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On/off switching in field assisted ion transport through a polymer membrane system

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ABSTRACT

In our previous work, we demonstrated ion selective transport through a single membrane. In this study, we adopted a new method by using a dual membrane system to improve the performance. Two gold-sputtered membranes were mounted between two independent glass cells. Then, polypyrrole (PPy) was electrochemically deposited on the gold side of each membrane. Benzylamine (BA) and Methylene blue (MB) were used as the probe materials in this membrane system. Since the PPy serves as a separator and an electrode, an electric field could be applied between the two membranes directly. Furthermore, a high electric field could be obtained between the two membranes even at a low applied potential because the distance between the two membranes is in microunits. As a result, the dual membrane system exhibited improved control and selectivity for the ions. Finally, the different transport mechanism for BA and MB was discussed in detail.

1. Introduction

Until now, electric field based separation methods such as capillary electrophoresis [1–5], gel electrophoresis [6–9], electro-osmosis [10–12], and membrane electrodialysis [13–17] etc. were frequently used in many fields of science because of their excellent separation ability. These methods can separate ions with different charges or different hydrated radii. Furthermore, electroosmosis can separate neutral molecules with different sizes. However, these methods require high voltages which can decompose the aqueous phase into H_2 and O_2. The strength of the electric field is proportional to the applied potential and inversely proportional to the distance between the two electrodes. The equation for the magnitude of an electric field E can be confirmed as follows.

$$E = -\frac{\Delta\phi}{d}$$

where $\Delta\phi$ is the potential difference and d is the distance between two electrodes. If d can be reduced to an extremely small value, a high electric field strength can be obtained between the two electrodes even with a low applied potential. But the short distance cannot provide good separation of the mediator for the ions. CPM such as PPy and Polyaniline can strongly affect the transport rate of ions when they are oxidized or reduced [18–25]. In addition, when they work as the separation mediator, the dense structure of the CPM can improve the separation ability for ions that have different sizes or different hydrated radii. Since the CPM can be used as the electrode and separation mediator, these advantages enable the potential use of CPM for electric field applied ion separation systems that can achieve "low applied potential and high separation ability".

In our previous work, we performed MB and BA transport controlling experiments using a CPM system and demonstrated the selectivity of the membrane for organic ions based on the specific adsorption property [26,27]. In this study, we tried to develop a new ion transport controlling system capable of providing better selectivity for separation by combining a PPy redox membrane with an electric field. Consequently, we successfully fabricated a dual PPy membrane system for ion selective transport based on the specific adsorption property. A pair of PPy membranes were polymerized one by one with PSS and DBS dopant ions. Each PPy membrane was used as an electrode and a separator. MB and BA transport experiments were performed with the system to identify the control ability and selectivity. A 4-electrode system was adopted to control the oxidation state of the PPy and the electric field applied between the two membranes. Combinations of potentials consisting of 0, +0.6, and −0.6 V were applied to the membranes. According to the results, the transport of BA through the dual membrane system was controlled by the applied potentials and the control ability was improved compared

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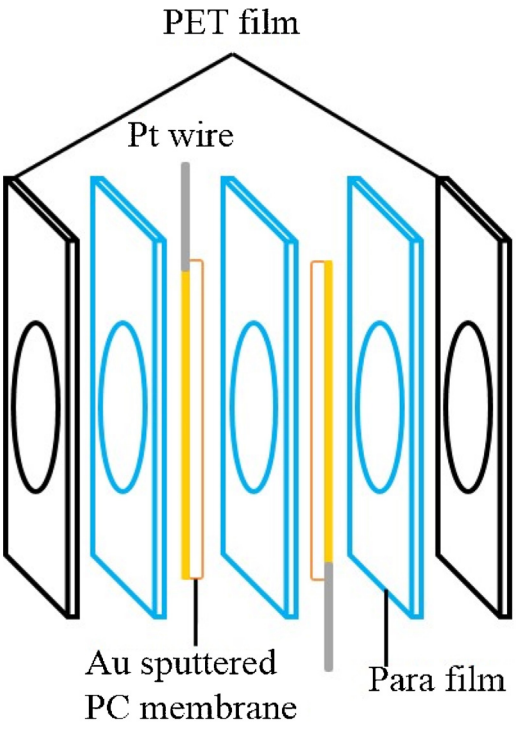

Fig 1. Dual membrane set up.

to the single membrane system we used previously. In contrast, MB was not transported through the dual membrane system at any potential condition. Finally, we propose a different transport mechanism for BA and MB through the dual membrane system in detail and a method for separating two ions using the dual membrane system.

