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Anion-exchange membranes derived from quaternized polysulfone and exfoliated layered double hydroxide for fuel cells

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ABSTRACT

Layered double hydroxides (LDH) are prepared by controlling urea assisted homogeneous precipitation conditions. Morphology and crystallinity of LDHs are confirmed by X-ray diffraction and scanning electron microscope. After LDHs are incorporated into quaternized polysulfone membranes, transmission electron microscope is used to observe the exfoliated morphology of LDH sheets in the membranes. The properties of the nanocomposite membranes, including water uptake, swelling ratio, mechanical property and ionic conductivity are investigated. The nanocomposite membrane containing 5% LDH sheets shows more balanced performances, exhibiting an ionic conductivity of 2.36×10^{-2} S cm^{-1} at 60 °C.

1. Introduction

As a kind of clean and highly efficient energy conversion devices, proton exchange membrane fuel cells are considered as promising candidates for stationary and mobile power applications. However, their wide applications are still retarded by the high cost and insufficient durability after research efforts of several decades [1]. Therefore, anion-exchange membrane (AEM) fuel cells are suggested because of their potential advantages such as faster electro-kinetics, enhanced material stability, and broader choice of fuels [2]. Furthermore, many efforts have been focused on searching materials of AEM and catalyst, membrane-electrode assembly (MEA) fabrication strategies, and cell operational technologies for AEM fuel cells [3]. Among them, studies on AEMs with high-performance have attracted considerable attention.

In the past several years, various AEM materials have been explored, including quaternized poly(ether ether ketone) [4,5], quaternized poly(sulfone) [6–8], imidazolium-functionalized poly (ether sulfone) [9], quaternized poly(ether-imide) [10], quaternized polybutadiene-*b*-poly(4-methylstyrene) [11], quaternized poly(2,6-dimethyl-1,4-phenylene oxide) [12–14], quaternized copoly(arylene ether sulfone)s [15–17], quaternized poly(aryl ether oxadiazole) [18], quaternized poly(tetraphenyl ether ketone sulfone) [19], quaternized poly(arylene ether ketone) [20], poly(arylene ether)s containing quaternary ammonium-substituted fluorene groups [21], quaternary phosphonium-functionalized poly(sulfone) [22], guanidinium-functionalized poly(2,6-dimethyl-1,4-phenylene oxide) [23], phenylguanidinium-functionalized perfluorinated polymer [24], permethyl cobaltocenium functionalized poly(sulfone) [25], modified commercial polymers by introduction of hydrophilic additives [26–30], grafting [31,32], reinforcement [33] and semi-interpenetrating polymer network [34]. The most extensively studied AEMs are based on homogeneous polymers, but the AEMs based on composite materials containing exfoliated nano-sheets are still rare.

Layered double hydroxides (LDH) are very stable under alkaline conditions because they are made in NaOH solution. Generally, LDH is composed of positively charged metal hydroxide sheets and interlayer anions between sheets, where interlayer anions can be exchanged. The ionic conductivity of LDHs can achieve the order of 10^{-3} S/cm [35]. As a consequence, LDH is fairly suitable for applications in AEMs.

Herein, Mg-Al based LDHs were synthesized in-house and were mixed with chloromethylated polysulfone (CMPSF) in dimethylacetamide (DMAc) to afford casting solutions. Thereafter, the nanocomposite AEMs based on quaternized polysulfone (QPSF) and exfoliated LDH sheets were fabricated and the effect of LDHs on the properties of nanocomposite AEMs was thoroughly elucidated.

2. Experimental

2.1. Chloromethylation of polysulfone

Polysulfone was chloromethylated using chloromethyl ether according to our previous study [29]. A typical procedure is as follows: 11 g polysulfone (Udel P3500, Solvay) was dissolved in 300 mL dichlor-

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omethane and then treated with 16 mL chloromethyl ether in the presence of 3 mL anhydrous tin chloride at 30 °C for 30 min to generate the chloromethylated polysulfone (CMPSF). At last, the mixture was precipitated in 3 L ethanol, followed by filtration, washing with water and evaporation.

2.2. Synthesis of LDH

LDH was prepared by controlling urea assisted homogeneous precipitation conditions [35]. 0.02 mol $Mg(NO_3)_2{\cdot}6H_2O$ and 0.01 mol $Al(NO_3)_3{\cdot}9H_2O$ with 0.30 mol urea were dissolved in 300 mL deionized water. The obtained clear solution was then transferred into a Teflon-lined autoclave without excluding CO_2 in the reaction mixture, sealed and kept at 95 °C for 24 h. After the reaction, the precipitate was recovered by centrifugation, followed by washing with deionized water for three times and with acetone. The sample was then dried in oven at 80 °C overnight.

