b Institute of Plasma Physics, Chinese Academy of Sciences, China

ARTICLE INFO

Article history:

Received 16 January 2016

Received in revised form 22 March 2016

Accepted 16 April 2016

Available online 19 April 2016

Keywords:

Anion exchange membrane

Plasma-grafting

Vinylbenzyl trimethylammonium chloride

Grafting efficiency

Plasma bombardment efficiency

ABSTRACT

A green and simplified plasma grafting approach was adopted for anion exchange membranes (AEMs) synthesis based on polyvinyl chloride powders in three steps: plasma bombardment, grafting and alkalization, avoiding the use of toxic chloromethyl ether and quaternization reagents. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses demonstrate the successful grafting of benzyltrimethylammonium groups into the polyvinyl chloride matrix. The plasma-grafted AEM exhibits satisfactory thermal stability, chemical stability and ionic conductivity, suggesting potential application in fuel cell. The plasma bombardment efficiency reaches up to 50% based on the FTIR and XPS results, meaning that one in every three syndiotactic CH₂-CHCl units is bombarded in the polyvinyl chloride matrix. But only a small part of plasma bombarded CH₂-CHCl units are grafted with (vinylbenzyl)trimethylammonium chloride (VBTAC) monomer, indicating that the grafting efficiency is the performance limiting factor in the plasma-grafted AEM synthesis. We anticipate this finding will provide guidance of plasma grafting technique for AEM preparations.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Although proton exchange membrane fuel cell (PEMFC) is a superior method to supply clean electricity at high conversion efficiency for stationary, electric vehicles and portable applications, the high cost of platinum-based catalysts is the primary obstacle to the commercialization of PEMFC technology [1]. Anion exchange membrane fuel cell (AEMFC) has attracted growing interest in the last decade due to the prospect of using non-noble metal electro-catalysts [2]. Different from traditional alkaline fuel cell, AEMFC uses solid anion exchange membranes (AEMs) instead of aqueous metal hydroxide solutions leading to an improved tolerance to CO₂ and elimination of electrolyte leakage problems during fuel cell operation [3]. As one of the key components of AEMFC, AEM serves dual functions of hydroxide ion transportation and reactant separation, and as a result, seriously affects the performance of AEMFC.

Great efforts have been devoted to the preparation of high-performance AEMs [4–8]. Among them, the grafting technique

has attracted great attention owing to the easy preparation of various pre-formed commercial polymers and monomers to yield the desired membranes. Furthermore, the highly toxic chloromethyl ether can be avoided when the chloromethylation reaction is displaced by grafting process. Some noteworthy developments came from Varcoe et al. who prepared AEMs by radiation-grafting of vinylbenzyl chloride or vinylbenzyl methylimidazolium chloride monomers onto fluorocarbon membranes, such as fully fluorinated poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), partially fluorinated poly(vinylidene fluoride) (PVDF) and poly(ethylene-co-tetrafluoroethylene) (ETFE), followed by quaternization [2,9–12]. Radiation-grafting approach has been also used to fabricate AEMs based on nonfluorinated polyethylene (PE) [13]. Another important AEM system was synthesized by plasma grafting approach. The plasma grafting approach as an effective and facile way can successfully introduce functional groups into the polymer matrix and at the same time has little impact on the stability of AEMs. Recently, we have reported a series of stable AEMs prepared by the plasma grafting methods [14–16]. The success of these grafted AEMs has inspired increasing interest in the grafting technique. It is known that in the grafting process, high-energy electron bombardment leads to the formation of reactive specie in the polymer matrix which acts as the initial active sites for grafting functional groups [17]. Although

* Corresponding author. Tel.: +852 3442 4626; fax: +852 3442 0688.

** Corresponding author. Tel.: +86 551 65591378; fax: +86 551 65591310.

E-mail addresses: hujue@ipp.ac.cn (J. Hu), mkh.leung@cityu.edu.hk (M.K.H. Leung).

there are some insights into how AEMs be fabricated by the grafting method, the study on grafting mechanism is limited. As one of the most important parameters, the efficiency of bombardment process is still unknown. More careful studies are still necessary to deeply understand the whole grafting process. Therefore, in this study we focus on the plasma grafting process of the plasma-grafted AEM preparation and the characterization of the plasma-grafted AEM.

The goal of the present work is to prepare AEMs by plasma-grafting approach using polyvinyl chloride (PVC) powders as the substrate polymer matrix and (vinylbenzyl)trimethylammonium chloride (VBTA) as the grafting monomer. This synthetic procedure can directly introduce ionic exchange groups (benzyltrimethylammonium groups) into the PVC matrix, leading to a simplified preparation procedure, and at the same time, avoiding the use of toxic chloromethyl ether and quaternization reagents. The chemical structure, ionic conductivity and stability of the plasma-grafted AEM were characterized to evaluate its potential application in fuel cell. The efficiencies of plasma bombardment and grafting processes are also investigated to gain a better understanding of the whole plasma-grafting process.

