Tuning the performance of anion exchange membranes by embedding multifunctional nanotubes into a polymer matrix

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ABSTRACT

Herein, a series of quaternized halloysite nanotubes (QHNTs) bearing different imidazoliums groups are prepared *via* distillation–precipitation polymerization and quaternarization, and then embedded into chitosan (CS) matrix to fabricate hybrid membranes. Systematic characterizations and measurements are performed to explore the relationships between the ligand of ammonium and the performance of hybrid membrane. It is found that QHNTs are well-dispersed within CS matrix, and the chain mobility of CS is promoted driven by repulsive interactions from QHNTs, in turn affording the increments of water uptake and area swelling. Together with the promoted chain mobility, low-barrier conduction pathways are formed along the QHNTs surface and then confer a significant enhancement in hydroxyl conductivity to hybrid membranes. For QHNTs, hydrophilic ligand could adsorb more water molecules and short ligand is more favorable for contacting with hydroxyl, both of which are beneficial for high hydroxyl conductivity. Particularly, incorporating 7.5% QHNTs with ester-type QA ligand endows the hybrid membrane with an 89% increase in conductivity from 0.009 to 0.017 S cm^{-1} at 90 °C and 100% RH. Yet under anhydrous conditions, the positive charge dispersity of QA and stereo-hindrance effect of the ligand are the predominant factors for hydroxyl ion hopping.

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1. Introduction

A fuel cell is an efficient energy conversion device which generates electric energy from chemical fuels and is considered to be promising for clean energy technology [1–3]. Among various fuel cells, proton exchange membrane fuel cell (PEMFC) is most developed for the attractive system efficiencies and environmental benefits. However, due to the use of noble metals as catalyst and expensive polyelectrolyte membrane (e.g., Nafion), the high cost prohibits its widespread commercial adoption [4,5]. By comparison, alkaline fuel cell (AFC) has renewed growing attention on account of its faster kinetic rate for oxygen reduction and lower methanol crossover [6–8]. These features endow AFC with the following advantages: (i) higher cell voltages; (ii) more alternative catalysts (especially the cheaper non-noble metal catalysts); and (iii) lower usage amount of catalysts [9–13]. As the key component in AFC, anion exchange membrane (AEM) should possess high hydroxyl conductivity, excellent mechanical stability, and outstanding thermal stability. Particularly, adequate hydroxyl conductivity is highly required for AEM, as it determines the performance of AFC including the operational fuel cell voltage and current output.

During the past decades, tremendous efforts have been devoted to enhancing the hydroxyl conductivity of AEM. Polymers tethering organic cations have been demonstrated as solid AEMs for AFCs. These organic cations have been obtained by introducing quaternary ammonium (QA) [14,15], guandinium [16], or phosphonium groups [17] through chloromethylation of aromatic rings or bromination on the benzylic methyl groups of the polymers, followed by the menshutkin reaction. Various polymers, such as poly (olefin)s [18], poly (styrene)s [19], poly (phenylene oxide)s [20,21], poly (phenylene)s [22], and poly (aryleneether)s [23] have been investigated, which display a wide range of hydroxyl conductivities. A high hydroxyl conductivity can be acquired under high loading amount of organic cations, however, it generally leads to excessive water swelling and hence a loss of mechanical strength [12,24]. By comparison, organic–inorganic hybrid membranes have attracted intensive interest due to their promising advantages in enhancing physicochemical properties and providing ionic conductivity [25–27]. The as-utilized inorganic materials include TiO$_2$ [28,29], SiO$_2$ [30], nanotubes [31–33], hydroxyapatite (HAP) [34], montmorillonite [35], etc. Yang et al. embedded the hydrophilic HAP into crystalline PVA, in which HAP interfered with the segment configuration of PVA and decreased the crystallinity of the membrane, thus reducing the transfer energy barrier and enhancing the ionic conductivity [36]. In addition, they fabricated quaternary PVA–Al$_2$O$_3$ hybrid membrane with enhanced hydroxyl

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conductivity through similar method [37]. However, the incorporation of inorganic fillers (e.g., SiO_2) into amorphous polymer matrix (e.g., quaternized chitosan) leads to the blockage for hydroxyl, resulting in the decrease of hydroxyl conductivity [38]. To address this issue, the filler materials bearing ion exchange groups have been adopted, which could provide additional ion hopping sites and conduction paths. For instance, Wang et al. prepared PVA/3- (trimethylammonium) propyl-functionalized silica hybrid membranes and found that 10% TMAPS could generate 70% increase of ionic conductivity [39]. Li and co-authors fabricated ionic liquid grafted carbon nanotubes (ILNTs) through radical polymerization, and noted that 0.3% ILNTs could elevate the conductivity of poly (2, 6-dimethyl-1,4-phenylene oxide) containing imidazolium membrane from 0.0129 to 0.0252 S cm^{-1} [40]. Despite of the advantages of functionalized filler-filled hybrid AEMs, the relevant investigation is seldom performed. In addition, the development of facile and general approach to fabricate efficient transfer channel remains a challenge at present.