2.3. Preparation of QPSF membrane and QPSF/ exfoliated LDH composite membranes

The QPSF membrane was fabricated by solution casting and the process was as follows. At first, the CMPSF was dissolved in dimethylacetamide (DMAc) and stirred to obtain a 15% w/v solution. Before casting, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was added into the CMPSF/DMAc solution as crosslinking agent (0.3 mL/10 g casting solution) to trigger partial crosslinking in membranes. Then the film was dried *in vacuo* at 80 °C for 24 h. The resultant membrane was immersed into 30 wt% trimethylamine (TMA) solution for 24 h to induce quaternary ammonium groups into the membrane. Thereafter, the membrane was put into 1 M KOH solution for 24 h, and the alkaline QPSF membrane was obtained. At last, the alkaline QPSF membrane was washed several times with distilled water, and naturally dried under ambient environment to avoid great shrinkage upnon water losing.

The QPSF composite membranes were also fabricated by solution casting. Firstly, required amount of dried LDH powder was dispersed in DMAc, and was vigorously stirred at room temperature for 48 h to form 2 wt% suspension. Then required amounts of CMPSF and DMAc were added in the prepared suspension to afford a 15% w/v solution. The formed dispersion was stirred at room temperature for at least 3 days. After ultrasonication for 1 h, the solution was dropped with TMEDA (0.3 mL/10 g casting solution) and vigorously stirred for 10 min. Then it was spread on a glass plate with a glass knife. The film was dried *in vacuo* at 80 °C for 24 h. The obtained composite membrane was sequentially treated with TMA, KOH solution and distilled water. The resulting composite membrane was designated as QPSF/ x% LDH membrane, where x was the content of LDH.

2.4. Structure characterizations

The FTIR spectra of samples were recorded using a VERTEX70 spectrometer. X-ray diffractometer (X'Pert PRO) was adopted to determine the change in d-spacing of LDH crystal. Cu Kα (λ=1.54 Å) was used as an the X-ray source at d-generator voltage of 45 kV and current of 80 mA. Samples were scanned in 2θ ranges from 5° to 60°, in steps of 0.02° and counting time 2 s per step. The surface of samples was examined through a scanning electron microscope (SEM, JEOL JSM-6510). After the sample was dried, it was vacuum-deposited with a thin Au film for the SEM examination. The morphology of samples was also examined through a transmission electron microscope (TEM, Tecnai G2 20). The dyed sample was embedded in epoxy resin and sectioned using a microtome to yield a 100 nm thick sample which was placed on copper grids for TEM images.

2.5. Water uptake

All membranes were vacuum dried at 100 °C before water uptake testing. Then the AEMs were soaked in deionized water for 24 h at a certain temperature. Weights of dry and wet membranes were measured. The water uptake content was calculated by

$$\text{uptakecontent}(\%) = \frac{\omega wet - \omega dry}{\omega dry} \times 100 \tag{1}$$

where ω_{dry} and ω_{wet} are the masses of dried and wet samples, respectively.

The length of dry and wet samples were measured. The swelling ratio was the average of the two measurements with an error within ± 3.0% and calculated from the length of films by

$$\text{swellingratio}(\%) = \frac{lwet - ldry}{ldry} \times 100 \tag{2}$$

where l_{dry} and l_{wet} are the lengths of dry and wet samples, respectively.

2.6. Mechanical properties

Tensile strength was measured by using INSTRON WN5566 Mechanical Testing Machine. The membrane samples were cut into 0.5 cm×5.0 cm and humidified in 100% relative humidity (RH) for 24 h at room temperature before testing. The samples were examined at an elongation rate of 10 mm min^{-1}. The tensile strength was calculated with the following equation:

$$\text{Tensile strength}=\frac{\text{Maximumload}}{\text{Crosssectionarea}}\text{Nmm}^{-2} \tag{3}$$

2.7. Hydroxide ion conductivity

Ion conductivity (σ) of the membranes was measured by two-probe AC method from 1 Hz to 500 kHz and 10 mV AC perturbation on an Autolab work station. A sample with size of 15 mm×15 mm was placed in an open, temperature controlled cell where it was clamped between two platinum electrodes. Specimens were soaked in deionized water at least 48 h prior to the test. The impedance measurements were performed in water with 100% relative humidity (RH) at desired temperature. The σ of the membranes in the transverse direction was calculated from the impedance data, using the formula:

$$\sigma = \frac{d}{R{\bullet}A} \tag{4}$$

where d and A are the thickness and face area of the sample, respectively. R is derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Z axis.

3. Results and discussion

3.1. LDH characterization

The XRD pattern of LDH was presented in Fig. 1. Strong diffraction peaks suggested the highly crystalline nature of LDH. The peaks of 2θ-angle values at 11.16°, 22.61° and 34.32° could be attributed to the basal, second and third-order reflections, respectively. Furthermore, as shown in Fig. 2, the typical plate-like morphology of LDH could be observed in the SEM image. These results were consistent with the literature [35], indicating the successful synthesis of LDH.

3.2. Morphology and structure of composite membranes

Fig. 3 displayed Tyndall effect of 2 wt% of LDH suspension in DMAc without CMPSF, Tyndall effect of casting solution for CMPSF/