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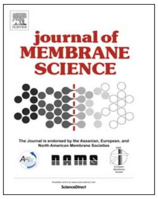

Mussel-inspired sulfonated polydopamine coating on anion exchange membrane for improving permselectivity and anti-fouling property

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ABSTRACT

Anion exchange membranes (AEMs) with high monovalent/multivalent anion perselectivity are essential for wide range applications (e.g., electrodialysis (ED)). In this work, we have proposed a facile surficial adhesive modification process to fabricate a highly permselective AEM for ED application. Firstly, a novel sulfonated dopamine (SDA) adhesive was synthesized, followed by coating this kind of polymer-like adhesive on commercial AEMs under alkaline and aerobic conditions. We have found that the SDA coating can significantly enhance the monovalent permselectivity (Cl^-/SO_4^{2-}), with a permselectivity of 34.02, which is much higher than the corresponding values of dopamine (DA)modified AEM (i.e., 11.59) and of the pristine AEM (i.e., 1.00). In addition, fouling experiments show that the transition time (the point time in fouling experiment when a voltage dramatically increases; that's to say, foulant dramatically occurs) of the optimum membrane is 112 min, indicating the superior anti-fouling property of SDA modified AEM, compared with pristine AEM (76 min). The facile fabrication process and superior performance of modified AEM suggest that as-prepared is potentially applicable in ED for separation of monovalent and multivalent anions.

1. Introduction

The crisis of water shortage has become an important worldwide concern [1,2]. Many strategies have been proposed to relieve the lack of nature water resource. With the advancement in science and technology, membrane separation technology as a novel water treatment technology not only has the function of separation and purification, but also shows the advantages of high efficiency, effective energy saving and short production process. Among which, reverse osmosis (RO) and nanofiltration (NF) are defined as the pressure-driven process [3–5], in which the solution flows directionally under pressure force and the ions with hydrated radius larger than the pore size of membrane will be intercepted while the smaller ones will easily go through the membrane, the diffusion and the electrical exclusion also plays a role in filtration process. Electrodialysis (ED) is a complementary technique in which the electrical driving force is exploited, and has been widely applied for water purification [6–8]. In the ED process, the ions in the solution migrate by using an electrical potential as the driving force, leading to the dilution of diluted compartment and concentration of concentrated compartment [9]. As a key component of ED, AEMs have been developed allowing for its application in the recovery of industrial wastewater, concentration of seawater, brine desalination etc. [9–14]. However, the shortage of monovalent selectivity causes the passing of harmful anions like F^- and NO_3^-, and the simultaneously removal of multivalent anions such as SO_4^{2-}. The residual of F^- and NO_3^- in solution is hazardous to the environment and human body. In addition, the removal of too much SO_4^{2-} will result in the formation of $CaSO_4$ in the concentrated compartment. As a result, the precipitated $CaSO_4$ significantly decreases the performance of the ED process [15].

It is well-known that the selectivity for monovalent anions is mainly through interactions between different anions and membrane properties (exchange groups, compact structure), such as electrostatic and sieving effect, which inhibits the transport of multivalent anions. Thus, polymers (e.g., polystyrene sulfonate) with negative charges have been usually used for surface modification to improve the membrane permselectivity [16–18]. Multilayer deposition of polymers rised in response to the proper time and conditions. Layer-by-layer assembly [19,20] is an effective method to alternately deposit polycations and polyanions onto the surface of membrane. With the accumulation of negative charges, AEMs are expected to an enhanced permselectivity due to the stronger electrostatic repulsion force. However, the tedious preparing process impedes its further application and development, despite the increment of permselectivity with the increasing number of depositions cycles. On the other hand, the stability of interface area of

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Nomenclature

SDA	polysulfonated dopamine
PSDA	polysulfonated dopamine
DA	dopamine
SDBS	sodium dodecyl benzene sulfonate
AEM	anion exchange membrane
CEM	cation exchange membrane
ED	electrodialysis
ATR-FTIR	attenuated total reflectance – Fourier transform Infrared spectroscopy
SEM	scanning electron microscope
IEC	ion exchange capacity
S	the membrane effective area cm^2
U	voltage of the membrane in V
R	resistance of the membrane expressed in $\Omega\ cm^2$
P	permselectivity of Cl^- and SO_4^{2-}

multi-layers may be loose due to the weak binding forces that are involved.

Inspired by the universal adhesion of mussels' protein, Messersmith et al. [21] have found that dopamine can be oxidized in alkaline aqueous solution and forms a polymer-like coating on a variety of materials with great adhesive strength. Many other studies have applied mussel-inspired coating for membrane surface functionalization [22–28]. Yang et al. [29] have fabricated a hydrophilicity-improved membrane for oil-in-water emulsion separation. Jiang et al. [30] modified membrane with dopamine followed with immobilizing poly(N-vinyl pyrrolidone) through strong hydrogen-bond, which effectively improves the membranes of antifouling and antimicrobial property. Lv et al. [31] modified a membrane by co-depositing of polydopamine and polyethylenimine to improve the salt rejection, and resultant membrane shows a good structural stability when immersed in ethanol or for long-term application of nanofiltration. Vaselbehagh et al. [18] coated the AEM with dopamine, leading to the enhanced permselectivity between Cl^- and SO_4^{2-}. Because of the amphotericity of DA with the isoelectric point at pH = 4 [32–34], the PDA layer exhibits negatively charged characteristic during the ED process.