Although the incorporation of functionalized inorganic fillers into polymer matrix may create ion transfer channels at the polymer/filler interface, the rational design of filler functionality based on hydroxyl ion transfer mechanism remains challenging. Actually, the filler functionality affects both the chemical environment and water environment of ion transfer channel, which are further in close relationship with ionic transfer mechanism. Generally, the transfer of hydroxyl ions through AEM obeys the following mechanisms [41]: Grotthuss mechanism, surface site hopping, diffusion and migration, and convection. Among them, the former two are regarded as predominant mechanisms. Grotthuss mechanism is assumed that the hydroxyl diffuses through the hydrogen-bonded networks formed by water. The transfer process follows the hydrogen bond rearrangement, re-orientation, and hydroxyl ion transfer by forming a tetrahedrally coordinated water cluster. Surface site hopping is related to the hydroxyl ion hopping from one cationic group to a neighboring one. This would to be the dominating transfer mechanism when the membrane is operated under anhydrous conditions. It reveals that water plays an indispensable role in the transfer of hydroxide. According to the aforementioned mechanisms, QA as the most employed hydroxyl ion carrier needs delicate design for intensifying Grotthuss mechanism and surface hopping mechanism. By varying the steric conformation and the polarity of the ligand on N atom of QA, its capacity of binding water molecule or hydroxyl ion can be tailored, and therefore the optimal ion transfer channel structures are expected to be acquired. However, the effect of ligand type of QA on the hydroxyl ion transfer channel environment has neither been theoretically predicted nor experimentally demonstrated.

In this study, novel polymer-nanotube hybrid AEM was prepared by embedding quaternized nanotubes into polymer matrix, in which the nanotubes might create continuous transfer pathways due to their high aspect ratios. Halloysite nanotubes (HNTs), naturally two-layered aluminosilicate clay mineral and available in abundance in the world, were chosen due to their excellent mechanical/thermal stabilities and sufficient Si–OH and Al–OH groups [42,43]. Imidazoliums were chosen as functional groups due to the good alkaline stability and high quaternarization reactivity from imidazole [44,45]. HNTs were quaternized via a facile distillation–precipitation polymerization followed by Menshutkin reaction using four chlorinated reagents. In such a way, four kinds of polymeric layer bearing high QA loading amount but different chemical structures were grafted on HNTs surface. Chitosan (CS) was chosen as membrane matrix due to its good film forming and mechanical properties as well as low cost [46,47]. To better investigate the function and transfer mechanism of QA, CS was not quaternized to minimize its influence on ionic conduction of the hybrid membrane. The microstructures and physicochemical

properties of the membranes were investigated in detail. Additionally, the hydroxyl conductivities and transfer mechanism of the membranes at different temperatures and humidity were systematically evaluated.

2. Experimental

2.1. Materials and chemicals

Halloysite nanotubes were refined from clay minerals in Henan province, China. CS with the deacetylation degree of 91% was purchased from Golden-Shell Biochemical Co. (Zhejiang, China) and used as received. 3-(Methacryloxy) propyltrimethoxysilane (MPS) was purchased from Aldrich and distilled under vacuum. 2, 2-Azobisisobutyronitrile (AIBN), ethylene glycol dimethyl acrylate (EGDMA) and acetonitrile were obtained from Kewei Chemistry Co. Ltd (Tianjin, China). Vinyl imidazole (VI), chlorobutane (CB), chlorodecane (CD), benzyl chloride (BC) and ethyl chloroformate (EC) were purchased from xi ya reagent in Shandong province, China. De-ionized water was used throughout the experiment.

2.2. Synthesis of the quaternized halloysite nanotubes (QHNTs)

QHNTs were synthesized via distillation-precipitation polymerization and quaternarization method. The detailed test method are as follows: HNTs (3.0 g) were dispersed into ethanol (160 mL), then water (15 mL) and aqueous solution of ammonium (12 mL) were added into the solution and stirring at room temperature (20–25 °C) for 24 h. Then, MPS (1.0 mL) was added into the mixture and being stirred for another 32 h. Subsequently, the MPS modified HNTs (M-HNTs) were purified by three cycles of centrifugation and followed by drying in vacuum oven at 40 °C. M-HNTs (0.30 g), EGDMA (0.30 mL), VI (0.60 mL), and AIBN (0.016 g) were dispersed into acetonitrile (80 mL) in a dried stand-up round bottom flask. The above mixture was heated and kept at 82 °C until half acetonitrile was distilled out. Afterwards, the N-vinyl imidazole grafted HNTs (VI-HNTs) was purified by centrifugation with washing by acetonitrile, and then dried in vacuum drying oven. VI-HNTs (0.6 g) was dispersed into absolute alcohol (100 mL), then quantitative of quaternary aminating reagent (CB, CD, EC, BC) (QA/VI=1:1, mol/mol) was added into the solution and the solution was refluxed under 80 °C for 8 h, QHNTs were purified by centrifugation with washing by ethanol and dried in vacuum oven. It should be noted that the preparation conditions of QHNTs were selected and controlled for achieving similar amount of QA for all the QHNTs. The as-synthesized QHNTs were designated as C_4-QHNTs, C_{10}-QHNTs, E-QHNTs, and B-QHNTs, respectively.

2.3. Preparation of CS control and hybrid membranes

CS (1.2 g) was dissolved into acetic acid aqueous solution (2%, 50 mL) under stirring at 80 °C for 2 h. Simultaneously, a certain amount of HNTs or QHNTs were dispersed into deionized water (10 mL) with ultrasonic treatment for 6 h, then added into CS solution drop-wise. The mixture was stirred vigorously at 80 °C for another 2 h. Subsequently, cooled down to room temperature (20–25 °C), a given amount of cross-linker glutaraldehyde (GA, 2%, v/v) aqueous solution was added to the mixture and stirred vigorously at room temperature (20–25 °C) for 3 h, and then ultrasonic treatment for another 30 min. The resultant mixture was cast onto a glass plate until the solvent evaporate at room temperature completely. For CS control membrane, the casting solution was prepared without the addition of nanofillers and the preparation process was as mentioned above. All the membranes were immersed into 0.5 mol L^{-1} KOH solution at room temperature for 24 h to obtain hydroxyl form