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A novel electric-field-accelerated ion-sieve membrane system coupling potential-oscillation for alkali metal ions separation

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ABSTRACT

A novel electric-field-accelerated ion-sieve membrane (EISM) system with potential-oscillation was set up for the selective separation of the alkali metal ions. The ion-sieve membrane was fabricated by coating a polypyrrole/polystyrenesulfonate composite on the stainless steel wire mesh (PPy/PSS/SSWM). In the EISM system, an external electric filed was applied by introducing a constant cell voltage on the two sides of the ion-sieve membrane to accelerate the directed transport of target ions through the membrane. Meanwhile, an extra pulse potential was applied on the PPy/PSS/SSWM membrane to adjust the ion binding ability of the PPy/PSS composite toward cations. As such, an enhanced "ion sieving effect" of the EISM system was achieved through the synergistic function of the constant cell voltage and potential oscillation, which resulted in the rapid transport of target cation across the membrane in a "leap-frogging" way. It is found that when an extra pulse potential of ±1.0 V (pulse width of 60 s) was applied on the EISM, the permeation flux of K^+ ions was increased by 7.42-fold with a constant cell voltage of 5 V. The permselectivities of the PPy/PSS/SSWM membrane for K^+/Li^+ and K^+/Cs^+ reached 3.29 and 3.45 respectively based on the optimized amplitude (±1.0 V) and frequency (pulse width of 60 s) of pulse potential.

1. Introduction

Selective transport of target ions through the polymer membranes is essential to many processes such as desalination, water purification, wastewater treatment, resource recovery, and energy production [1–3]. In general, the ion selectivity and permeability are two crucial parameters in the membrane-based ion separation process. However, there is a trade-off between these two parameters in the general polymer membranes [2,4]. This compromise leads to an "upper bound" for ion separation performance; therefore many efforts have been devoted to surpass the "upper bound" (i.e., to enhance the ion selectivity and permeability simultaneously). In general, the ion selectivity and permeability of membrane are dominated not only by the characteristics of target ions including ionic species, valence, radius or hydrated radius, hydration free energy, but also by the characteristics of the membrane such as the composition and structure, the steric configuration of binding sites, the distribution of ionic channels, and the affinity between the target ion and the functional group in the membrane. In natural systems, the protein ionic channels in the cell membrane can efficiently recognize and guide the target ions transportation based on the precisely arranged arrays of charged amino acids [1,5]. Motivated by these discoveries, scientists have devoted to synthesize some nonbiological ionic channels for highly selective ions separation using the functional-group modified homogeneous polymer membranes [6–8]. To improve the ion selectivity, some mixed matrix membranes were also fabricated by doping with inorganic materials, such as zeolites [9,10], metal-organic frameworks (MOFs) [11], and carbon materials [12,13], because of the size selectivity of their lattices towards the target ions. Besides, it is worth noting that the development of the novel electrochemically-assisted membrane separation system is also an efficient and economical way to improve the ion separation performance based on the charge characteristics of the ions. In electrodialysis, the ions can be selectively transported from the dilute

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compartment to the concentrated compartment through an ion exchange membrane under the driving force of a cell voltage applied on the two sides of it [14]. Such an electrodialysis has been used for the desalination of seawater to produce fresh water [14,15]. Furthermore, Kaya et al. reported a novel electro-driven membrane for the removal of chromium ions by using a constant DC electric current instead of electric voltage to improve the ions selectivity and stability [16].

Recently, a novel electric-field-accelerated ion-sieve membrane (EISM) system based on the potential-oscillation technique has been applied for the selective separation of target ions [17–20]. This new membrane separation technology is effective and environment-friendly, which was in fact originated from the electrochemically switch ion exchange (ESIX) technique [21]. In the ESIX process, the reversible uptake and release of the target ions can be realized by electrochemically adjusting the redox state of the electroactive ion exchange materials (EIXMs). Because the electric field provides the main propelling force during the ion exchange process, the EIXMs can be applied for the rapid separation of the target ion with a dilute concentration but without the secondary pollution. To date, the discovered EIXMs mainly involve organic conducting polymers, inorganic compounds with mixed-valence transition metals and organic-inorganic hybrid materials [21]. These materials have been fabricated as the electroactive films to selectively separate the different target ions, such as Li^+ [22], Cs^+ [23], Ni^{2+} [24], Pb^{2+} [25], Y^{3+} [26], F^- [27] and ClO_4^- [28]. However, in the ESIX process, the selective separation of target ions and the regeneration of the electroactive film have to be performed separately. To solve this problem, Murray et al. reported an "ion gate membrane" made of the conducting polypyrrole (PPy), one of the typical EIXMs, to realize the continuous operation [29]. On this base, Wallace et al. developed a series of ion transport systems based on the PPy membrane [30–33]. Their researches indicate that the ion flux can be significantly improved by the electrical modulation of the PPy membrane between its oxidized and reduced states. These works motivated us to develop a novel EISM system in which two ingenious strategies were employed to improve the ion selectivity and permeability simultaneously. (i) An external electric filed was generated by applying a constant cell voltage on a pair of auxiliary electrodes placed on the two sides of the EISM to accelerate the directed transport of the target ion through the membrane. (ii) The EISM was made of the EIXMs instead of the conventional ion exchange materials. Meanwhile, a pulse potential was applied on this EISM to control their redox states. Because of the unique ESIX function of EIXMs, the strength of the affinity between the EIXMs and the target ions can be adjusted periodically during the ion transport process, which can further improve the ion flux of the EISM based on a unique "ion sieving effect" induced by the potential oscillation. Furthermore, a high selectivity of EISM can be achieved easily by choosing a suitable EIXM with unique selectivity for the target ion [21].

