



Plasma graft-polymerization for synthesis of highly stable hydroxide exchange membrane



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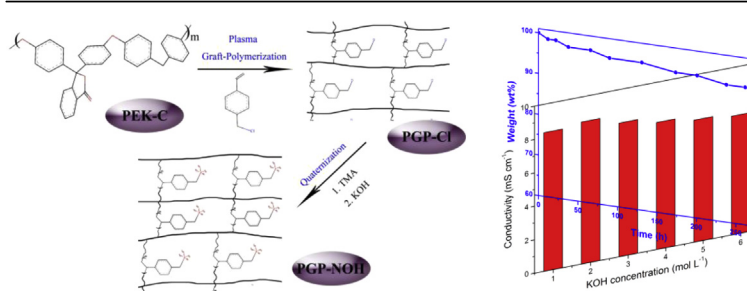
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HIGHLIGHTS

- Successfully introduced functional groups into PEK-C matrix via plasma graft-polymerization.
- Plasma graft-polymerization enables high preservation in polymer backbone and functional groups.
- The obtained membranes possess high chemical stability.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel plasma graft-polymerization approach is adopted to prepare hydroxide exchange membranes (HEMs) using cardo polyetherketone powders (PEK-C) and vinylbenzyl chloride. The benzylic chloromethyl groups can be successfully introduced into the PEK-C polymer matrix via plasma graft-polymerization. This approach enables a well preservation in the structure of functional groups and formation of a highly cross-linked structure in the membrane, leading to an improvement on the stability and performance of HEMs. The chemical stabilities, including alkaline and oxidative stability, are evaluated under severe conditions by measuring hydroxide conductivity and weight changes during aging. The obtained PGP-NOH membrane retains 86% of the initial hydroxide conductivity in 6 mol L⁻¹ KOH solution at 60 °C for 120 h, and 94% of the initial weight in 3 wt% H₂O₂ solution at 60 °C for 262 h. The PGP-NOH membrane also possesses excellent thermal stability (safely used below 120 °C), alcohol resistance (ethanol permeability of 6.6 × 10⁻¹¹ m² s⁻¹ and diffusion coefficient of 3.7 × 10⁻¹³ m² s⁻¹), and an acceptable hydroxide conductivity (8.3 mS cm⁻¹ at 20 °C in deionized water), suggesting a good candidate of PGP-NOH membrane for HEMFC applications.

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1. Introduction

Fuel cells (FCs), which are expected to provide clean and efficient energy sources for stationary, automobile and portable

electronic device applications, have attracted considerable attention as means of securing a sustainable future for mankind [1]. Among the several different types of FCs, polymer electrolyte fuel cell (PEFC) as a potential future power source for zero-emission vehicles has been the most developed one in the past two decades due to its rapid startup and high power density [2,3]. Since the development of perfluorinated cation exchange membranes, such as Nafion[®], PEMFCs are considered to be one of the most

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important technologies in the 21st century [4]. To date, significant efforts have been devoted to the development of proton exchange membrane fuel cells (PEMFCs). However, to become commercially viable, PEMFCs have to overcome a number of scientific and technological barriers: high cost by exclusive use of platinum-based catalysts and membranes, serious fuel crossover, serious corrosion and low durability in acidic environment [3,5]. Hydroxide exchange membrane fuel cell (HEMFC) is another type of PEMFC that uses hydroxide exchange membrane (HEM) as the polymer electrolyte, in which hydroxide ions instead of protons are transported through the membrane. Compared with its acid analogue, several merits for HEMFC have been suggested: (i) potential for use of non-precious metal catalysts due to the structure insensitive for electro-oxidation of fuels in alkaline environment; (ii) lower fuel permeability due to the opposite direction of electro-osmotic drag; (iii) lower overpotential associated with many electrochemical reactions in alkaline condition; (iv) less serious corrosion and potentially simplified water management [6–9].

In HEMFC, the HEM is a critical component which can seriously affect the performance of the whole system. Unluckily, there is no equivalent commercially available HEM for HEMFC to Nafion® in PEMFC. Since the membrane features are far from HEMFC requirements, the researches of development on HEMs performance become crucial. Significant efforts have been focused on a noteworthy HEM system by performing a chloromethylation reaction on the polymer backbone to form benzylic chloromethyl groups, followed by quaternization and alkalization [6,10,11]. However, in the chloromethylation reaction, the chloromethyl groups are not always located into the expected position on the polymer backbone, which leads to serious side reactions and inaccurate ion-exchange capacity (IEC) values for membrane [12]. Furthermore, the chloromethylation reaction has other shortcomings, including its sluggishness and the requirement of large quantities of carcinogens, such as chloromethyl ether and dichloromethyl ether [11,13]. Another important development came from Varcoe and co-workers who prepared HEMs by radiation-grafting vinylbenzyl chloride (VBC) onto polymer matrix, such as poly(ethylene-co-tetrafluoroethylene) (ETFE), poly(vinylidene fluoride) (PVDF), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), and so on, which has been proved to be an effective way to avoid chloromethylation reaction [14–17]. However, due to the high energy level of the radiation, irradiation damage occurred in the polymer matrix to a certain extent, which could seriously affect the membrane's structure, and more importantly, the stability [14]. It is well known that in most HEMFC systems to date, alkaline was still added to the fuel, leading to an extremely severe circumstance for HEM operation. Since the HEM works in such strong alkaline and oxidative environment, new method for synthesizing HEM with excellent stability is promising [18].