2. Experimental

The chemicals, apparatus and gold modified membrane preparation methods used in this study were described in our previous work [27]. The basic set up for the dual membrane system is shown in Fig. 1. Two PC membranes sputtered with gold were overlapped PC side to PC side and a para film with a punched hole of 1 cm diameter was placed between them. Gold sputtering was performed at 20 mA for 10 min and a piece of platinum wire was contacted with each gold side to create an electric connection.

The PPy polymerization cell is illustrated in Fig. 2. Polymerization for the two membranes was performed one after another in a polymerization solution containing 0.1 M pyrrole, 0.1 M PSS and 0.001 M DBS. First, the three electrode system was connected as step 1 and polymerization was performed by applying 0.8 V to the membrane. Then, the reference and counter electrodes were connected as step 2 and the polymerization was repeated. The two independent PPy membranes prepared using this method can be used for two electrodes. SEM analysis was performed on the PPy surface.

After polymerization, cyclic voltammetry (CV) analysis was performed for the dual membrane system in 0.1 M $NaNO_3$ electrolyte to check the redox ability of the PPy on the PC membrane (result is not shown). A 4-electrode system was adopted as shown in Fig. 3. The concentrations of the MB and BA ion for permeating are commonly 0.1 M. Independent potentials can be applied to the dual membrane system. A constant potential of 0 V was applied to E2 (electrode 2) while CV analysis with a potential window of −0.8 V–0.6 V was performed for E1 (electrode 1) over 5 cycles. Ion transport experiments were also

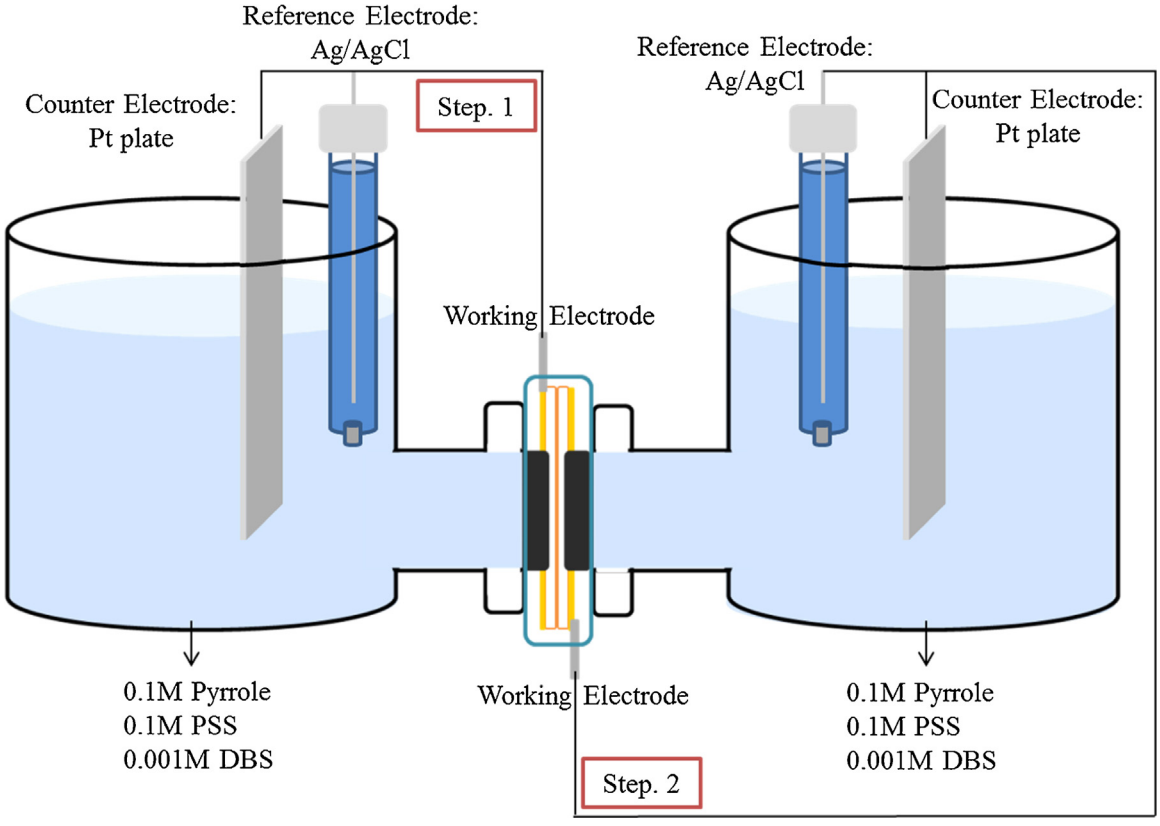

Fig. 2. Cell contribution for dual PPy membrane preparation process. Polymerization potential is 0.8 V.