



High-performance layered double hydroxide/poly(2,6-dimethyl-1,4-phenylene oxide) membrane with porous sandwich structure for anion exchange membrane fuel cell applications

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ABSTRACT

Herein, we present a porous-sandwich-structure anion exchange membrane (AEM) to improve the comprehensive performance of the AEM. A series of porous-sandwich-structure AEMs based on triple-cation side chain poly(2,6-dimethyl-1,4-phenylene oxide) (TC-QAPPO) membrane were synthesized by spraying quaternary-ammonium-modified layered double hydroxide (QA-LDH) on the surface of the TC-QAPPO membrane. Compared with the TC-QAPPO membrane, the QA-LDH/TC-QAPPO composite membranes show higher alkaline stability, hydroxide conductivity, and dimensional stability than those of TC-QAPPO membrane. The QA-LDH layer exhibits an impressive ion conductivity and alkali resistant ability, acting as a protective layer to protect the TC-QAPPO membrane from being attacked by hydroxide. The porous structure was designed to accelerate the ion conductivity in QA-LDH layer. The QA-LDH/TC-QAPPO membranes with low swelling ratio exhibits a maximum hydroxide conductivity of 122 mS/cm at 80 °C. A long-term stability test demonstrates that the QA-LDH/TC-QAPPO membranes have a maximum retention (85.4%) of hydroxide conductivity in 1 M KOH at 80 °C for 500 h. Besides, the QA-LDH/TC-QAPPO membrane achieves a maximum power density of 267 mW/cm² at current density of 554 mA/cm² at 60 °C. The porous-sandwich-structure strategy provides a new and reliable method to prepare high-performance AEMs for alkaline fuel cell applications.

1. Introduction

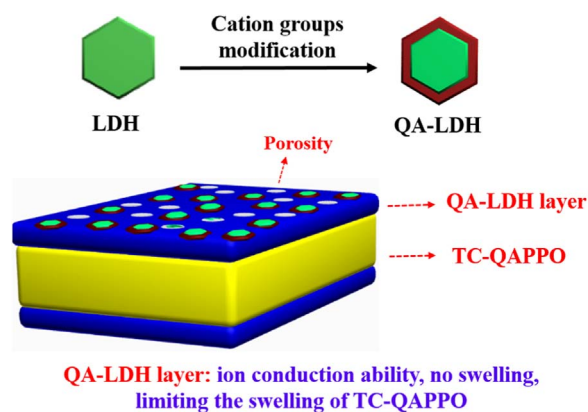
To overcome the reliance on precious platinum catalysts, researchers have paid much attention to anion exchange membrane fuel cells (AEMFCs) as a promising alternative to proton exchange membrane fuel cells (PEMFCs) in recent years due to their advantages in utilizing non-noble metal catalysts and having faster cathode reaction kinetics under alkaline conditions [1–3]. Anion exchange membrane (AEM) is a pivotal component of AEMFCs, acting as both ionic conductor and gas barrier [4,5]. An ideal AEM should simultaneously possess high ion conductivity, sufficient chemical stability and dimensional stability, and excellent mechanical properties [6–8]. A number of polymers, such as polyethersulfone [9], polystyrene [10], polyphenyl ether [11], polybenzimidazole [12], and fluorinated polymers [13], and different cationic groups, for example, quaternary ammonium [14], imidazolium [15], phosphonium [16], sulfonium [17], ruthenium [18], and cobaltocenium [19,20], were explored to prepare high-performance AEMs in the past few years. Unfortunately, most of the AEMs suffer from insufficient ion conductivity and chemical stability,

impeding the practical applications of the AEMs for fuel cells [21–24]. Zhuang and coworkers focused on the quaternary ammonia polysulfone demonstrated that AEMs with suitable microphase separation possess much higher ion conductivity. Currently, Hickner and coworkers revealed the strategy of multi-cation side chain in AEM can simultaneously improve the ion conductivity and alkaline stability of the AEM due to reducing the functionalized degree of the benzylammonium structures in AEM while constructing the hydrophilic/hydrophobic phase separation in AEM [25–28].

On the other hand, organic-inorganic hybrid AEMs, which combine the advantage of polymer and inorganic materials, have received much interest in the past few years. A number of inorganic materials, such as SiO₂ [29], TiO₂ [30], ZrO₂ [31], Al₂O₃ [32], montmorillonite [33], nanotubes [34], and layered double hydroxide (LDH) [35], have been used as fillers to improve the ion conductivity, mechanical properties, and chemical stability of AEMs. Especially, in our early reports [30], modifying inorganic materials with cation groups is a logical method to obtain high loading of cationic groups in AEMs as well as maintain the structural stability of AEMs. In general, high ion conductivity of an

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Scheme 1. the porous sandwich structure of QA-LDH/TC-QAPPO composite membrane.

AEM requires high ion exchange capacity (IEC), but the high IEC results in excessive water uptake and swelling ratio [36–39]. Recently, Zhu and coworkers reported that the cation groups modified inorganic materials have ion conduction ability and water absorption capacity. Besides, the cation groups modified inorganic materials are difficult to swell in aqueous solution, exhibiting a potential application in preparing the high-IEC AEM with low swelling ratio [30]. The traditional method of utilizing an inorganic material in AEMs is directly doping it into polymer solution. However, the application of inorganic materials in AEMs is limited by the dispersion of the inorganic materials in polymer matrix. The doping amount of inorganic materials should not exceed 20% of the polymer mass, and even 10% will be detrimental to the ion conductivity of the AEMs [40–42].

