Journal of Power Sources 326 (2016) 466–475

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Preparations of an inorganic-framework proton exchange nanochannel membrane

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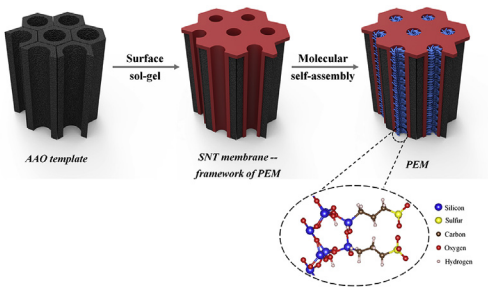
HIGHLIGHTS

- A PEM composed of straight and aligned proton conducting nanochannels is prepared.
- The proton conductivity of the nanochannel membrane reaches 11.3 mS cm^{-1} at 70 °C.
- The activation energy for proton transfer is 0.06 eV assisted with water molecules.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 April 2016
Received in revised form
17 June 2016
Accepted 7 July 2016
Available online 15 July 2016

Keywords:
Proton exchange membrane
Inorganic material
Proton conductivity
First-principles study

ABSTRACT

In this work, a proton exchange membrane composed of straight and aligned proton conducting nanochannels is developed. Preparation of the membrane involves the surface sol-gel method assisted with a through-hole anodic aluminum oxide (AAO) template to form the framework of the PEM nanochannels. A monomolecular layer (SO_3H–$(CH_2)_3$–Si–$(OCH_3)_3$) is subsequently added onto the inner surfaces of the nanochannels to shape a proton-conducting pathway. Straight nanochannels exhibit long range order morphology, contributing to a substantial improvement in the proton mobility and subsequently proton conductivity. In addition, the nanochannel size can be altered by changing the surface sol-gel condition, allowing control of the active species/charge carrier selectivity via pore size exclusion. The proton conductivity of the nanochannel membrane is reported as high as 11.3 mS cm^{-1} at 70 °C with a low activation energy of 0.21 eV (20.4 kJ mol^{-1}). First-principle calculations reveal that the activation energy for proton transfer is impressively low (0.06 eV and 0.07 eV) with the assistance of water molecules.

1. Introduction

Proton exchange membranes (PEMs) have attracted much attention due to their widespread utilization in electrochemical energy systems such as fuel cells [1–4], batteries [5,6] and electrolyzers [7,8]. The most commonly used PEMs are composed of polymer-based materials, such as perfluorosulfonic acid [9], with which the most famous example is commercialized under the trade name Nafion, sulfonated polyether ether ketone [10] and acrylamide-*tert*-butyl sulfonic acid [11]. With significant headway being made in nanofluidic science, nanostructured polymer membranes, which contain self-organized ion nanochannels driven by the incompatibility of hydrophilic and hydrophobic polymer moieties, have seen substantial development in recent years [12–16]. For

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http://dx.doi.org/10.1016/j.jpowsour.2016.07.022
0378-7753/

example, Watanabe et al. [17] synthesized quaternized aromatic multiblock copolymers with well-developed ion nanochannels; Ran et al. [18] developed a rod-coil graft copolymer comprising of hydrophobic rigid main chains and hydrophilic flexible graft chains; Titvinidze et al. [19] prepared a series of multiblock copolymers consisting of highly sulfonated poly (phenylene sulfone) and poly (phenylene ether sulfone) segments as the PEM, in which the spontaneous phase separation results in ordered and continuous ion nanochannels; Bae et al. [20,21] reported poly (arylene ether sulfone ketone) multiblock copolymer membranes exhibiting highly sulfonated hydrophilic blocks, where distinct hydrophilic/hydrophobic phase separations were observed to form distinct ion nanochannels. The nanostructured membrane displays remarkable advantages: the well-defined nanochannels exhibiting long-range order morphology can significantly enhance the ion mobility by reducing the morphology barrier, and in turn improve the proton conductivity [22,23]. In addition, the issue of fuel permeation, which plagues many electrochemical energy systems, can be solved via size exclusion effect in such a confined microenvironment [24–26]. While promising, limitations for this type of nanostructured polymer membranes need to be addressed. First, nanoscale morphology of polymer-based PEMs proves difficult to be controlled with precision. Second, swelling is observed from dry to hydrated state during operation, causing a volumetric discrepancy and disturbing the nanostructure. Membrane properties, such as permeability and stability, are thus affected. Meanwhile, it should be mentioned that the “nanochannels” of this polymer membrane are separated hydrophilic phases with ionic clusters rather than true paralleled and straight channels.

