



Development of acid block anion exchange membrane by structure design and its possible application in waste acid recovery



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ABSTRACT

Nowadays, excess quantities of industrial waste acid with low concentration have become not only a serious threat to environment but also a huge resource waste. Electrodialysis (ED) should have played important roles therein. However, the substantial proton leakage of anion exchange membrane (AEM) seriously deteriorates its work performances. In this report, the water uptake of AEM is controlled for alleviating the problem by material selection, for example, hydrophobic skeleton and weakly basic anion exchange groups. Of note, two kinds of membrane structures are designed and investigated. One is the semi-interpenetrating network which is achieved by blending PVDF with DMAEMA and DVB copolymer, the other is a so-called microphase-separated structure which is driven by the polarity difference of segments of the side-chain-type membrane material, PVDF-g-PDMAEMA. Series of electrodialysis experiments confirm that the as-prepared AEMs do exhibit remarkable acid block property. In particular, PVDF-g-PDMAEMA AEM displays more outstanding comprehensive properties, such as area electrical resistance, anti-swelling and limiting current densities. Based on comparison of results achieved in electrochemical characterizations, morphology observations and measurements of water uptake and acid adsorption, it is concluded that the microphase separation of the hydrophilic and hydrophobic segments contributes to the formation of ion nanochannels and then induces some consequential confinement effects.

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1. Introduction

As is well known to all, excess quantities of waste acid with low concentration are produced during industrial production, for example, more than 25 million tons per year in China according to a roughly estimation [1]. Nowadays, many techniques have been put forward to treat and recover the waste acid [2]. Among them, diffusion dialysis (DD) has been widely regarded as a cost-effective, low-energy-consuming and environmentally friendly manner for the recovery of waste acid and received extensive applications [3]. However, its limitations are also obvious. Above all, as a spontaneous separation process driven by concentration gradient, DD generally displays a relatively low processing capability and efficiency, especially at low waste acid concentration [4]. Besides, a large amount of water is required to accept acids during DD process and then results in some problems, such as consumption of plenty of purified water and low concentration of recovered acids, which has nearly no immediate engineering significance [5].

As a result of the directional migration of ions driven by electric field, electrodialysis (ED) can well circumvent the above problems encountered in DD and should have played important roles in the recovery and concentration of waste acid. However, a lot of practices have shown that the proton leakage of anion exchange membrane (AEM) seriously deteriorates the ED process and even results in failure to recovering acid with a relatively high concentration [6]. Required by these, a substantial effort has been focused on the exploration of proton transport behavior in AEM and development of the acid block AEM.

Relevant researches have concluded that proton mobility is an order of magnitude higher than those of other cations in aqueous solution via some special transport mechanisms, such as Vehicle mechanism and Grotthuss mechanism. For the former protonated water forms clusters and the proton moves through the medium as a water cluster by molecular diffusion, while for the latter protons move from oxygen to oxygen by simultaneously breaking and forming hydrogen bonds [7]. It can be seen clearly that water plays an important role in the proton transport whatever its involvement may have been. Therefore, the moderate reduction of proton leakage has been accomplished by diminishing water uptake of AEM,

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for instance, the adoption of weakly dissociated anion exchange groups [8], the introduction of hydrophobic groups [9] and the enhancement of crosslinking degree [10]. However, the relevant results also indicated that the achievement in acid block property was often in the sacrifice of membrane conductivity. For example, Zheng and Barber copolymerized ethylenically unsaturated aliphatic or aromatic tertiary amine monomer with vinylbenzyl chloride and other crosslinking monomer to prepare AEM [11]. Although the proton leakage was reduced, the membrane electrical resistance increased by several times when compared to those of the conventional ones. On the other hand, it has been noticed that the proton leakage of some commercial AEMs, even specially being manufactured for restraining H^+ transport, usually becomes serious with the increase of acid concentration [12]. Pourcelly's kinetic study on electrotransport of HCl in AEM has pointed out the rate constant of the penetration of anions decreased while that of proton remained practically constant as the acid concentration increased in the aqueous solution [13]. Therefore, it is necessary to further facilitate anion transport in AEM at the same time of inhibiting proton transport. As known to all, a most-straightforward approach to strengthen Donnan exclusion for protons and simultaneously facilitate the transport of anions is to increase the corresponding ion exchange capacity (IEC). However, a higher IEC usually increases water uptake and leads to an excess swelling, which must be detrimental to acid block.

Recent studies on membranes for fuel cells have confirmed many times that the transport of counter-ions can be facilitated in the ion nanochannels induced by microphase separation because of the simultaneous improvements of their mobility and concentration therein [14,15]. Moreover, it is reasonable to hypothesize that relatively high local concentration of the fixed charges due to the confinement effect in nanochannels will be favor to enhance the Donnan exclusion and then retard the transport of co-ions, namely protons. Therefore, the formation of so-called microphase-separated morphology is expected to break through the bottleneck problems encountered in the preparation of acid block AEM.

