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The improvement of comprehensive transport properties to heterogeneous cation exchange membrane by the covalent immobilization of polyethyleneimine

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A B S T R A C T

In this work, a three-step modification scheme was devised to covalently immobilize the polyethyleneimine (PEI) multilayers for improving the comprehensive transport properties of a heterogeneous cation exchange membrane (CEM), including the grafting of carboxyl groups, the PEI immobilization by amidation reaction and glutaraldehyde-induced PEI multilayers deposition. Firstly, the changes in surface chemical composition and morphology after modification were investigated by attenuated total reflection-Fourier transform infrared spectroscopy and scanning probe microscope. Then, the membrane properties corresponding to different modification steps were comprehensively evaluated by the measurements of ion exchange capacity, water content, salt permeability coefficient, membrane electrical resistance, limiting current density and so on. Especially, in order to simulate the possible applications in the reclamation of the industrial effluents from the hydrometallurgy processes and the comprehensive utilization of seawater, respectively, some electrodialysis experiments for H^+/Zn^{2+} system and Na^+/Mg^{2+} system were performed to estimate and compare the monovalent selectivity of the membrane samples. Furthermore, the alteration of surface heterogeneity after modification was explored by current–voltage curves and chronopotentiometric curves. The experimental results showed that the modification scheme proposed in this work can make significant contributions to a heterogeneous CEM, such as the endowment of monovalent cation permselectivity, the improvement of surface homogeneity for ameliorating concentration polarization, the ability to impeding salt diffusion and even the possibility of extending membrane life-span.

1. Introduction

It is well known that the electrodialysis technology specializes in the common desalination and concentration of electrolyte solutions. As the core of an electrodialysis process, ion exchange membrane (IEM) has made great progress in its comprehensive properties over past several decades and even some of them have attained almost limiting values [1]. However, the relevant applications, such as the reclamation of the effluents produced from the hydrometallurgy or electroplating processes and the comprehensive utilization of sea water, thirst for the cation exchange membrane (CEM) with high proton leakage or selectivity to monovalent cations. Up to now, much attention has been attracted whether from academic or practical points of views. Several approaches have been proposed to adjust the affinity of relevant cations with the membrane or/and their migration speeds in the membrane phase, including the alteration of the membrane morphology [2–4], manipulation of the membrane hydrophobicity and hydrophilicity [5,6], the employment of special ion exchange groups [7], and the formation of a thin cationic or neutral layer on membrane surface. In view of the perfect properties of the current commercial membranes and the advantage of the obtained monovalent selectivity, the last one is often employed to prepare monovalent perm-selective CEMs.

According to the published reports, the modification materials are mainly focused on the some polyelectrolytes, such as polyethyleneimine (PEI), polyaniline [8–14], polypyrrole [15,16], polyallylamine [17,18], chitosan and its derivatives [19–22]. Thereinto, PEI is particularly notable due to its relevant characteristics, including water solubility, high reaction activity and high content of amine

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groups. For example, Amara, etc. used PEI to endow monovalent selectivity to CEM by immersion, electrodeposition, and electroadsorption method [23,24]. However, the detachment of the modified layer from base membrane seems to be unavoidable because only the relatively weak interactions (mainly electrostatic attraction) exist between them [25]. Hence, the studies on the covalent grafting of a modified layer on the membrane surfaces become very important. Vallois et al. deposited a PEI layer on the membrane surface by the plasma polymerization technique involving an ethylene/ammonia monomers mixture [26]. Takata et al. immobilized a PEI layer on membrane surface by means of the formation of the sulfonyl–amide bond [27]. Although series of relatively good experimental results were obtained, there is plenty of room for improvement. For example, the former always raised relatively high demands for equipment and manipulation. But for the latter, the modification began with the precursor of a CEM and was performed with a great sacrifice of ion exchange capacity. This will certainly result in a high electrical resistance and low current efficiency of the modified membranes. Thus, there is an urgent need to develop novel methodology for the preparation of monovalent selective CEMs with the advantages such as simple operation, high efficiency and low cost.

On the other hand, as far as we know, the heterogeneous IEMs was still widely applied in the industrial electrodialysis processes (ED), especially for water recovery and wastewater reclamation, due to its typical advantages such as low cost, easy manufacturing, favorable oxidative stability, good mechanical strengths and good dimensional stability. Accordingly, many attempts have also been made for improving selective separation properties of heterogeneous CEMs between mono-valent and multi-valent cations [20,28,29]. Simultaneously, the surface heterogeneity, an inherent disadvantage resulting from membrane-manufacturing methods, was another dilemma for a heterogeneous IEM at present because it was generally regarded as one of the important reasons for bringing about concentration polarization and thereby reducing the limiting current during a practical ED process.