It is currently feasible to obtain inorganic materials with designable architecture and tunable pore structures, where the inorganic material itself is free of swelling. Hence, one method to overcome the limitations of the polymer membrane is to adopt the use of inorganic material based PEM. In this work, a silica nanotube (SNT) membrane, the framework of the PEM, is prepared by a surface-sol-gel (SSG) method assisted with a through-hole anodic aluminium oxide (AAO) template. The size of the nanochannel can be controlled by the SSG condition. The nanochannels shape the proton-conducting pathway and the assembly of the inner walls with a monomolecular layer (SO_3H–$(CH_2)_3$–Si–$(OCH_3)_3$) enhances the ion exchange capacity, allowing the Grotthuss transport mechanism to be achieved. As a result, a PEM composed of straight, aligned and size-controllable proton conducting nanochannels is developed. The basic fabrication process of the inorganic framework proton exchange nanochannel membrane is illustrated in Fig. 1.

2. Experimental methods

2.1. Fabrication of the silica based nanochannel membrane

Commercially available through-hole AAO template with pore diameters of 30 nm and a thickness of 30 μm was used. The surface sol-gel (SSG) synthetic method was used to fabricate the SiO_2 nanotube (denoted as SNT) membrane. The AAO template was first immersed in a 99% $SiCl_4$ solution (Sigma-Aldrich) for 4 min and subsequently rinsed with hexane and immersed in fresh hexane for 30 min to remove any unbound molecules. The template was then placed in methanol/hexane (1:1) and ethanol for 5 min respectively to replace the hexane, and dried under a stream of N_2. The experimental procedures were completed in an argon-filled glovebox to avoid undesired hydrolysis of $SiCl_4$. Finally, the template was placed into the deionized water for 5 min to make the adsorbed $SiCl_4$ molecules hydrolyze to form SiO_2. The aforementioned method describes one cycle of SSG. In total, four cycles were carried out for the synthesis of the silica nanotube membrane.

2.2. Functionalization of the nanochannel membrane

The fabricated nanochannel membrane (evacuated at 393 K) was placed in dry toluene solution with 0.5 vol% 3-mercaptopropyltrimethoxysilane (MPTMS) at ambient temperature for 100 h to allow diffusion of the MPTMS molecules into the nanochannel to react with the nanopatterned Si–OH on the inner walls of the SNTs. The membrane was subsequently rinsed with toluene to remove residual MPTMS and dried under a stream of N_2. The –SH end groups assembled on the nanochannel were then converted to $-SO_3H$ groups by mild oxidation with 35 wt% H_2O_2 at ambient temperature for 48 h. The membrane was then washed with water and ethanol, respectively, and acidified with 0.1 M H_2SO_4, followed by thorough washed with water and dried.

2.3. Characterization

The morphologies of the nanochannel membrane were observed by a high resolution scanning electron microscope (SEM). The SNTs, which act as the membrane framework, were observed by a transmission electron microscopy (TEM) fitted with energy-dispersive X-ray spectroscopy (EDS). The functionalization of the inner wall was confirmed by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and time of flight secondary ion mass spectrometry (ToF-SIMS). The membrane proton conductivity was measured with a potentiostat (EG&G Princeton, model M2273). The prepared nanochannel membrane was sandwiched by a pair of gold-coated stainless steel electrode. This setup was then clamped by a home-made module and immersed in deionized water. The proton conductivity was measured by the potentiostat through an AC impedance method. The spectra were recorded at a frequency range from 1000 kHz to 1 Hz with wave amplitude of 10 mV. The proton conductivity σ can be obtained from:

$$\sigma = \frac{L}{R_\Omega \times A} \tag{1}$$

where L represents the thickness of the membrane, A is the surface area of the membrane and R_Ω is the membrane resistance which was obtained by calculating the intercept of the high frequency region.

2.4. Computational methods

All density functional theory (DFT) based first-principles studies were performed using ABINIT code [27,28]. The electron-ion interactions were described by the projector augmented wave (PAW) method [29], and the electronic exchange correlation effect was implemented within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) type [30]. The valence electrons were expended on a plane wave basis with a 22 Ha energy cutoff. The Brillouin zone integration was sampled using a $4 \times 4 \times 4$ and $2 \times 2 \times 1$ Monkhorst-Pack [31] k-point mesh for bulk and surfaces, respectively. A 20 Å vacuum along z-direction was used to avoid the interaction between adjacent supercell in the slab model. The Self-Consistent-Field (SCF) cycles were continued until the tolerance for differences of forces reached 4.0×10^{-5} Ha/Bohr on two successive cycles, and the maximal absolute force tolerance for structural optimization was set to be 4×10^{-4} Ha/Bohr.

First-principles studies of amorphous silica are challenging due to lack of periodicity in the system. Previous investigations used a variety of crystalline structures to model the structure of amorphous silica and demonstrated high feasibility [32–36]. In this work, α-quartz SiO_2 with hexagonal crystal structure is used to