Such an EISM system provides an effective tactic for the separation of target ion with high flux and high ion selectivity to break the trade-off. In this system, the synergy between the pulse potential applied on the membrane and the constant cell voltage plays an important role in the high-efficiency ion transport through the EISMs. Hence, it is important to investigate the mechanism of ion transport under this complex electrochemically-assisted system. In addition, the EIXMs are other important factor to dominate the ion separation performance of the EISM. Among the EIXMs, PPy is one of promising membrane materials owing to its good film-forming property and electrochemical activity in the neutral solution [34]. In general, the PPy doping with small counterions (A_S^-) such as Cl^- ions can generate an electrically switchable anion exchange material [35]. Conversely, the cation exchange behavior can be achieved by incorporating large counterions (A_L^-) such as polystyrene sulfonate (PSS^{n-}) because of their immobility in the PPy matrix. These two processes are summarized in the following Eqs. (1) and (2):

$$\mathrm{PPy}^+ \cdot A_S^- + e^- \leftrightarrow PPy + A_S^- \tag{1}$$

$$\mathrm{PPy}^+ \cdot A_L^- + C^+ + e^- \leftrightarrow PPy \cdot A_L^- \cdot C^+ \tag{2}$$

Therefore, the PPy can be tailored as cation or anion exchanger by doping different counterions. In this study, in order to investigate the ion transport mechanism of the EISM system, the PPy/PSS composite was selected as the electroactive cation exchange material and electrochemically polymerized on the stainless steel wire mesh (SSWM) to fabricate the PPy/PSS/SSWM membrane. The SSWM is an ideal substrate for preparation of electroactive membrane because of its good conductivity and mechanical property. More importantly, because the conducting PPy is a typical anticorrosion material to maintain the metal in the passivity domain, the electrochemical corrosion of SSWM can be avoided effectively during the redox process [36]. Potassium ions are important to maintain fluid and electrolyte balance in the body as an essential macromineral in human nutrition, thus making their selective separation and detection should be rather important for biomedical diagnosis and environmental remediation [37]. Herein, the alkali metal ions of K^+, Li^+ and Cs^+ served as the ion microprobe to test the permselectivity of the membrane. The mechanism of alkali metal ions transport through the EISM was studied. Furthermore, the effects of the operation parameters including the cell voltage and the pulse potential on the permselectivity of the PPy/PSS/SSWM membrane were systematically investigated.

2. Experimental

2.1. Materials and instruments

Pyrrole (Sigma-Aldrich) was purified by distillation under reduced pressure and stored in nitrogen atmosphere prior to use. Sodium polystyrenesulfonate (NaPSS, Mw ca. 70000, Sigma-Aldrich) was used as received. Other chemicals were analytical grade and purchased from National Medicine Group Chemical Reagent Co., Ltd. (China). Aqueous solutions were prepared using Millipore deionized water (18.2 MΩ cm).

Electrochemical experiment was performed using a potentiostat (Princeton Applied Research, VMP3, USA) and a DC regulated power supply (APS-1501D, China). The morphology and elemental compositions of the PPy/PSS/SSWM membrane were examined with a scanning electron microscope (SEM, Hitachi SU8010, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS) detection system. The cation concentrations in the aqueous solution were determined by an ion chromatography (DX-600, DIONEX, USA).

2.2. Preparation of PPy/PSS/SSWM membrane

A SSWM (4 cm × 4 cm, 400 mesh) was used as the conductive substrate. It was pretreated with anhydrous alcohol to remove the organics on the surface, and then immersed in 0.1 mol L^{-1} sulfuric acid solution for 10 min to remove the metal oxides on the surface, finally washed with deionized water and dried in a nitrogen atmosphere prior to use. The PPy/PSS membrane was electrodeposited on the surface of the pretreated SSWM in a freshly prepared solution containing 0.2 mol L^{-1} pyrrole monomer and 0.1 mol L^{-1} NaPSS (calculated by the molar mass of sodium 4-styrenesulfonate monomer) via potentiostatic method with a