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Potential dependent transport property of BA through a polypyrrole-modified membrane and its selectivity for the organic ions

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ABSTRACT

It is well established that mixture of inorganic ions including heavy metals can be simply separated into components by using a conducting polymer membrane (CPM) system because each component has a unique charge or size of hydrated radius. However, studies about organic ion separations with the CPM system were hardly found even though organic ions are used in so many fields. Unlike inorganic ions, organic ions usually have complex characters can cause some specific interactions with the membrane and the specific interactions can affect their transport. However, in the case that the specific interactions are weak enough, the organic ion transport may be similar to that of inorganic ions. Thus, investigation of the organic ion transport should be done case by case. In this study, we investigated the transport phenomenon of an organic ion which has weak specific interactions with the membrane under different applied potentials and demonstrated its transport mechanism in detail. Benzylamine (BA) was chosen as the transporting ion and the experimental results showed that its transport was similar to that of inorganic ions even though it has different characters with them. In addition, we compared the transport property of BA to that of methylene blue (MB) which has a strong specific interaction with the membrane under same applied potential and suggested a possibility that organic ions could be separated based on the membrane selectivity.

1. Introduction

The membrane based ion separation (MBIS) method has been developed and utilized in many fields of chemistry, such as environmental cleaning, heavy metal recycling, etc. The use of conducting polymer for MIBS is known as an economical and easy implementation method compared to other techniques for ion separation. This method has been mainly used for inorganic ion separation including heavy metals. Since the transport rate of ions through the same membrane depends on the charge [1–6] or size of the hydrated radii [7–13], charge-based ion separation as well as size-based ion separation can be achieved by using the MBIS method. However, unlike inorganic ions, organic ions have many complex characteristics that can strongly affect their transport property in different ways. These can differentiate the transport tendency of organic ions from inorganic ions. Thus, organic ion separation processes by using MIBS are also important and need to be developed on a case-by-case basis.

Martin et al. prepared a gold-modified membrane for ion separation [14]. The gold-modified membrane contains many cylindrical gold nanotubes that run through the whole membrane. Thus, when ions are transported through the gold nanotubes under the applied potentials, their transport rate can be controlled by the electrostatic interaction between the ions and the polarized gold surface. In addition, ion transport through a self-assembled monolayer (SAM) of thiol molecules on a gold surface can be controlled by adjusting the solution pH. Because the charge of the tail groups of the SAM would be changed by the given pH conditions, thus the ion transport could be affected by the electrostatic interaction between the ions and the charged SAM. Wallace and co-workers prepared a polypyrrole (PPy) membrane for ion separation. It can be simply prepared by an electrochemical method and the surface characteristics can be easily controlled by applying redox potentials to the membrane [8,9]. PPy will be charged or discharged by the applied potentials and the electrostatic interaction is also the dominant factor for controlling ion transport. Meanwhile, the dense polymeric structure of PPy is also important for improving the selectivity of ions with different hydrated radii. The counterions introduced during the polymerization process can affect the growing morphology [15–17] as well

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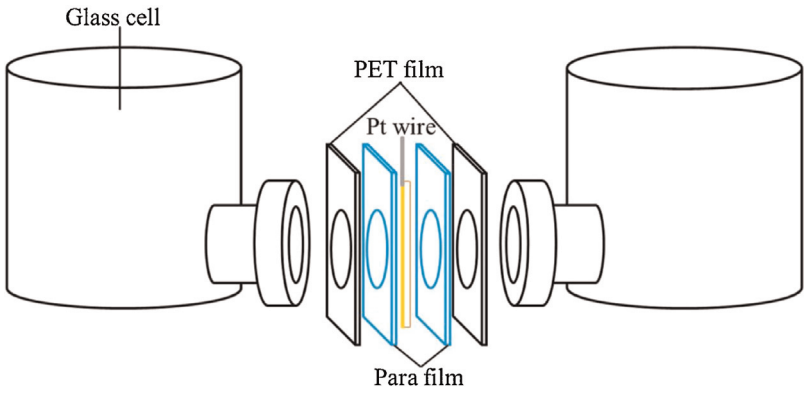

Fig. 1. Cell contribution for electrochemical characterization and ion transport experiment performed in this study.

as the redox property [8,9] of the PPy. Large organic counterions ensure homogeneous growth of PPy and the PPy membrane can be used to control cation transport. In addition, when using Poly (sodium 4-styrenesulfonate) (PSS) and sodium dodecylbenzene-sulfonate (DBS) as the counterions, the electrical conductivity, mechanical strength, and cation flux property of the PPy membrane are essential for ion separation [11].

