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Titanate nanotube array membranes filled with polyelectrolyte brushes for proton conduction

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ABSTRACT

Development of effective ion conductors with high volumetric stability is essential for micro-electrochemical devices. Herein, we report the synthesis of orderly aligned proton conductors based on polyelectrolyte brushes grafted on the surface of free-standing and through-hole TiO_2 nanotube array membranes. The proton conductivity observation of the formed membranes with partially and fully filled polymers indicates that the ionic segments close to the surface play major role on proton transportation through membranes. The formed membrane exhibits promising proton conductivity at elevated temperature (0.125 S cm^{-1} at 140 °C) and the proton conductivity remains stable within the test period of time (100 h). The results provide a potential nanotechnology for preparation of orderly aligned ionic conductors not only for transportation of proton but also for other ions.

1. Introduction

Portable electronic devices have been widely used and updated with an inconceivable speed, which makes more strict demands on portable power sources. Although lithium-based batteries have dominated the market, battery manufacturers are still facing growing pressure to increase the energy density of portable power sources [1]. Micro-fuel cell has thus been aroused much interests as the optimum alternative of lithium based batteries since it has advantages including high energy conversion efficiency, zero emission, and high-energy density [2–4]. Particularly, the energy density of micro-fuel cell exceeds that of lithium-based batteries by an order of magnitude. However, to realize fuel cell microminiaturization, development of electrolyte membrane with high dimensional stability and great ionic conductivity is prerequisite [2].

Of various types of electrolyte membranes developed, electrolyte membrane with orderly aligned channels has been recognized as an effective ion conductor [2,5,6]. In the pioneer work conducted by Kanamura et al., proton-conducting polymer, poly(2-acrylamido-2-methyl-1-propanesulfonic acid), was introduced into pre-synthesized macroporous silica matrix to form ion-conducting membranes with orderly aligned channels using "pore filling" technique [5]. The accordingly assembled fuel cell exhibited comparable electrochemical performance to the cell from Nafion membrane. Later on, Moghaddam et al. reported an inorganic–organic composite membrane fabricated by grafting an organic electrolyte monolayer onto the inner wall of porous silica membrane through self-assembly [2]. The formed composite membrane exhibited higher proton conductivity than Nafion membranes under both dry and humidified conditions. Although the preparation process is quite complicated, it is obvious that ion conductor with orderly aligned channels can enhance ion transportation in membranes.

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Since its birth in 1999 [7], free-standing and through-hole TiO_2 nanotube (FT-TiNT) array membrane has attracted great attention due to its potential applications in photochemistry and biomedical applications [8–13]. Moreover, the existence of surface hydroxyl groups on FT-TiNT makes surface modification possible and also facilitates ion transportation [14–16]. In addition, the good volumetric stability can perfectly meet the requirement of micro-fuel cells or lithium based batteries. Herein, we report the fabrication and ionic conductivity of orderly aligned proton conductor using FT-TiNT array membranes as matrix and surface-attached polymers as electrolyte, as shown in Fig. 1. The polyelectrolyte chains were directly grown from the surface through surface-initated polymerization ("grafting from" technique) [17]. Due to the confined structure of polymer chains and high grafting density, the synthesized material exhibited promising ionic conductivity particularly at elevated temperature.

2. Experimental

2.1. Materials and method

Sodium 2-acrylamino-2-methylpropane sulfonate (AMPS, 50 wt% in water) and titanium foils (99.7%, 0.25 mm) were purchased from Sigma Aldrich. 4,4′-Azobis(4-cyanovaleric acid), ally alcohol, and hexachloroplatinic acid were obtained from Alfa Aesar. Toluene was distilled over sodium under a nitrogen atmosphere using benzophenone as an indicator. Water was deionized through a Milli-Q system (Barnsted Nanopore, 18.2 $M\Omega\ cm^{-1}$). All the other chemical reagents with analytical grade were purchased from Sinopharm and used as received. The azo type initiator, dimethylchloro–silylpropyl-4-isobutyr onitrile-4-cyanopentanoate, was synthesized according to previous works [18,19].

2.2. Synthesis of free-standing and through-hole titanate nanotube array membranes

FT-TiNT array membranes were prepared using anodic oxidation process as reported in literature with slight modification [9]. Potentiostatic anodic oxidation was typically performed in a two-electrode electrochemical cell using Ti foil as working electrode, a platinum plate as counter electrode at 0 °C. Prior to use, Ti foils was washed with detergent and followed by ultra-sonication treatment for 10 min in acetone and rinsed thoroughly using water. To eliminate defects on the surface, Ti foils were pre-anodized in an electrolyte solution containing 0.3 wt% NH_4F and 2 vol% deionized water in ethylene glycol at 60 V for 2 h. The resulting TiNT array layers were then removed by ultra-sonication in 1 M HCl aqueous solution. Subsequently, the textured Ti substrates were anodized again in the same composition of electrolyte at 60 V for 24 h. To obtain through-hole TiNT array membrane, a larger anodic voltage (150 V) was applied for 5 min at the end of the anodization. After immersed in methanol for 48 h, the sample was exposed in air and the freestanding membrane gradually separates from the Ti substrate [20].

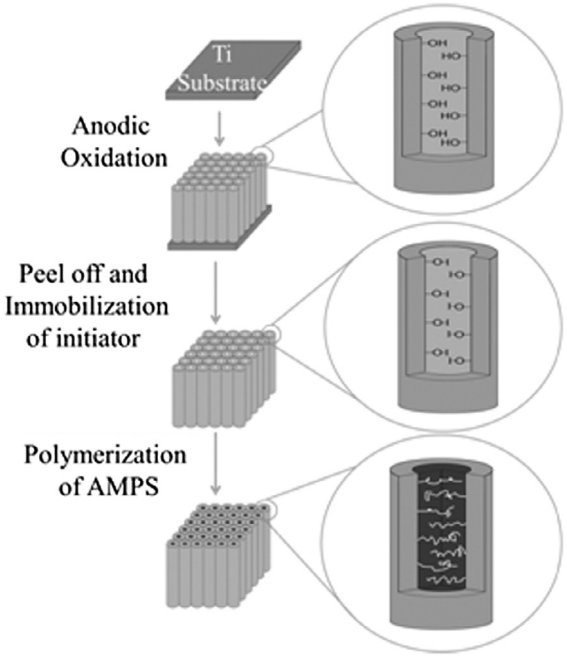

Fig. 1. Schematic illustration of the synthesis of orderly aligned proton conductors.