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Proton-conducting nanocomposite membranes based on P(VDF-co-CTFE)-*g*-PSSA graft copolymer and TiO₂-PSSA nanoparticles

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ABSTRACT

Bifunctional TiO₂ nanoparticles with hygroscopic and proton-conductive properties were synthesized by grafting proton-conducting polymer, i.e. poly(styrene sulfonic acid) (PSSA) from TiO₂ nanoparticles via surface-initiated atom transfer radical polymerization (ATRP). These bifunctional TiO₂-PSSA nanoparticles were blended with poly(vinylidene fluoride-co-chlorotrifluoroethylene)-graft-poly(styrene sulfonic acid), i.e. P(VDF-co-CTFE)-*g*-PSSA to give proton-conducting membranes for high temperature fuel cells. FT-IR, UV-visible spectroscopy and X-ray diffraction (XRD) results revealed bifunctional properties of TiO₂-PSSA nanoparticles due to successful grafting of PSSA chains. Ion exchange capacity (IEC) of P(VDF-co-CTFE)-*g*-PSSA/TiO₂-PSSA membranes was not significantly changed irrespective of TiO₂-PSSA concentrations, representing almost fixed SO₃⁻ concentration in the membranes. In contrast, water uptake and proton conductivity of membranes continuously increased with increasing TiO₂-PSSA concentrations, presumably due to hygroscopic, soft conducting property of nanoparticles. The results of thermal gravimetric analysis (TGA) also showed that all the membranes were stable at least up to 280 °C.

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1. Introduction

Because of the interesting transport and physico-chemical properties, polymer electrolytes have attracted considerable attention in many applications such as lithium rechargeable batteries [1], dye-sensitized solar cells [2] and facilitated olefin transport membranes [3]. In particular, proton-conducting polymer electrolyte membranes have been extensively investigated for the applications to fuel cells during the last decade [4–10]. The most common polymer electrolyte membranes used in fuel cells applications are perfluorinated polymer membranes, i.e. the Nafion series from DuPont. These membranes are chemically inert in the oxidizing/reducing atmospheres of fuel cells and have demonstrated a long-term

stability under fuel cell operating conditions with excellent proton conductivity [11]. However their commercialization to fuel cells is limited to some degree by certain disadvantages such as high cost, high methanol permeability, and low proton conductivity at high temperature/low humidity conditions. These problems have initiated world-wide research activities for developing new materials for proton exchange membranes, ranging from partially fluorinated to non-fluorinated fully aromatic materials in order to reduce costs, since the production of the fluorinated monomers is the most cost intensive step in the production of such materials [12–15].

The operation of fuel cells at elevated temperatures is attractive because it can significantly reduce CO poisoning of the electrode catalysts and the need for noble metal catalysts.

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Elevating the operating temperature would also enhance the electrode reaction kinetics, which consequently results in the increase of fuel cell efficiency. Hybrid organic/inorganic composite membranes are being widely developed for high temperature fuel cell applications, because many of the inorganic materials are capable of operating at a much higher temperature than a pure polymer [16–18]. The incorporation of inorganic compounds into the neat polymer membranes enhances proton conductivity, water retention, and mechanical strength at high temperatures. One of the approaches is the incorporation of hydroscopic and proton-conductive inorganic particles such as zirconium dioxide (ZrO_2), titanium dioxide (TiO_2) and silicon dioxide (SiO_2) into a polymeric matrix [19–21].

In this work, we aim to prepare proton-conducting nanocomposite membranes based on a graft copolymer electrolyte and bifunctional inorganic TiO_2 nanoparticles for high temperature fuel cell applications. Graft copolymer electrolyte comprises poly(vinylidene fluoride-co-chlorotrifluoroethylene), P(VDF-co-CTFE) backbone and poly(styrene sulfonic acid) (PSSA) side chains, which was synthesized using atom transfer radical polymerization (ATRP). Bifunctional inorganic TiO_2 nanoparticles grafted with PSSA were also prepared via surface-initiated ATRP technique. Several characteristics of the resulting P(VDF-co-CTFE)-*g*-PSSA/ TiO_2 -PSSA membranes, e.g. ionic exchange capacity (IEC), water uptake, proton conductivity, and thermal properties are reported in this paper.

