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Layer by layer self-assembly fabrication of high temperature proton exchange membrane based on ionic liquids and polymers

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ABSTRACT

The multicomponent membranes based on the polymer of sulfonated polyetheretherketone (SPEEK) as polyanion, the polymer of polyurethane (PU) and ionic liquid (IL) cation of 1-butyl-3-methylimidazolium ($bmim^+$) as polycations were fabricated with layer by layer (LBL) self-assembly technique. After 100 layers deposition, the $(SPEEK/PU/SPEEK/bmim)_{100}$ membranes were obtained and they showed the potential as membrane electrolytes working in proton exchange membrane fuel cell (PEMFC). Phosphoric acid (PA) molecules were doped in $(SPEEK/PU/SPEEK/bmim)_{100}$ membranes anductivity of $(SPEEK/PU/SPEEK/bmim)_{100}$/60%PA membranes could reach 1.03×10^{-1} S/cm at 160 °C, which was higher than the value of 6.27×10^{-2} S/cm for the comparative $(SPEEK/PU)_{210}$/60%PA membranes under anhydrous conditions. Moreover, $(SPEEK/PU/SPEEK/bmim)_{100}$/PA membranes exhibited the satisfactory mechanical property. The tensile stress was 2.38 MPa for $(SPEEK/PU/SPEEK/bmim)_{100}$/PA membranes at room temperature. This research indicated that the properties of multicomponent LBL self-assembly membrane electrolyte could be optimized through adjusting the components.

1. Introduction

As an energy conversion device, fuel cells could convert chemical energy to electrical energy with high efficiency and less pollution [1]. In the field of fuel cells, proton exchange membrane fuel cell (PEMFC) is considered to be a promising candidate because of its high energy conversion efficiency, low-cost fabrication and high capability, etc. [2–4]. As the key component of PEMFC, proton exchange membranes (PEMs) are in charge of transporting protons and blocking the direct contact of fuels and oxidants [5]. At current, PEMFC is generally operated below 80 °C with humidified gases, which could probably induce the power density decrease as well as the cost of PEMFC systems increase [6]. Over the past decades, many effects have been devoted on improving the working temperature of PEMFC [7–9]. High temperature PEMFC possesses some advantages of high reaction kinetics, high tolerance to fuel impurities, simplified water and heat management, etc. [10,11]. Therefore, the attraction of designing and preparing PEMs with robust proton conducting properties at elevated temperatures and low humidity is growing in the recent years [12,13].

Generally, the structures and properties of components dominate the performance of membrane electrolytes. Besides that, the method of membrane preparation could determine the deposition of components, affecting the property of PEMs. As the most common method, solution casting has been frequently reported to prepare membranes owing to its convenient operation, strong versatility and rapid membrane forming [14,15]. However, the prepared PEMs are usually dragged from the disordered dispersion of components [16]. The membrane electrolytes with the good dispersion of components were still expected to meet the demands for application in PEMFC. Layer by layer (LBL) self-assembly technique as the easy and effective method to prepare functional membranes with the regular nanostructure under molecular alignment has been frequently mentioned in the field of PEMs [17]. In theory, two or more polymers could form the polymer complex or membranes with LBL self-assembly technique owing to the interaction forces such as electrostatic interaction, van der Waals force and hydrogen bonds, etc. At current, most of the researches focused on modifying membranes on surface with depositing some thin layers of polymers or inorganics to improve the property of membrane electrolytes. Hammond PT deposited polyelectrolyte multilayers on a porous support using LBL self-assembly technique and successfully fabricated extremely thin composite membranes for serving as PEMs in fuel cell [18]. Na H reported that the sulfonated poly(arylene ether ketone) bearing carboxyl groups (SPAEK-C) membrane was modified by alternating deposition of the oppositely charged polyaniline (PANI) and phosphotungstic acid (PWA) via LBL self-assembly technique in order to prevent the methanol crossover in direct methanol fuel cell (DMFC) [19]. Similarly, He GH fabricated the composite membranes through LBL self-assembly of chitosan (CS) and PWA on the surface of sulfonated poly(phthalazinone ether sulfone ketone) (SPPESK)

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membranes. They developed LBL self-assembly technique as a promising method in preparation and modification of membrane electrolytes as PEMs [20]. Moreover, the Nafion® series membranes have also gained much attention with depositing some polymers on surface for hindering methanol permeation [21]. The multilayered PEMs were prepared by alternating deposition of poly(diallyl dimethyl ammonium chloride) and highly sulfonated poly(phenylene oxide) on the surface of Nation-212 membranes. The composite membranes showed the decreased methanol permeability and increased overall selectivity compared to the pristine Nafion® membranes [22].

The novel ultra-thin membranes or multi-functional membranes preparing from the alternative deposition of small molecules were promising since they could offer the possibility to combine properties of different components. In this research, the $bmim^+$ cations from 1-butyl-3-methyl imidazolium chloride (bmimCl) are introduced into the LBL self-assembly process of the negatively charged sulfonated polyetheretherketone (SPEEK) matrices and the positively charged polyurethane (PU) matrices. The electrostatic interaction and hydrogen bonds between the components are described and the simulated diagrams are shown in Fig. 1. For PU matrices, a large number of amine groups guarantee phosphoric acid (PA) molecules to be absorbed owing to the formed intermolecular hydrogen bonds. Although SPEEK matrices are incapable of capturing PA molecules [23], they are selected on account of the high thermal stability, excellent mechanical behavior and low cost [24]. Comparing to $(SPEEK/PU)_{210}$ membranes, the $bmim^+$ cations provide a possibility to optimize the property through partially replacing PU matrices in $(SPEEK/PU/SPEEK/bmim)_{100}$ membranes. More PA molecules are thus doped owing to the intermolecular hydrogen bonds between the imidazolium rings of $bmim^+$ cations and PA molecules. Therefore, $(SPEEK/PU/SPEEK/bmim)_{100}$/PA membranes show the better performance on proton conductivity even proton conductivity stability.

