

표면개질된 다공성 알루미나 막의 이온이동 특성평가

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Characterization of ion transport properties of surface-modified porous alumina membranes

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1. Introduction

With advances in membrane preparation techniques, ion exchange membranes (IEMs) are widely used in analytical and biomedical fields, and water purification applications. As IEMs are utilized in various industrial fields, mechanical, thermal and chemical stabilities of membranes are more important. One of the most interesting materials to substitute organic membranes is porous alumina membranes (PAMs) owing to their unique material properties, such as high pore density, thermal stability and uniform pore size. It is well known that surface charge characteristics as well as pore morphology are important factors in membrane performance. Functionalization of pore wall with charged groups leads to improvements in IEM properties.

In this study, amine groups were grafted on the pore surface by silane coupling reaction with hydroxyl groups of alumina surface, and further quaternized to yield positive charges. We have examined structural properties by scanning electron microscopy (SEM), and confirmed the surface functionalization by fourier transform-infrared (FT-IR) spectroscopy. IEM properties were investigated for the prepared alumina membranes using electrochemical techniques: zeta-potential, electric membrane resistance and transport number.

2. Experimental

Anodisc[®] 25 porous alumina membranes with 0.02 μm pore size were purchased from Whatman. Functionalization precursors were N,N-(Dimethylaminopropyl)trimethoxysilane (N1-TMS) and N1-(3-Trimethoxysilylpropyl)diethylenetriamine (N3-TMS) from Sigma Aldrich. Solutions for surface reaction were prepared using absolute ethanol (Sigma Aldrich), acetic acid (KANTO Chemical), and sodium acetate (SAMCHUN Chemical). Methyl iodide (>99.5%) and butyl alcohol (>99%) were obtained from Sigma Aldrich and DAEJUNG Chemical, respectively, and used as received. Electrolyte solutions were prepared from reactant grade chemicals and DI water.

Surface modification of PAM was conducted using silane coupling reaction. 5 v/v% solutions of N1-TMS or N3-TMS in absolute ethanol was prepared. Each solution was mixed with a 0.1 M acetate buffer solution (pH=5.1) to make a 5 v/v% solution in the buffer. PAMs were silanized by soaking in

these mixtures for 3 hr at room temperature. After silanization, the membranes were rinsed with pure ethanol and DI water several times, and then cured at 120 °C in a vacuum oven for 3 hr.[1] Quaternization process was performed using a 20 wt.% solution of methyl iodide in butyl alcohol for 48 hr.

Infrared spectroscopy measurement (Nicolet 6700, Thermo Scientific) was used to verify the attachment of functional groups on the alumina surface, and structural property of membrane pore is examined by SEM (JSM6700F, JEOL). Experiments for electrical properties of modified PAMs were performed using a two-compartment cell. The potential difference across the membrane was measured using digital multimeter (DM3601, RIGOL Technologies) and two Ag/AgCl electrodes prepared from silver wire.

For measuring transport number, the NaCl concentration in a dilute compartment was varied from 0.001 to 1.5 M, while the concentration in a concentrated compartment was 5 times higher. The transport number(t_-) was calculated from the following equation:[2]

$$V_M = (2t_- - 1) \frac{RT}{F} \ln \left(\frac{a_2}{a_1} \right) \quad \text{Eq. (1)}$$

Streaming potential measurements were performed using the experimental set-up described in Fig. 1.[3] Each compartment of half cells were filled with 1.00 mM KCl solution at neutral pH, and the potential difference across the membrane (ΔE) was measured for varying transmembrane pressure (ΔP). The streaming potential (v) was calculated from the slope of ΔE versus ΔP , and the corresponding zeta potentials (ζ) were estimated from the Helmholtz-Smoluchowski equation ignoring the curvature of pore surfaces:

$$v \equiv \frac{\Delta E}{\Delta P} = \frac{\varepsilon \zeta}{\eta k_b} \quad \text{Eq. (2)}$$

where ε is electrical permittivity, η is the viscosity of solution, and k_b is the bulk conductivity of the electrolyte solution.