Introducing reverse charges is a commonly-used method to fabricate a monovalent anion selective AEM. Due to the electrostatic repulsion, the modified conventional membrane will perform good monovalent anion selectivity and anti-fouling property [27,35–39]. In this work, we have established a simple and convenient self-adhesion strategy to improve the permselectivity of an AEM. A modified dopamine with sulfonyl groups has been firstly synthesized, followed by depositing it on an AEM to self-polymerize a stable negatively charged coating layer. The performance of modified AEMs has also been investigated by testing the Cl^-/SO_4^{2-} selectivity at constant current in ED. Moreover, the modified AEMs with the stable active layer structure exhibits considerably improved salt rejection.

2. Experimental

2.1. Materials

Both commercial anion exchange membranes AEM-Type I and cation exchange membranes CEM-Type II were purchased from Fujifilm Corp. Japan, and Table 1 shows their parameters. dopamine hydrochloride, 1,3-propanesulfonate and tris (hydroxymethyl) aminomethane (Aladdin industrial Corporation, Shanghai, China), were used as received. Ammonia solution was received from Longshan Chemical Co., Ltd. Inl. Trading Dept. (Hangzhou, China). Sodium dodecyl benzene sulfonate (SDBS) is a model organic foulant commonly used to investigate fouling of AEMs in the ED process and it remains negatively charged over the entire pH range [32]. All the other reagents and solvents were brought from commercial sources and used as received without further purification. Distilled water was used throughout.

2.2. Preparation of sulfonated dopamine

Sulfonated dopamine was synthesized according to Chung's work [40], as shown in Scheme 1. In detail, 1.1376 g (6 mmol) dopamine hydrochloride (DA) was dissolved into150mL ethanol in a 250 mL flask, then416 μL (3 mmol) 28 wt% aqueous ammonia and 799 mg 1,3-propanesulfonate (6.5 mmol) were slowly added. After heating to 50 °C and stirring for 18 h, white precipitate was observed in the bottom of flask. Thereafter, the mixture was filtered, and the resultant precipitate (SDA) was washed with ethanol 3 times, followed by drying under vacuum at 40 °C. ^1H NMR spectra measurement was taken to confirm the chemical structure of SDA (D_2O was employed as the solvent). Both DA and SDA were dried at 25 °C.

Fig. 1 shows ^1H NMR spectra of dopamine and SDA. Five resonances of dopamine protons (d′, e′, f′, g′ and h′) can be observed [41]. The disappeared signals of hydroxy and amidogen protons (reactive hydrogen) can be due to the addition of D_2O, resulting in the vibration between reactive hydrogen and D_2O, and new peak of DOH appeared at about 4.7–4.8. When 1, 3-propanesulfonate was introduced, the signals of homologous protons of the sulfonyl dopamine slightly shifted and the new peaks could be observed. Signal a, signal b and signal c were assigned to the protons of $-CH_2-CH_2-CH_2-SO_3H$, respectively, suggesting the successful introduction of sulfonated groups. The results demonstrate the ring-opening reaction of 1, 3-propanesulfonate and grafting reaction into the amino.

2.3. Modification of AEM

The commercial original AEM was rinsed with NaOH solution (0.2 M) and HCl solution (0.2 M) alternately, to remove the residual impurities absorbed on membrane surface. Parallel experiments were also undertaken with SDA and DA, respectively, for the purpose of comparison. Herein, SDA and DA were dissolved in tris (hydroxymethyl) aminomethane-HCl (Tris-HCl) buffer solutions (pH = 8.5), respectively. Subsequently, for example of dopamine/Tris-HCl solution, the solution was added to a custom-designed experimental setup (see Fig. S1 in Supporting information) assembled with a certain area of pristine AEM and then kept stirring as the set time (0 h, 4 h, 8 h, 12 h, 24 h, and 48 h). At the very beginning, a transparent dopamine/Tris-HCl solution was observed. After stirring for several minutes, the solution became darkish brown, due to the self-formed polydopamine in aerobic and alkaline environment [21]. Meanwhile, a visible black aggregation could be observed in dopamine aqueous solution, indicating the non-uniform polymerization and deposition on the membrane surface. Finally, the surface of DA modified AEM (denoted as DA/AEM) shows the color of black brown. Similarly, SDA modified AEM (denoted as SDA/AEM) was also taken. However, sulfonated dopamine/Tris-HCl solution became transparent without visible aggregation inside, suggestive of the homogeneous coating on surface of membrane. The as-prepared membrane was taken out and thoroughly with pure water, and finally stored in deionized water for use.

Table 1
Characteristics of commercial homogeneous AEM and CEM (commercial data).

Membrane type	Thickness (μm)	Area resistance($\Omega\ cm^2$)	pH stability
AEM-Type I	125	1.3	2–10
CEM-Type II	135	2.7	4–12