More recently, we have developed a novel plasma grafting approach to prepare HEM, which is demonstrated to be a mild and efficient method for introducing benzylic chloromethyl groups onto the polymer backbone and preserving the polymer structure [19]. To further improve the stability of the membrane, a cross-linked structure is needed [4]. Herein, plasma graft-polymerization was adopted to synthesize HEMs. In the plasma graft-polymerization process, exciting species within plasma bombard with the polymer matrix to create active sites for binding of functional groups, and in the same time, attack with monomer to prepare active species for polymerizing of high cross-linked structure on the polymer matrix [20]. By employing the plasma graft-polymerization approach, benzylic chloromethyl groups can be efficient introduced into the polymer backbone. In addition, this approach enables a well preservation in the structure of the polymer backbone and functional groups, leading to an improvement

on the stability and performance of HEMs [21]. Furthermore, since the plasma bombardment, grafting and polymerization processes simultaneously occur in gaseous phase, HEM synthesis can be simplified and the problem of liquid waste pollution is expected to be resolved.

The object of the present study is to prepare HEM by the plasma graft-polymerization approach using cardo polyetherketone (PEK-C) powders as the substrate polymer matrix and VBC as the monomer. The chemical structure, physicochemical and electrochemical characteristics of the obtained membranes, including ionic exchange capacity, water uptake, swelling degree, thermal stability, alkaline stability, oxidative stability, ionic conductivity and ethanol permeability, were evaluated.

2. Experimental

2.1. Materials

Cardo polyetherketone (PEK-C) powder (particle size around 50 μm) was obtained from Xuzhou Engineering Plastic Factory (China). Vinylbenzyl chloride (VBC, 95 wt%) was received from Alfa Aesar®. Trimethylamine (TMA, 33 wt%), potassium hydroxide (KOH, AR grade), ethanol (EtOH, AR grade), hydrochloric acid (HCl, 37 wt%) and dimethylformamide (DMF, AR grade) were purchased from Shanghai Chemical Reagent Store (China). High purity hydrogen (H_2 , 99.999%), and argon (Ar, 99.999%) were obtained from Shangyuan Gas Co. Ltd. (China). Deionized water was used in the experiments. All reagents were used as received without further purification.

2.2. Synthesis of plasma graft-polymerized hydroxide exchange membranes

There are two steps in preparation of plasma graft-polymerized HEMs, as shown in Scheme 1: (i) plasma graft-polymerization of VBC monomer into PEK-C polymer matrix; (ii) quaternization of benzylic chloromethyl groups into benzytrimethylammonium cationic groups ($-\text{N}^+(\text{CH}_3)_3\text{OH}^-$).

The plasma graft-polymerization process was carried out in an inductively coupled plasma (ICP) system, depicted in Fig. 1. The device consists of a cylindrical Pyrex glass tube, a radio frequency (RF) power supply, a monomer heater with temperature controller, gas mass flow controllers and a mechanical booster pump. The ICP sustained by a RF power supply inside the brass coil. There are two pieces of Nylon screens in the middle of the Pyrex glass tube with a gap of 100 mm where PEK-C powders located in. Before plasma polymerization of VBC monomer, PEK-C powders were treated by argon plasma under the discharge power of 150 W for 10 min. VBC monomer carried by hydrogen was inlet into the reactor through the gas lines, which were wrapped by heating wires to prevent the polymerization and condensation of VBC on the inner walls of gas lines. The experimental details of plasma graft-polymerization process were: 20 W for the discharge power, 20 Pa for the partial pressure of argon, 60 Pa for the reactor total pressure and 2 h for the reaction time.

The obtained PEK-*gp*-PVBC (PGP-Cl) powders (2 g) were dissolved in DMF to form a 10 wt% solution. A part of the solution was cast onto a flat, clean glass plate and dried in vacuum oven at 50 °C for 12 h and then further dried in vacuum oven at 80 °C for 12 h, after which the film (PGP-Cl) was removed from the glass plate by immersing it in deionized water. In the quaternization process, the rest part of the solution (PGP-Cl) was bubbled with TMA gas at a flow rate of 100 mL min^{-1} for 0.5 h. The resulting quaternized PGP-Cl (PGP-NCl) solution was cast into film using the same condition of preparing PGP-Cl membrane. In order to replace the Cl^- anion in

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