Membrane resistance was determined by using electrical impedance spectroscopy (EIS) instrument (ZIVE SP2, ZIVE LAB) with 0.50 M NaCl solution filled in the both compartments of the cells. The range of alternating current frequency was from 0.1 to 10⁶ Hz.

3. Results and Discussion

Anion exchange membranes treated with N1-TMS, and N3-TMS (N1-AEPAM and N3-AEPAM, respectively) were prepared via silane coupling reaction and quaternization, and the surface functionalization of each step was qualitatively confirmed by infrared spectroscopy. The FT-IR spectra of the membranes before and after quaternization are depicted in Fig. 2.

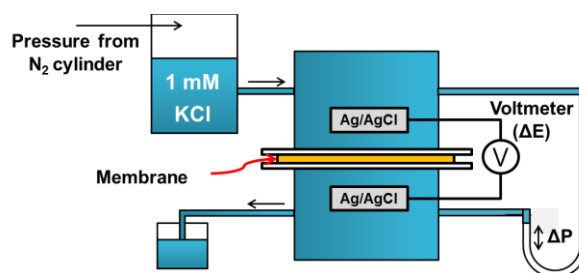


Fig.1. Apparatus to measure streaming potential

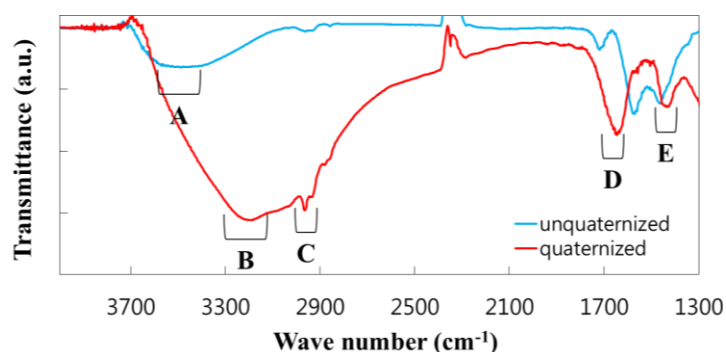


Fig.2. FT-IR Spectra of N1-AEPAM before and after quaternization
A. Broad N-H stretch, $3400\text{-}3600\text{ cm}^{-1}$. **B.** Broad $[-\text{N}(\text{CH}_3)_3^+]$ C-N stretch, $3100\text{-}3300\text{ cm}^{-1}$. **C.** Aliphatic C-H stretch, $2925, 2850\text{ cm}^{-1}$. **D.** The N-H bend (scissoring), 1620 cm^{-1} . **E.** The C-N stretch, 1420 cm^{-1} .

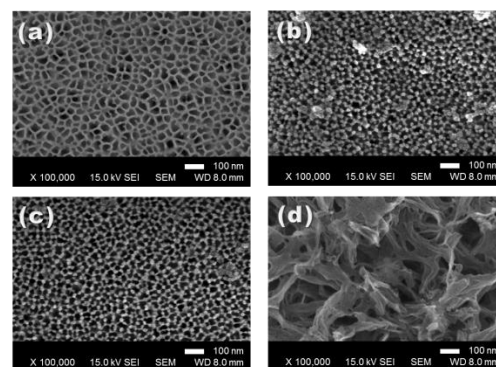


Fig. 3. SEM images of top surface of PAM (a), and N1-AEPAM modified using different synthesis concentration conditions, (b) 5 v/v % , (c) 8 v/v % , and (d) 10 v/v %.

The broad band at $3400\text{-}3600\text{ cm}^{-1}$ appeared upon silanization with N1-AEPAM, and it is assigned to N-H stretch of the amine group attached to PAM surface. After quaternization, the band decreased in intensity, and the broad band at $3100\text{-}3300\text{ cm}^{-1}$ was significantly increased. The latter band assigned to $[-\text{N}(\text{CH}_3)_3^+]$ C-N stretch[4] indicates that the membrane surface was successfully functionalized with quaternary ammonium form.

