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Highly charged hierarchically structured porous anion exchange membranes with excellent performance

Erigene Bakangura, Congliang Cheng, Liang Wu, Yubin He, Xiaolin Ge, Jin Ran, Kamana Emmanuel, Tongwen Xu*

CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, PR China

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ABSTRACT

Fabrication of Porous Anion Exchange Membranes for ion transport and ionic selectivity has gained tremendous attention as a prospect for broad application in separation and energy conversion. In this work, we developed a novel strategy to fabricate highly charged hierarchical porous anion exchange membranes (AEM) with high performance. The membranes were prepared by coupling quaternized poly (2-dimethylaminoethanol-N-2,3-dimethylphenyl oxide) (QDAPPO) and an organosilane ionic liquid (IL). The electrostatic ionic interactions provide the porous system. When applied in acid recovery, the obtained membranes achieved a high separation factor of 86.5 with proton dialysis coefficient of 0.027 m h^{-1} at 25 °C. This unique efficiency is about 4.7 times that of commercial membrane. More interestingly, the strategy presents in this work tackle the great challenge of fabricating highly charged, thinner and dimensional stable AEM.

1. Introduction

The environmental impact of world population growth is diverse because the rapid demand of food, energy and commodities increases the expansion of industries productions which lead to environmental pollution and rapid decline of the natural resources. Major industries such as metal processing, mining, pulp and paper, paintings, agriculture, vehicles, chemical and food, and electrical power plants produce acidic wastewaters contained toxic heavy metals and detrimental chemicals [1–3]. To ensure sustainable human society development, there is an increasing global concern for the wastewaters treatment within industrial production processes [4–6]. Traditional techniques such as neutralization, crystallization, distillation, thermal decomposition and solvent extraction for wastewater treatments [7–10] focus on purification rather than recovery of resources, and therefore loss enormous amount of energy stored in wastewaters while consuming additional external energy for their operating processes. Membrane based technologies like diffusion dialysis, membrane distillation, electrodialysis, microbial desalination cell, reverse electrodialysis that recover resources and/or energy from wastewaters are more promising for wastewater treatments, sustainable and environmental friendly [11–18]. Diffusion dialysis, an attractive and commercial viable technique due to its low cost and requires minimum energy during operations [5,19–21], was selected to investigate the performance of AEMs in this work. It is noteworthy that the major challenges of membrane based techniques for wastewater treatment and acid recovery has been the fabrication of cost-effective anion exchange membranes (AEMs) with optimum desired characteristics including high permeation, high selectivity and long-term stability.

In membrane based gradient techniques for acidic wastewater treatment, AEM should selectively allow the passage of anions across the membrane while limiting the transport of the cations and thus to successfully recover acid, the proton (H^+) should cross the AEM taking advantage of its small radii and high mobility than other cations (i.e. Fe^{2+}, Cr^{2+}, Mn^{2+}). AEMs are usually prepared by attaching cationic groups (i.e. quaternary ammonium (QA), Imidazolium (Im), phosphonium and guanidine) on polymer architectures [22–24]. Compared to their counterpart proton exchange membranes (PEM), the fabrication of high performance AEMs is more challenging because the fundamental characteristics of cationic head groups and the intrinsic nature of anions such as low dissociation, low mobility and various shape compared to cations [25]. Firstly, tailoring microphase separated morphology is much easier in PEM than in AEM because the acidity of anionic functional groups is much higher than the basicity of cationic groups. Secondly, low mobility of anions leads to lower ionic transport and poor selectivity of AEMs [22]. A facile straight forward strategy to increase the ionic transport is via increasing the

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* Corresponding author.
E-mail address: twxu@ustc.edu.cn (T. Xu).

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ion exchange capacity (IEC) which unfortunately is usually associated with excessive membrane swelling and compromise of mechanical properties [26]. Thirdly, flexibility of AEMs becomes low as increasing the IEC in rigid aromatic polymers backbone, especially at low humidity that can make the operation failure or maintenance difficulty [27–30]. In order to increase the ion transport and selectivity while preserving the membrane dimensional integrity, previous works attempted to fabricate AEMs with controlled microphase separated morphologies [31,32] or crosslinking polymer chains to enhance the dimensional stability toward high IEC [28,33–37]. Although these techniques succeed to increase the ionic transport, particularly when external electrical potential is applied for ion transport like in case of electrodialysis, the membrane mass transport is very lower for feasible application in membrane techniques based on concentration gradient like diffusion dialysis. For example, the commercial available DF-120 (a dense AEM with fiber as substrate) has a proton dialysis coefficient (U_{H^+}) of only 0.009 m h^{-1} and selectivity of 18.5 at 25 °C.

To assure the high ion and mass transport of AEMs, porous membranes have been proposed for versatile applications owing to their high surface area responsible to boost the membrane permeability [11,19,38]. Porous asymmetric (Ultra-filtration, UF) membranes prepared via phase inversion routes have been mostly utilized for diffusion dialysis [39,40]. Porous asymmetric AEMs prepared through immersing brominated poly(phenylene oxide) in multisilicon copolymer solution and in tertiary amine solutions for cationic functionalization followed by sol-gel reaction exhibited an improved U_{H^+} value of 0.020–0.025 m h^{-1} and a separation range from 25 to 45 at 25 °C [40]. Very recently, Wang et al. [41,42] reported macroporous asymmetric membrane with high U_{H^+} values prepared via phase inversion of BPPO crosslinked by N,N,-tetramethylethylenediamine (TEMED) or poly(ethyleneimine) (PEI). The TPPO-4h membrane (BPPO crosslinked by TEMED) of 1.43 meq g^{-1} exhibits a high proton dialysis coefficient of 0.043 m h^{-1} and a high separation of 73.8 at 25 °C. Consider the obtained high U_{H^+}, the performance of these membranes were counterbalanced with the diffusion of ferrous ions (Fe^{2+}) which increased as a results of wide pores and high water uptake. Additionally, porous asymmetric (UF) membranes usually have a thick layer (ca. $>300\ \mu m$) responsible for weakening mass transport and sometime lead to operation difficulty. Despite that, fabrication of thin layer porous membranes is still a major challenge limiting the optimization of membrane performance.