2. Experimental

2.1. Materials

Hydrophilic ionic liquid (IL) of bmimCl was purchased from Sinopharm Chemical Reagent Co., Ltd., China. 3 wt% bmimCl was obtained by dissolving bmimCl into de-ionized water. Poly (ether ether) ketone (PEEK) powder was received from Jida High Performance Materials Co., Ltd. China. For 3 wt% PU aqueous solution, it was prepared by diluting 30 wt% cationic PU aqueous dispersion (molecular mass approximately 92,000, from Hepce Chem, South Korea). Moreover, 70 wt %–30 wt% PA solutions were obtained by dissolving 85 wt% PA solution into de-ionized water respectively. All chemicals were used as received without further purification.

2.2. Membrane preparation

2.2.1. Sulfonation of PEEK polymer

The electrophilic aromatic substitution reaction of PEEK with H_2SO_4 was performed to synthesize the polymer of SPEEK [25]. About 5 g PEEK powder was added in batches into 100 mL of concentrated H_2SO_4 and stirred for 1 h at room temperature. Subsequently, the viscous mixture was stirred for 2 h at 60 °C and poured into ice water mixture with manual stirring. The resulting white-colored SPEEK precipitate was washed by de-ionized water for 5 times and then dried in vacuum oven for 2 days at 60 °C. The sulfonation degree (SD, the number of sulfonic acid group/repeating unit of SPEEK) value of SPEEK polymer was 47% in this research. The SPEEK solution with the concentration of 3 wt% was used by dissolving SPEEK polymer into de-ionized water.

2.2.2. Fabrication of $(SPEEK/PU/SPEEK/bmim)_{100}$, $(SPEEK/PU)_{210}$ membranes and PA doped membranes

For $(SPEEK/PU/SPEEK/bmim)_{100}$ membranes, the glass substrates were firstly treated with piranha solution (4 ppm Fe^{2+}, 3 wt% H_2O_2) bearing the negative charges on surface and they were subsequently dipped into cationic PU solution, SPEEK solution, bmimCl solution and SPEEK solution to complete the monolayer self-assembly of components. The membranes were prepared after repeating 100 multilayer deposition processes. It was important to note that the glass substrates were rinsed in de-ionized water to remove the residual PU, SPEEK or $bmim^+$ on surface after each step of self-assembly process. For comparison, $(SPEEK/PU)_{210}$ membranes were fabricated by depositing PU and SPEEK with 210 cycles. $(SPEEK/PU/SPEEK/bmim)_{100}$ and $(SPEEK/PU)_{210}$ membranes peeled off the substrates while the glass surface was corroded immersing into 1 wt% hydrofluoric acid. Moreover, the PA doped membranes were prepared through immersing $(SPEEK/PU/SPEEK/bmim)_{100}$ and $(SPEEK/PU)_{210}$ membranes into 30 wt%, 40 wt%, 50 wt%, 60 wt% and 70 wt% PA solutions in a conical flask with cover for 24 h at room temperature separately.

2.3. Fourier transform infrared spectra

For $(SPEEK/PU/SPEEK/bmim)_{100}$ and $(SPEEK/PU)_{210}$ membranes, the Fourier transform infrared (FTIR) spectra were obtained on a Vertex 70 Spectrometer (Bruker optics Company, Germany). The infrared rays pierced membranes with air as blank.

2.4. Thermal and chemical stability

Thermal stabilities of $(SPEEK/PU/SPEEK/bmim)_{100}$ membranes, $(SPEEK/PU)_{210}$ membranes and PA doped membranes were measured by a thermogravimetric analyzer TGA 290C (Netzsch Company,

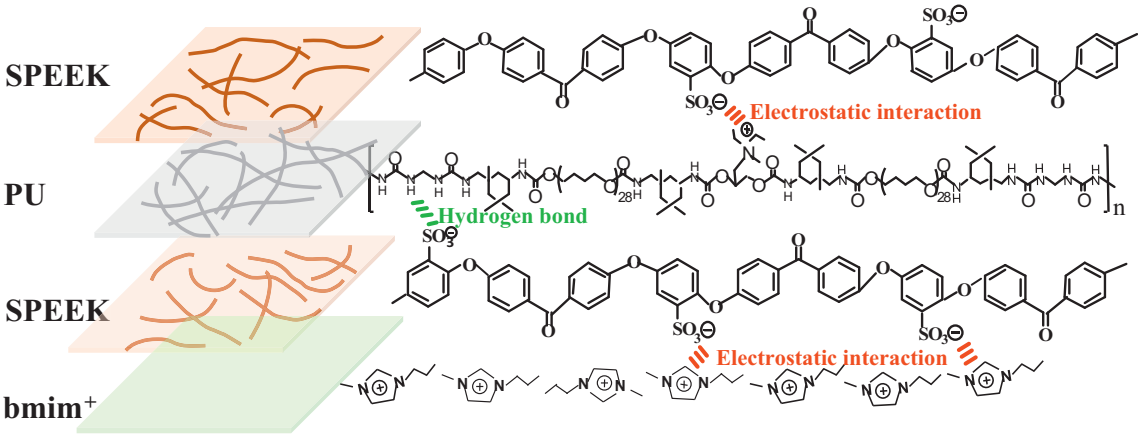

Fig. 1. The diagrammatic sketch of the interaction force between SPEEK and PU, SPEEK and $bmim^+$ in one layer of the LBL membranes.