In this work, inspired by the sandwich structure, we change the traditional way of doping inorganic materials in AEMs by presenting a porous-sandwich-structure AEM. The porous sandwich structure of AEM is based on quaternary-ammonium-modified LDH (QA-LDH) and triple-cation side chain poly(2,6-dimethyl-1,4-phenylene oxide) (TC-QAPPO) membrane, as shown in Scheme 1. The porous sandwich structure of the QA-LDH/TC-QAPPO composite membranes shows higher IEC values and lower swelling ratio than those of the TC-QAPPO membrane. The QA-LDH layer on the surface of the TC-QAPPO membrane not only possesses an ion conduction ability, but also improve the dimensional stability of the TC-QAPPO membrane. The porous structure of the QA-LDH layer was designed to accelerate the ion conductivity in QA-LDH layer. Atomic force microscope (AFM) was used to investigate the microphase morphology of the TC-QAPPO membrane. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) linear scanning were used to reveal the porous sandwich structure of the composite membranes. The performance of the QA-LDH/TA-QAPPO composite membranes was evaluated, and the results demonstrate that the composite membranes have higher hydroxide conductivity, alkaline stability, and fuel cell performance, better mechanical properties and dimensional stability compared to the TC-QAPPO membrane.

2. Experimental section

2.1. Materials

Iodomethane, γ -aminopropyltriethoxysilane, 1-bromo-2,5-pyrroli-dione (NBS), benzoyl peroxide (BPO), 1,5-dibromopentane, trimethylamine, and N,N,N,N-tetramethyl-1,6-hexanediamine were purchased from J&K and used as received. Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) was purchased from Nanya Chemical Company (Nanjing, China). All the solutions were stored over 4-Å molecular sieves. All other chemicals were purchased from the Beijing Chemical Reagent Store (China) and used without further purification.

2.2. Synthesis of quaternary ammonium modified LDH (QA-LDH)

γ -aminopropyltriethoxysilane (2.336 mL, 0.01 mol) was added to a 100 mL round-bottomed flask, and excessive iodomethane (3 mL) and 2.76 g K_2CO_3 (0.02 mol) were added. Then, the solution was continuously stirred at room temperature for 24 h in a N_2 atmosphere. Subsequently, 100 mL of ethanol was added to the above solution, and the undissolved precipitate was removed. Then the solvent was removed by rotary evaporator to obtain a residue, and the residue was washed with ethylether for three times to get a yellow liquid. Then the liquid was dried in a vacuum oven at 60 °C for 12 h to obtain N, N, N-trimethylpropyltriethoxysilane ammonium chloride (TMPSA). The structure of the TMPSA was confirmed by 1H NMR as shown in Fig. S1.

The synthesis of hexagonal Mg-Al-LDH was according to the early reports [43,44], the hexagonal Mg-Al-LDH nanoplatelets with an average particle size of 50 nm were used to modify with the TMPSA (as shown in Fig S2). Typically, Mg-Al-LDH (2 g) was added to an ethanol solution under magnetic stirring. After the LDH was homogeneously dispersed into the solution, 0.6 g of TMPSA was added, and then the solution was refluxed for 6 h at 110 °C. Subsequently, a white solid was obtained by centrifuging the solution, and the solid was carefully washed three times by ethanol. Finally, the solid was dried in an oven at 50 °C to obtain QA-LDH. The structure of QA-LDH was confirmed by TEM, TGA, and XRD, which are shown in Fig. S2, Fig. S3, and Fig. S4.

2.3. Synthesis of 1-(N', N'-dimethylamino)–6, 11-(N, N, N-trimethylammonium) undecane bromide

Synthesis of (5-bromopentyl) trimethylammonium bromide: 1, 5-dibromopentane (13.62 mL, 0.1 mol) was dissolved in 120 mL tetrahydrofuran, and then the excessive trimethylamine gas was slowly injected into the solution for 3 h at room temperature. The solution was stirred at room temperature for additional 7 h, and a white precipitate was observed during the reaction. Finally, the white precipitate of (5-bromopentyl) trimethylammonium bromide was obtained by filtration and purified by ethyl acetate for three times with a yield of 73%. 1H NMR spectrum of the precipitate is shown in Fig. S5.

N, N, N', N'-tetramethyl-1, 6-hexanediamine (10.75 mL, 0.05 mol) was added to the 50 mL acetonitrile in a three-necked flask. Subsequently, 14.45 g of (5-bromopentyl) trimethylammonium bromide was dissolved in 60 mL acetonitrile, and then dropped into the three-necked flask. Subsequently, the reaction solution was stirred at 40 °C for 24 h. Whereafter, the solvent in solution was removed by rotary evaporators, and then the residual was purified by hexane for three times to remove excessive diamine. Finally, a viscous white precipitate of 1-(N', N'-dimethylamino)–6, 11-(N, N, N-trimethylammonium) undecane bromide was obtained with a yield of 61%. The structure of the precipitate was confirmed by 1H NMR as shown in Fig. 1(b).

2.4. Polymer synthesis

The synthesis of brominated PPO (BPPO) was presented in our previous work [30,45]. The degree of bromination (DB) is 40% at the benzyl position, which was determined by 1H NMR as shown in Fig. 1(a). The BPPO (0.7 g, 4.63 mmol) was dissolved in N, N-dimethylformamide (DMF) at room temperature. Then 1-(N', N'-dimethylamino)-6, 11-(N, N, N-trimethylammonium) undecane bromide (0.48 g, 1.04 mmol) was dissolved in DMF solution and added into BPPO solution. Subsequently, the mixed solution was heated at 65 °C for 96 h. After the reaction, the solution was poured into deionized water to precipitate the polymer, and the polymer was washed by deionized water for three times. A yellow solid was obtained after the polymer was dried in an oven. Finally, the solid was dissolved in DMF again, and the solution was cast on a flat glass plate to obtain triple-cation side chain PPO membrane (TC-QAPPO).

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