



Grafting distance and molecular weight dependent proton conduction of polymer electrolyte brushes



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ABSTRACT

Proton conducting materials having reasonable proton conductivity over wide range of relative humidity are of great importance for their application in electrochemical or energy storage devices. Herein, we show that polymer electrolyte brushes on titanate nanotubes fabricated by surface-initiated free radical polymerization technique are effective proton conductors under both hydrated and anhydrous conditions. Both grafting distance and molecular weight of surface-attached polymer electrolyte chains exhibit significant influence on proton conductivity of the formed polymer brushes. With the decrease in average grafting distance of surface-attached polymer chains, the proton conductivity of the synthesized polymer brushes initially increases and then decreases after reaching a maximum value. Non-monotonic behavior of proton conductivity with the increase in molecular weight is also observed. Under optimized conditions, the proton conductivity values of the formed polymer electrolyte brush reach 0.095 S cm^{-1} under 100% relative humidity and 0.01 S cm^{-1} under anhydrous conditions at 140°C .

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) that is an electrochemical device to convert chemical energy stored in fuels directly into electricity has been emerged as a potential practical and viable alternative to the depleting fossil energy resources due to its green nature and high power density [1–4]. One of the key materials for PEMFC assembly is the proton conducting membrane, which functions as proton conductor and reaction gases separator as well [5]. The ideal proton conducting membrane is a nanomaterial with hydrophilic pores through which protons are transported. The often applied proton conducting

membrane in fuel cells is Nafion produced by DuPont, which is composed of a hydrophobic polytetrafluoroethylene backbone and perfluoroether side chains terminated with hydrophilic sulfonic acid groups. Although the precise microstructure of Nafion membrane is still in argument, it is well accepted that the interconnected hydrophilic channels for proton transportation are formed inside the membrane through micro-phase separation induced by hydrophobic backbone and hydrophilic sulfonic acid groups on the side chain of ionomers [6,7]. Accordingly, humidification is generally required for practical applications of fuel cell assembled from Nafion membrane to ensure the expansion of ionic channels by penetration of water molecules for effective proton conduction. The thus-applied humidifier in PEMFC to keep Nafion humidified can not only decrease the power density, but also increase the cost of the system [8]. In addition, Nafion membrane is not suitable for elevated temperature appli-

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cations as the hydrophilic channels could be deformed above the glass transition temperature of Nafion ionomers (about 110 °C) [6]. This brings the question whether the micro-phase separation induced ionic channels in proton conducting membranes are necessary [9,10].

Over the last ten years, many efforts have been devoted to organic–inorganic hybrids as alternative solid proton conducting materials to enhance the proton conduction under reduced humidification levels or at elevated temperatures as discussed in recent topical reviews [11–15]. Particularly, immobilization of organic or polymeric molecules onto hard surfaces exhibits enhanced thermal and chemical stability, improved water retention ability, and according less humidity-dependent proton exchange capacity [16–23]. For instance, Moghaddam et al. designed and fabricated a proton conducting membrane by self-assembly of an organic monolayer with sulfonic acid end groups on the surface of micro-porous silica matrix [16]. It was observed that proton conductivity of the formed membrane is independent on the relative humidity applied and is slightly higher than that of Nafion 117 membranes under hydrated state. Under reduced humidification conditions, the proton conductivity of the formed membrane is two to three magnitudes higher than that of Nafion under the same condition. Another example is polymer electrolyte brushes grown directly from the inner surface of microporous silica matrix through surface-initiated polymerization [17]. It was concluded that the short distance between two neighboring sulfonic acid groups induced by high density of sulfonic acid groups inside the brush leads to an efficient proton transporting pathway through the membrane. However, the grafting distance or grafting density of the anchored polymer chains was not given in their reports, resulting in difficulty to evaluate the effect on humidity-dependent proton conductivity.

We have recently reported that polymer electrolyte brushes grown on the outer surface of titanate nanotubes (TiNTs) can be saturated by water molecules at low humidification levels for effective proton transport because of the short grafting distance between anchored polymer chains [24]. In this paper, we systematically investigated how the grafting distance and molecular weight of surface attached polymer electrolyte chains affect the proton conductivity of polymer electrolyte brushes. It turns out that proton conductivity exhibits non-monotonic behavior with the increase in molecular weight or grafting density of anchored polymer chains. With optimized structure, the highest proton conductivity reaches 0.095 S cm^{-1} under hydrated state and 0.01 S cm^{-1} under dry state at 140 °C. The results suggested that polymer electrolytes with confined structures are potential effective proton conductors operated at elevated temperature and low relative humidity, particularly for micro-fuel cell applications.

2. Experimental

2.1. Materials

Sodium 2-acrylamido-2-methylpropane sulfonate, hexachloroplatinic acid, laevulinic acid, and allyl alcohol

were purchased from Alfa Aesar. Phosphorous pentachloride, potassium cyanide, and triethylamine were received from Kermel Chemical Reagent Ltd. (Tianjin, China). Titanium dioxide powder (P25) was purchased from Evonik Degussa, Germany. Toluene was distilled under a nitrogen atmosphere from sodium using benzophenone as an indicator. Water was deionized through a Milli-Q system (Barnsted Nanopore, resistivity = $18.0 \text{ M}\Omega \text{ cm}^{-1}$). All the other solvents and chemicals were reagent grade and were used as received. The initiator, dimethylchloro-silylpropyl 4-isobutyronitrile-4-cyano pentanoate, and the titanate nanotube substrates were synthesized according to literatures [25,26]. The synthesized TiNTs for grafting of polyelectrolyte have the inner diameter of 5 nm, wall thickness of about 1.4 nm, and the Brunauer–Emmett–Teller (BET) surface area of $321 \text{ m}^2 \text{ g}^{-1}$ calculated from adsorption–desorption isotherms, as reported in our previous work [26].

2.2. Self-assembly of initiator on titanate nanotubes

To a suspension of TiNTs (1 g) in anhydrous toluene (50 ml), a solution of initiator with desired amount in anhydrous toluene (20 ml) was added under an atmosphere of nitrogen. Triethylamine (1 ml) was added to the mixture as catalyst for surface attachment and the mixed suspension was stirred overnight at room temperature. The surface modified TiNT was centrifuged and carefully washed with toluene, ethanol, and acetone. The products were dried at room temperature under vacuum for 4 h.

2.3. Formation of polyelectrolyte brushes

Under an atmosphere of nitrogen, initiator modified TiNTs (1.5 g) was suspended in aqueous solution containing of desired amount of sodium 2-acrylamido-2-methylpropane sulfonate in a Schlenk flask. The mixture was degassed through 5 freeze-thaw cycles under vacuum to remove trace of oxygen and polymerized at 60 °C for a period of time. After polymerization, samples were separated by centrifugation and washed with 0.1 M HCl aqueous solution 4 times (each washing step for 30 min) to transfer the sodium salt to acid form. After extracting the non-attached polymers with methanol using a Soxhlet apparatus for 15 h, the resulting white powders were dried at 80 °C under vacuum overnight. Free polymers in solution were dried using lyophilizer and were used for determination of molecular weight. The acid-form polymer electrolyte brush synthesized here was denoted as polyAMPS brush.

2.4. Characterization

Elemental analysis was carried out to determine the grafting density of surface attached initiator monolayer. Weight average Molecular mass of free polymers in solution was determined by gel permeation chromatography (GPC-SEC system, SUPERA water column, Agilent) calibrated with polyacrylic acid–sodium salts (PAA-10). Fourier transform infrared spectra (FTIR, Bio-Rad FTS

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