In this work, we report a novel strategy to tailor hierarchical mesoporous AEMs (HMPA) with high performance for rapid acid recovery. HMPA takes advantage of the highly charged nanosized pores in gradient structure with a moderate thickness to simultaneously enhance the selectivity and mass transport. To prepare HMPA, poly (2,3-dimethylphenyl-N-(2-hydroxy-N,N-dimethylethanaminium chloride)) or quaternized poly(2-dimethylaminoethanol-N-2,3-dimethylphenyl oxide) (QDAPPO) and 3-methyl-1-(3-(triethoxysilyl) propyl)-1H-imidazolium chloride (Ionic liquid, IL) were covalently crosslinked via sol-gel reaction followed by thermal treatment at high temperature. By contrast to reported works, hierarchical porous membranes for gas separation and responsive membranes have been recently prepared by using template method or immersing IL based membranes into ammonium solutions [43–46]. More interestingly, the strategy presents in this work tackle the great challenge of fabricating highly charged AEM with thin layer and good dimensional stability.

2. Experimental

2.1. Materials

1-(2-(dimethylamino) ethanol (DMAE) was purchased from J&K chemicals Ltd and was used without further purification. Sodium sulfates, sodium chloride, Toluene, ethylacetate, NMP, diethyl ether, were purchased from Shanghai Sino Pham Chemical Reagent Co. Ltd. (P. R. China). Bromomethylated (2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) of 52 bromobenzyl ($–CH_2–Br$) was provided by Tianwei Membrane Corporation Ltd.(Shandong, P. R. China). It was purified before use by dissolving in N-methyl-2-pyrrolidone (NMP), precipitating in deionized water, and drying in 30 °C vacuum oven. Diionized water was used throughout the experiments.

2.2. Synthesis of quaternized poly(2-dimethylaminoethanol-N-2,3-dimethylphenyl oxide) (QDAPPO)

1.104 g (4.2 mmol) of 1-(2-(dimethylamino) ethanol (DMAE) was all at once added to a solution of 2 g (5.56 mmol) BPPO in 30 mL of NMP into 50 mL bottom flask. The mixture was stirred at room temperature for 16 h and then poured in toluene to precipitate the product. The precipitate was filtered, washed several times by ethylacetate and final by diethylether and then dried at 40 °C for 48 h in air circulating oven. The completed substituted polymer was confirmed by ^1H NMR as determined from integration ratio of methylene and aromatic protons.

2.3. Synthesis of 3-methyl-1-(3-(triethoxysilyl)propyl)-1H-imidazolium chloride (Ion liquid, IL)

IL was prepared by following the method reported elsewhere [47] and described as follows. 1-Methylimidazole (2.060 g, 25.085 mmol) and (3-chloropropyl) triethoxysilane (6.042 g, 25.091 mmol) dissolved in toluene (20 mL) were refluxed for three days. Immediately after stop stirring and heating, viscous oil decant at the bottom of flask and then the toluene can easily removed by pouring. The obtained viscous oil was washed several times by toluene and diethylether anhydrous to remove unreacted reagents. The solvents were completely removed under reduced pressure and drying for 24 h at 60 °C to afford the title product as viscous oil. The IL is soluble in other polar solvent (i.e. DMSO, Acetonitrile). The chemical structure was confirmed by ^1H and ^{13}C NMR (see Fig. S1 and S2, ESI).

2.4. Membrane preparation

1 g of polymer (QDAPPO) was dissolved in 10 mL of DMSO. Appropriate amount of IL (10%, 20%, 30% and 40% wt of QDAPPO) was added to the polymer solution at room temperature and allow to mixture for 30 min prior to subsequently add TEOS (1:1 ratio corresponding to loaded IL) and 2–3 drop of 1 M HCl in DMSO. The above mixture was stirred at 45 °C for 24 h, casted on glass plate and dried at 60 °C for 12 h to remove the solvent. The membrane was peered off the glass plate and thermally treated from 70, 90, 110 and 120 °C (1 h at each temperature) and at 130 °C for 3 h to assure the complete sol-gel reaction and remove of tapped solvent. The obtained thermal treated membrane was immersed in water for 24 h and then in 2 M NaCl to convert the Br- ions into Cl^- ions. The membranes were noted as QDA-ILx where x presents the percentage ratio of IL and TEOS to QDAPPO.

2.5. Polymer and membrane characterization

Nuclear Magnetic resonance (NMR) spectra were recorded on a Bruker AVANCEII spectrometer with TMS as an internal standard. Scanning electron microscopy (SEM) images were observed by using scanning electron microscopy (XT30ESEM-TM-PHILIP). The samples for SEM (for cross-sectional) were prepared by freezing and breaking samples in nitrogen liquid whereas the sample for surface imaging were prepared by directly cutting a clean membrane into small pieces. Thermal behavior was carried out on NETZSCH STA 449F3 thermogravimetric analyzer (TGA). Samples,