In this study, we attempted to demonstrate the control of a simple organic ion transport through a PPy membrane and to elucidate the transport mechanism in detail. Benzylamine (BA) was chosen as the transporting ion because as a simple organic material it has a weak adsorptive property and keeps its ionic form in neutral solvent. As a result, its transport tendency is similar to the inorganic ions used in other research studies [2,12] even though it is an organic ion. In addition, we compared the transport of BA to the transport of methylene blue (MB) because those chemicals differ in specific adsorption properties. We successfully controlled BA transport through the membrane by applying two kinds of constant potentials +0.6 and −0.6 V to the membrane. Furthermore, when applying a constant potential of −0.6 V to the membrane, the transport rate of BA was about 1400 times faster than that of MB. Thus, the results can provide a possibility that organic ions have weak specific interactions with the membrane can also be selectively separated from the strong specific interactive ones such as MB, commassie brilliant blue R-250 (CB), orange G (OG), Eosin Y (EY), tartrazine, etc [18–24].

2. Experimental

Pyrrole was purchased from Sigma–Aldrich (USA) and distilled prior to every polymerization process. Track-etched poly carbonate membrane (diameter: 47 mm, pore size: 1.2 μm, porosity: 14.7%) used as the template was from Millipore (USA). Poly (sodium 4-styrenesulfonate) (PSS) and sodium dodecylbenzenesulfonate (DBS) were obtained from Sigma–Aldrich (USA) and $NaNO_3$ was from DAEJUNG (Korea). Methylene blue (Junsei, Japan) and benzylamine (Sigma–Aldrich, USA) were used as the transporting species for electrochemical ion transport processes. All solutions used in this study were prepared with deionized (DI) water (18 MΩ).

Membrane preparation and system structure are described elsewhere [25]. Including some changes and details, the system used in this study is shown in Fig. 1. In brief, the gold layer was sputtered on the poly carbonate (PC) membrane by using a current of 10 mA for 20 min. Electric contact with the membrane was made by using a Pt wire. All electrochemical experiments were performed with a three electrode system. Pyrrole was polymerized with 0.1 M PSS and 0.001 M DBS at 0.8 V for 30 min. After washing with DI water, the cells were filled with 0.1 M $NaNO_3$ and kept the membrane in it for 1 h. Then, a redox treatment for the membrane was performed by using the cyclic voltammetry (CV) method and the morphology was identified by scanning electron microscopy (SEM). The concentrations of the transported ions were detected by a high performance liquid chromatography (HPLC).

Ion transport experiments were also performed with the U-tube cell shown in our previous work. The concentration of the ions for permeating is 0.1 M and during the transport experiment, the solutions in both cells were stirred. In order to control the transport rate of BA, two constant potentials of +0.6 and −0.6 V were applied alternately to the membrane. Ion transport experiments of BA and MB were then performed by applying a constant potential of −0.6 V to the membrane for a long time. The concentration change of the ions in the receiving half-cell (RC) was detected by HPLC for a specific time period.

3. Results and discussion

SEM analysis was performed on the PPy/PSS/DBS membrane after redox treatment in 0.1 M $NaNO_3$. The surface images of the

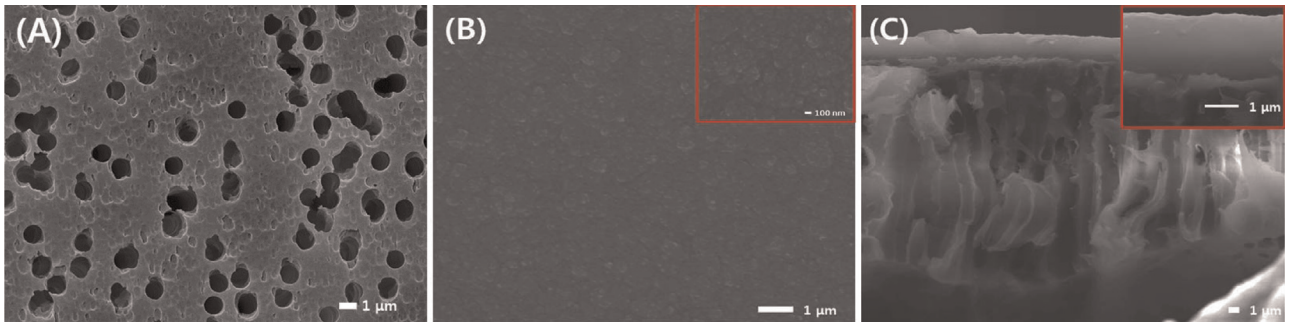

Fig. 2. SEM image of (A) gold sputtered membrane surface, (B) PPy/PSS/DBS surface and (C) PPy/PSS/DBS cross section.