Therefore, we think a surface modification on a heterogeneous IEM by a homogeneous polyelectrolytes layer may contribute to improving its comprehensive transport properties, such as monovalent ion permselectivity and amelioration of concentration polarization. In this study, a three-step modification scheme was proposed and demonstrated in Fig. 1. Firstly, the carboxylic acid groups were introduced to membrane surface by means of the chemical reactions of azidobenzoate (Az) groups, such as hydrogen abstraction and insertion into double bonds, under UV-light irradiation [22,30,31]. Then, the covalent grafting of PEI on membrane surface can be carried out by the amidation reaction taking place between the carboxyl groups and the amine groups of PEI in the presence of 1-ethyl-(dimethylaminopropyl) carbodiimide (EDC) and N-hydroxyl succinimide (NHS). At last, the density of amine groups on membrane surface was further adjusted by glutaraldehyde (GA)-induced PEI multilayers deposition. Thereinto, GA supplied aldehyde groups not only for the cross-linkage of the grafted PEI layer but also for the next coming PEI layer. During the experiments, morphological observations, chemical composition analysis, transport properties measurements and the other related electrochemical characterizations were performed to investigate the effects of different modification steps. More specifically, series of electrodialysis experiments with respect to two kinds of systems, such as H^+/Zn^{2+} system and Na^+/Mg^{2+} system which were used to simulate the hydrometallurgy application and the seawater concentration application, respectively, were conducted to evaluate the monovalent selectivity of the modified CEMs.

2. Experimental section

2.1. Materials

The heterogeneous CEM, a product of Zhe-jiang Qianqiu Environmental Protection & Water Treatment Co. Ltd. (China), was selected as the base membrane in this study. Simultaneously, a heterogeneous anion exchange membrane (AEM) produced by the same company was also employed in the relevant electrochemical characterization experiments. Their main characteristics were listed in Table 1. Branched PEI (Mw: 10,000), EDC (>98.5%) and NHS (>99%) were obtained from Aladdin. 4-azidobenzoic acid (Az, >97%) was purchased from TCI. Other reagents, such as NaCl, $MgCl_2$, H_2SO_4, $NaSO_4$, $ZnSO_4$, EDTA, HCl, NaOH, Tetrahydrofuran (THF), methanol and GA (30 wt% solution in water) were used directly without any further purification. The indicators, Eriochrome Black T (EBT) and Xylenol Orange (XO), were newly prepared and stored at low temperature.

2.2. The preparation of the monovalent selective CEM

Firstly, the bare CEMs (area: 5 cm × 5 cm) were thoroughly cleaned with HCl solution (0.05 mol/l), NaOH solution (0.05 mol/l), pure water and methanol in turn. Then, the CEMs were immersed in the 20 mmol/l Az solution in THF for about 30 s at room temperature. After being drained the excess of Az solution well, the membrane samples were irradiated by 254 nm UV-tube light for 30 min. Subsequently, the samples were again immersed in 500 ml methanol solution in which 1 g PEI, 1.16 g EDC and 0.42 g NHS were homogeneously dispersed. During the reaction process, the solution was shaken continuously 72 h later at room temperature, the membrane samples were taken out and washed thoroughly with distilled water. Next, the membrane samples were sequentially immersed into GA solutions (0.5%) and PEI (2 g/l in 1 mol/l NaCl solution) for 30 min with a thorough rinse in pure water at each interval. It was worth pointing out that the modification process was ended up with an immersion in GA solution. At last, the modified CEMs were stored in a 0.025 M NaCl solution for further examinations.

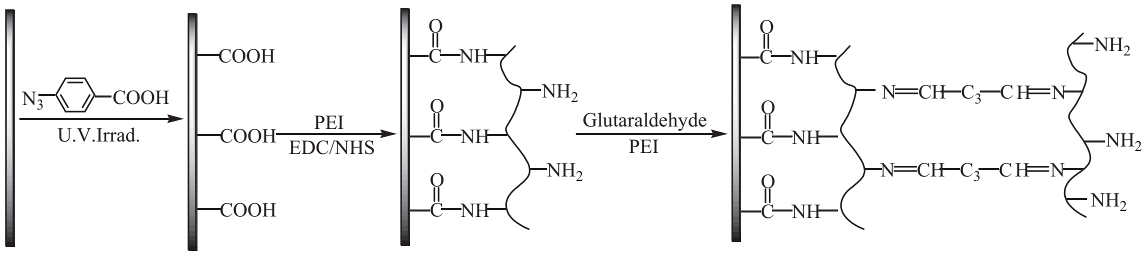

Fig. 1. The schematic diagram for CEM modification by the covalent immobilization of PEI.