2. Experimental section

2.1. Preparation of plasma-grafted anion exchange membranes

PVC powders with a particle size of approximately 50 μm were used as the polymer substrate to prepare AEMs. There are three steps in preparation of plasma-grafted AEMs, as shown in Scheme 1: plasma bombardment of PVC substrate, grafting of VBTA (Sigma-Aldrich[®]) monomer with $-\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ groups onto PVC matrix, and alkalinizing of $-\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ groups into $-\text{N}^+(\text{CH}_3)_3\text{OH}^-$ groups. The plasma bombardment process (step 1) was carried out in a low-pressure plasma discharge system which consisted of a glass vacuum bottle, an inductively coupled coil electrode, a radio frequency power supply with corresponding power coupling, a stirring device and a vacuum pump. The inductively coupled plasma sustained by a 13.56 MHz power supply outside the glass bottle using high purity argon (99.999% purity) as the working gas. PVC powders were placed in the plasma discharge centre with continuous magnetic stirring during this process. The experimental parameters were 100 W for the input power, 20 Pa for the total pressure and 30 min for the treatment time. In the next step (step 2), the plasma treated PVC powders were rapidly immersed in 10 wt% VBTA aqueous solution with excess VBTA monomer and stirred at 60 °C for 48 h. The obtained PVC-g-VBTA (PVC-TAC) powders were dissolved in

dimethylformamide (DMF, Shanghai Chemical Reagent Store) to form 10 wt% solution, and then cast onto a flat and clean glass plate. After drying in vacuum oven for 12 h at 60 °C, a polymer film was formed. In the last step (step 3), the PVC-TAC film was soaked in 1 M potassium hydroxide (KOH) aqueous solution for 48 h to alkalinize the $-\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ groups (trimethylammonium chloride, TAC) into $-\text{N}^+(\text{CH}_3)_3\text{OH}^-$ groups (trimethylammonium hydroxide, TAH). Then, the alkalinized PVC-g-PVBTA membrane (PVC-TAH) was washed with deionized water and soaked in deionized water with frequent water changes for at least 48 h to remove the trapped KOH.

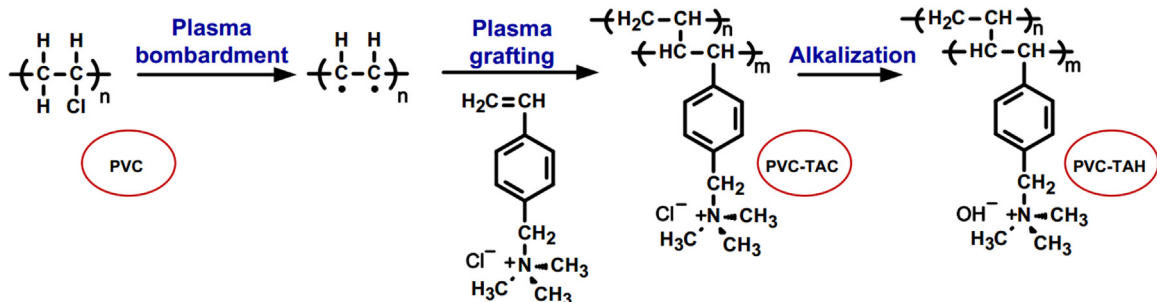
2.2. Characterization of membranes

To analyzing the effect of plasma bombardment on materials structure, PVC and plasma bombarded PVC powders were tested by Fourier transform infrared spectroscopy (FTIR). The chemical structure of PVC and PVC-TAH membrane were further analyzed by attenuated total reflection FTIR (ATR-FTIR). The FTIR spectra were recorded on a Nicolet NEXUS 870 spectrometer after 40 scan in the range of 4000~400 cm^{-1} . The ATR-FTIR spectra were presented after 256 scans with spectral resolution of 2 cm^{-1} in the range of 4000~670 cm^{-1} . All the spectra were subtracted the contribution of CO_2 and H_2O . The chemical structure of PVC and PVC-TAC membrane were also tested by X-ray photoelectron spectroscopy (XPS) to analyse the plasma-grafting process. The XPS analysis was conducted using a Thermo ESCALAB 250 spectrometer using an Al $\text{K}\alpha$ X-ray source (1486.6 eV). The pass energies were set at 70 eV and 20 eV for survey spectra and core level spectra, respectively. All of the binding energies were calibrated with respect to the C 1s band of graphitized carbon at 284.6 eV and the spectrometer energy scale calibration was checked by setting Ag 3d_{5/2} at 368.26 eV. Thermogravimetric analysis (TGA) measurements were carried out using a DTG-60H analyzer. Accurately weighted (about 10 mg) samples, which placed in a Pt crucible, were heated to 800 °C under constant nitrogen purging at 10 ml min⁻¹ at a constant heating rate of 10 °C min⁻¹.

2.3. Water uptake, swelling ratio, ion-exchange capacity and ionic conductivity measurements

Water uptake (WU) was determined gravimetrically by soaking the dry weighted samples separately into deionized water for 24 h. Then the samples were taken out and weighted after wiping away the surface water. Water uptake was calculated by:

$$\text{WU}(\text{wt}\%) = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \quad (1)$$



Scheme 1. Synthesis of plasma grafted anion-exchange membrane based on PVC powder substrate and monomer containing quaternary ammonium groups.

Download English Version:

<https://daneshyari.com/en/article/182860>

Download Persian Version:

<https://daneshyari.com/article/182860>

[Daneshyari.com](https://daneshyari.com)