Tuning electrodialytic transport properties of heterogeneous cation exchange membrane by the addition of charged microspheres

CrossMark

Bei-bei Wang, Meng Wang *, Kai-kai Wang, Yu-xiang Jia

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Qingdao, 266100, China
College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, 266100, China

HIGHLIGHTS

- Cation exchangers with small size and narrow size distribution were fabricated.
- Charged microspheres were used as additives for preparing heterogeneous membranes.
- A method for improving heterogeneous membrane properties was proposed.

ARTICLE INFO

ABSTRACT

In this study, the sulfonated polystyrene microspheres (MPs) which embraced much smaller particle size and narrower size distribution than those of conventional resin powders (RPs) were synthesized and employed as ion-exchangers exclusively or additives to prepare heterogeneous cation exchange membrane (CEM). Thereupon the effects of the incorporation of the charged MPs on the properties of heterogeneous CEM were investigated. Firstly, the morphologies of the synthesized MPs and the corresponding CEMs were examined by SEM observation. Then, the membrane properties were comprehensively evaluated by the measurements of ion exchange capacity, water uptake, transport number, salt permeability coefficient, membrane resistance, limiting current density and so on. Moreover, surface homogeneity was explored by means of the chronopotentiometric analyses. The experimental results showed that the required amount of RPs can be reduced significantly by adding moderate MPs while achieving the similar or even higher membrane conductivity at almost no sacrifice of other membrane properties. Moreover, the surface homogeneity was also enhanced, which can effectively alleviate the concentration polarization behavior at the membrane/solution interface. All these experimental results indicated that the added MPs can make good connections among the conductive regions both in membrane body and at membrane surface and then facilitate ion transport.

© 2015 Published by Elsevier B.V.

1. Introduction

Heterogeneous ion exchange membrane (IEM) which consists of micron-sized ion exchange particles and neutral polymer matrix was successfully prepared just after ion exchange resins were developed in the 1930s [1–2]. Although being inferior to homogeneous IEM in electrochemical properties, heterogeneous IEM is still widely used due to its typical advantages, such as low cost, easy manufacture, favorable oxidative stability, good mechanical strengths and dimensional stability [3]. Especially in the low value-added industrial electrodialysis processes, such as water recovery and wastewater reclamation, the membrane price and membrane mechanical stability often arouse more interests. Therefore, both academia and industry have paid more attention to

improve the work performance of heterogeneous IEM, for examples, exploring the effects of the surface heterogeneity on the electrochemical properties of IEM [4–5], putting forward novel membrane-fabricating methods [6–9], and developing new membrane materials for binder, ion exchanger and additive [10–16].

Therein, how to decrease membrane resistance seems to be a problem that has to be dealt with during the preparation of heterogeneous IEM. It is well known that the membrane conductivity can be effectively enhanced by increasing the content of the ion exchangers. However, this often results in a devastating loss in membrane strength and shape stability. Hence, some endeavors have been made to break through the trade-off between the above membrane properties. For instance, Oren et al. innovatively prepared a heterogeneous membrane with a highly ordered distribution of ion exchange particles by the aid of ac electric field [17]. Their experimental results showed that the ordered particle chains can facilitate the ion transport and then reduce the required amount of ion exchange material in membrane

* Corresponding author at: Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Qingdao, 266100, China.
E-mail address: wangmeng@ouc.edu.cn (M. Wang).

preparation. Accordingly, not only was the mechanical property improved but also the membrane conductivity was kept or even increased. However, it can be anticipated that the reduction in ion-exchange materials and their ordered arrangement in membrane body may result in an increase of the inert area at membrane surface. Thus, this must deteriorate the surface homogeneity and further induce concentration polarization at the membrane/solution interface, which will decrease the limiting current density in a practical electrodialysis process. Moreover, Vyas et al. prepared heterogeneous IEM by using the conventional resin particles with a relatively small size and observed somewhat decrease of membrane resistance [18–19]. However, it was worth noting that the reduction in resin particle size was limited because of some inherent technical restrictions which must be faced during the traditional grinding process, such as the highly crosslinking structure of the resin particles and the aggregation of resin powders. Hence, it seems to be unavoidable for the conventional preparation of heterogeneous IEM that the numerous inert regions were formed among the resin particle aggregates.

In this study, the sulfonated polystyrene MPs which embraced much smaller size and narrower size distribution than those of the commercial RPs were synthesized and used for the preparation of a heterogeneous cation exchange membrane (CEM). Hopefully, the charged MPs can be effectively filled into the inert regions which were formed during the random accumulation of RPs and then made good connections among resin particle aggregates. Accordingly, a facilitated ion transport could be expected. In particular, the MPs which embraced a lower exchange capacity than that of the commercial RPs were selected deliberately in this study in order to distinguish the size effects of MPs on electrodialytic transport properties of the heterogeneous CEM, especially the membrane conductivity and surface homogeneity.