SEM was employed to characterize the morphology of prepared membranes. To investigate the influence of synthesis condition on the structural changes, a series of experiments were performed under different synthesis conditions of varying reactant concentrations. The photomicrography results are presented in Fig. 3. As the concentration of silanizing agent was increased from 5 to 8 v/v %, the pore sizes on membrane top surfaces were considerably reduced from those of untreated membrane. It also can be seen that 10 v/v % concentration resulted in organic silica layer on the surface via polymerization of silanizing agents.

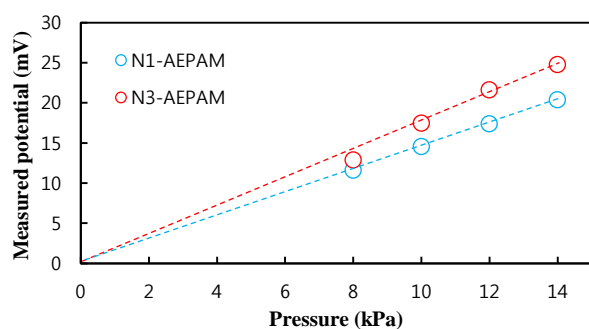


Fig.4. Streaming Potential with N1- and N3-AEPAM

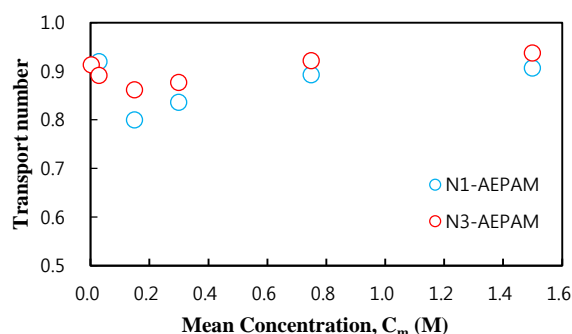


Fig. 5. Transport number of N1- and N3-AEPAM

Streaming potential measurements were performed to determine the zeta potential of the treated membrane surfaces. A plot of ΔE versus ΔP with N1- AEPAM and N3-AEPAM is shown in Fig. 4. The zeta potentials were calculated from streaming potential by using Eq. (1), and each value was estimated 31.25 mV and 38.44 mV for N1- AEPAM and N3-AEPAM, respectively. The surface areas

per attached grafted ion correspond to 3.06 nm^2 and 2.33 nm^2 .

Fig. 5 shows the change in transport number with varying concentration of NaCl solutions separated by N1-AEPAM and N3-AEPAM membranes. The transport number decreased with an increase in arithmetic mean concentration of NaCl solution up to 0.2 M, and it exhibited a slight increase with increasing electrolyte mean concentration above 0.2 M. The result also shows the effect of amine group number contained in the precursor; the transport number slightly increased from 0.91 for a single amine group to 0.94 for three amine groups at $C_m = 1.5 \text{ M}$.

Electrical resistances of N1-AEPAM and N3-AEPAM were examined in 0.5 M NaCl solution, and these were measured as $6.75 \Omega \cdot \text{cm}^2$ and $7.29 \Omega \cdot \text{cm}^2$, respectively.

4. Conclusion

In this study, surface modification of PAMs has been implemented with an aim to explore the feasibility of utilizing PAMs for anion exchange applications. The treated PAMs were examined by infrared spectroscopy technique to confirm the surface reaction leading to the attachment of quaternary ammonium cations to PAM surfaces. SEM was employed to analyze the surface morphology of membranes, and this approach was proven helpful to optimize synthesis conditions.

We have conducted a series of electrochemical measurements to characterize ion transport properties of fabricated membranes: zeta potential, transport number, and membrane resistance. The results show that anion exchange membranes in this study have higher selectivity for anions at high concentration and lower electrical resistance than other commercial ion exchange membranes.

Ion selectivity is expected to be further improved by reducing pore size and optimizing surface functionalization techniques, and it is believed that functionalized alumina membrane may surpass commercial polymer IEM in ion exchange properties in the near future.

References

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