In this report, we attempted to endow the acid block property to AEM via the adjustment of membrane morphology, namely, formation of a microphase-separated morphology. Herein, PVDF was chosen as the backbone of the synthesized membrane material in view of its hydrophobicity and stability in acidic environment. In order to reduce water sorption of the AEM, 2-(N,N-dimethylamino) ethyl methacrylate (DMAEMA), an aliphatic tertiary amine monomer, was selected as grafting side chains. Accordingly, it can be expected that a microphase separation would be driven by the polarity difference between the hydrophilic and hydrophobic segments during the membrane formation. For comparison, another AEM with similar chemical composition but different membrane morphology, a semi-interpenetrating network, was also prepared and investigated in this work. Hopefully, a new way may be opened up for the preparation of acid block AEM with excellent comprehensive properties.

2. Experimental section

2.1. Materials

PVDF powder (FR904) was purchased from Shanghai 3F New Materials Co., Ltd. DMAEMA (Aladdin reagent company, 98%), was passed through an inhibitor removal column before use. DVB (Aladdin reagent company, 80%) was washed by NaOH solution (3 wt.%) to remove the inhibitor. 2, 2'-azobisisobutyronitrile (AIBN, Aladdin reagent company) was purified by recrystallization. Other reagents, such as N,N-dimethylformamide (DMF), HCl, KOH, NaOH,

KCl, NaCl, H_2SO_4 and ethanol were used as received. Three kinds of typical commercial AEMs, including Qianqiu AEM, Tingrun AEM, and FAB AEM, were selected for comparison. Their basic information can be found in Table 1. In addition, the cation exchange membrane (CEM, FKB, FuMA-Tech GmbH, Germany) was used together in the ED process for acid concentration experiments.

2.2. Preparation of membrane material and membranes

The PVDF-g-PDMAEMA copolymers were synthesized via radical graft copolymerization between alkali-treated PVDF and DMAEMA using AIBN as initiator by means of a modified procedure based on some previous reports [16–18]. A Schematic illustration for the graft copolymer synthesis was illustrated in Fig. 1. Then, a solution composed of PVDF-g-PDMAEMA copolymer (15 wt.%) and DMF was prepared and cast onto a leveled glass plate. At last, the membrane entitled as AEM-1 in this work was fabricated by complete evaporation of the solvent at 60 °C for 24 h. After being activated thoroughly by an immersion into 2 M HCl for more than 24 h, AEM-1 was kept in 0.25 M NaCl solution for the subsequent characterizations.

For comparison, a blend membrane composed of PVDF and the copolymer of DMAEMA and DVB were prepared as follows. According to the composition of AEM-1, a specified amount of PVDF and DMAEMA were dissolved completely in DMF to achieve a 15 wt. % homogeneous solution by continuously stirring under 40 °C for two hours. Then, specified amounts of DVB and AIBN were added. Subsequently, the above solution was stirred at 80 °C for 5 h under nitrogen atmosphere to reach a complete reaction. After film-casting and complete evaporation of solvent at 60 °C for 24 h, a blend AEM entitled as AEM-2 in this work was eventually fabricated. Similar to the case of AEM-1, AEM-2 was also kept in 0.25 M NaCl solution for the subsequent characterizations after being activated by 2 M HCl for more than 24 h.

2.3. Characterization of membrane material and membranes

In order to confirm the successful synthesis of PVDF-g-PDMAEMA, Fourier transform infrared spectra (Nicolet iN10 IR Microscope) and 1H NMR spectra (Bruker AVANCEIII 400 instrument) of the nascent PVDF and the synthesized copolymer were collected and compared. Furthermore, the surface phase behaviors of the as-prepared AEMs were observed by an Environment Control Scanning Probe Microscope (SPM, SII Nanonavi E-Sweep) using the tapping mode with the silicon cantilever (AN-NSC01) under ambient conditions. Besides, small angle X-ray scattering (SAXS) profiles of the AEMs were also recorded using a SAXSess-MC2 X-ray scattering spectrometer (Anton Paar, Austria) at room temperature.

In view of the weak alkalinity of tertiary amine groups existing in the as-prepared AEMs, IECs of membrane samples were measured and compared in different pH environments, including pH = 1, 3 and pure water, by spectrophotometric (SP) method in this work [19]. That was, the number of moles of NO_3^- ions exchanged by Cl^- ions was determined spectrophotometrically using UV-1600PC (Mapada, China) at a wavelength of 210 nm. And then, the IEC value, the ratio of displaced ions to the weight of a dry membrane sample, can be calculated. Moreover, the quantities of ion exchange groups presented in the weakly basic AEMs were confirmed again by means of elemental analysis (EA, Vario EL Cube, Elementar, Germany).

Similarly, AC electrical resistances of membrane samples were measured in a working solution of 0.1 M HCl by means of the impedance measurement using a four-electrode technique. The detailed configuration of the electrochemical cell was described in Fig. 2. As can be seen, the cell was composed of two compartments of equal

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