2. Experimental

2.1. Materials

Styrene (St, CP, Sino-pharm Chemical Reagent Co., Ltd) and divinyl benzene (DVB, AR, Xi-ya Reagent Research Center) were purified before being used. Azodiisobutyronitrile (AIBN, CP, SHANPU Chemical Reagent Co., Ltd) was recrystallized by means of the common procedures. Polyvinylpyrrolidone (PVP, K-value: 27.0-32.4, Sino-pharm Chemical Reagent Co., Ltd), polyvinyl chloride (PVC, K-value: 65-68, Aladdin Chemistry Co., Ltd), tetrahydrofuran (THF, AR, Fu-yu Chemical Reagent Co., Ltd), anhydrous ethanol, concentrated sulfuric acid and sodium chloride were commercial products and used directly without further purification. A noteworthy fact is that the RPs employed in this work was no other than the ion-exchangers used in the normal industrial production of heterogeneous IEMs, a conventional sulfonated copolymer of St and DVB. Deionized water was used throughout this study.

2.2. Preparation

2.2.1. The preparation of MP and its post-sulfonation

A typical dispersion polymerization process with a weight ratio of [St]:[DVB]:[PVP]:[AIBN] = 100:1:10:3 in anhydrous ethanol was carried out at 70 °C in nitrogen for 24 h along with a continuous stirring at a rate of 270 r/min. During the process, the MPs were formed gradually and kept growing while suspending in anhydrous ethanol. After being washed with anhydrous ethanol several times, the MPs were dried thoroughly in vacuum at room temperature. Subsequently, the MPs were sulfonated by the concentrated sulfuric acid at 50 °C in nitrogen for 4 h. At last, the obtained sulfonated MPs were washed repeatedly with deionized water till neutrality.

2.2.2. The fabrication of heterogeneous CEMs

In this study, the heterogeneous CEMs were prepared by solution casting technique using THF as solvent and PVC as binder. The

preparation scheme was schematically demonstrated in Fig. 1. Above all, all the membrane materials were dried thoroughly at 50 °C for more than 48 h. Then, a certain amount of PVC was dissolved in THF along with continuous stirring. Subsequently, the synthesized MPs and/or the commercial RPs which have been dispersed in THF in advance were added proportionally into the above PVC/THF solution. In order to achieve a good dispersion of MPs and RPs in THF, the above casting solution were further sonicated before being poured on a glass plate for film formation. The compositions of the investigated membrane samples and their corresponding thicknesses were demonstrated in Table 1. After a solvent evaporation at an ambient temperature for more than 48 h, the membrane was immersed in the distilled water to remove the residual THF again. At last, the membranes were kept in NaCl solution for further examinations.

2.3. Characterization

2.3.1. Morphological observation

The synthesized MPs and the corresponding membranes were observed by scanning electron microscope (Field Emission Scanning Electron Microscope, Hitachi S-4800). Before the examination, the membrane samples were kept in vacuum at room temperature for several days to remove water gradually and then sputtered with gold. The particle size distribution was analyzed in a statistical way with the help of software (Nano Measurer 1.2.5) on the basis of the SEM observation. Of particular note was that the particle sizes were measured in the same direction, especially for the commercial resin particles. In addition, the thickness of the prepared membrane was measured in dry form by a digital display microcalliper (0–25 mm/0.001 mm, Cheng-du San-he Measure Tools Co., Ltd.).

2.3.2. Water uptake (WU)

After removing excess sodium chloride by a thorough immersion in pure water, the membrane samples were wiped quickly and carefully with a filter paper to remove the free water attached to membrane surface and weighed immediately for obtaining the wet weight (m_{wet}). Then, the membrane samples were dried in vacuum at 40 °C until reaching a constant weight, i.e. the dry weight (m_{dry}). The water uptake is defined as the ratio of the difference between wet weight and dry weight to the dry weight.

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\% \tag{1}$$

2.3.3. Ion exchange capacity (IEC)

Firstly, all the membrane samples were adequately equilibrated in 1 M HCl to achieve the H-type exchange groups. Then, they were washed thoroughly with deionized water until reaching neutrality. Subsequently, the samples were immersed in 1 M NaCl solution for 24 h and washed thoroughly with deionized water again. Finally, the amount of hydrogen ions exchanged by sodium ions was determined by titration using 0.01 M NaOH as titrant and phenolphthalein as indicator. Moreover, similar to the WU measurement, the dry weight of membrane samples can also be obtained. Hence, the IEC can be calculated as the ratio of total charge (α, mmol) to its dry weight (m_{dry}):

$$IEC = \frac{\alpha}{m_{dry}} \tag{2}$$

2.3.4. The transport number

The investigated membrane was fastened between two compartments into which two NaCl solutions with different concentration ($C_1 = 0.5$ M and $C_2 = 0.1$ M) were fed, respectively. Then, the membrane potential (E_{mem}) can be read from a multimeter by aid of a couple