2. Experimental

2.1. Materials

P(VDF-co-CTFE) (PVDF SOLEF[®] 31508/1001) was kindly provided by Solvay. Commercial TiO_2 (P25) was purchased from Degussa. 2-Chloropropionyl chloride (CPC, >97%), triethylamine (TEA, >99.5%), 4-(dimethylamino) pyridine (DMAP, >99%), methylene dichloride (MC, >99.8%), 4-styrene sulfonic acid sodium salt hydrate (SSA), dimethyl sulfoxide (DMSO), copper (I) chloride ($CuCl$), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) were purchased from Aldrich and used as received without further purification.

2.2. Synthesis of TiO_2 -PSSA nanoparticles

TiO_2 -PSSA nanoparticles were synthesized by two-step reaction; 1) synthesis of TiO_2 -Cl nanoparticles and 2) grafting of PSSA from TiO_2 -Cl nanoparticles.

First, 3.68 g of DMAP was mixed with 20 ml of MC and 2.8 ml of TEA at 0 °C with ice in a 500 ml round bottom flask. Next, 4.8 ml of CPC in 20 ml of MC was added to the solution. And then, 20.0 g of TiO_2 in 100 ml MC was added dropwise to the solution. It was purged with nitrogen for 30 min. The mixture was allowed to be stirred at room temperature for 24 h. After the reaction, the resulting solution was precipitated into methanol and the product was separated by centrifuge. Finally, TiO_2 -Cl nanoparticles were obtained and dried in a vacuum oven overnight at room temperature.

Second, 8 ml of SSA was dissolved in 10 ml of DMSO in a 100 ml flask. 0.0264 g of $CuCl$ and 0.072 ml of HMTETA were

added to the solution, and then 2 g of TiO_2 -Cl nanoparticles were added sequentially. The solutions were purged with nitrogen for 30 min. The mixture was placed in a 90 °C oil bath for 24 h. After graft polymerization, the resulting solution was precipitated into methanol and the product was separated by centrifuge. The product was washed with methanol several times to remove impurity. Finally, TiO_2 -PSSA nanoparticles were obtained and dried in a vacuum oven overnight at room temperature.

2.3. Synthesis of P(VDF-co-CTFE)-*g*-PSSA graft copolymer

P(VDF-co-CTFE)-*g*-PSSA graft copolymer was synthesized via single-step ATRP reaction using CTFE units as a macro-initiator, according to the previous work [22]. Briefly, 2.0 g of P(VDF-co-CTFE) was dissolved in 50 ml NMP in a round flask at 80 °C. Separately, 11 g of SSA were dissolved in 40 ml DMSO at 80 °C and added to P(VDF-co-CTFE) solution. After making homogeneous solution, 0.16 g of $CuCl$ and 0.4 ml of HMTETA were added and the reaction flask was sealed with a rubber septum. After N_2 purging for 30 min, the reaction vessel was immersed in an oil bath at 120 °C. The reaction was allowed to proceed for 24 h. After polymerization, the resultant polymer was diluted with DMSO. After passing the solution through a column with activated Al_2O_3 to remove the catalyst, it was precipitated into methanol. The polymer was purified by redissolving in DMSO and reprecipitating in methanol. Finally, the P(VDF-co-CTFE)-*g*-PSSA graft polymer was dried in a vacuum oven overnight at room temperature.

2.4. Membrane preparation

The nanocomposite membranes consisting of P(VDF-co-CTFE)-*g*-PSSA graft polymer and TiO_2 -PSSA nanoparticles with various weight ratios were prepared using a solution casting method. The graft polymer and TiO_2 -PSSA nanoparticles with different concentrations, i.e. 0, 2, 4, 6, 8 wt% of nanoparticles relative to total membrane, were dissolved in DMSO together to form a transparent solution. After complete dissolution, the polymer solutions were cast onto a glass dish. The solutions were dried in a convection oven at 80 °C for 48 h, and then in a vacuum oven at 100 °C for 24 h. The membranes with TiO_2 -PSSA concentrations higher than 8 wt% did not show a free-standing film.

2.5. Ion exchange capacity (IEC)

The IEC values of membranes were measured by the classical titration method. The membranes were soaked in 1.0 M NaCl solution for 24 h before measuring IEC. The protons released due to the exchange reaction with Na ions were titrated against 0.01 M standardized NaOH solution, using phenolphthalein indicator. The IEC of the graft copolymer membranes was calculated using the following equation:

$$IEC(\text{meq/g}) = \frac{X \times N_{\text{NaOH}}}{\text{Weight}(\text{polymer})} \quad (1)$$

where X is the volume of NaOH consumed and N_{NaOH} is the normality of NaOH.

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