Bull. Soc. Sea Water Sci., Jpn., 63, 381 − 386 (2009)

Bulletin of the Society of
Sea Water Science, Japan

特集「第60年会：技術交流セクション」
技術交流ポスター賞受賞
（報文）

# Ion Transport Properties of Anion Exchange Membranes Prepared from Poly (Vinyl alcohol) and Poly (Allylamine)

Megumi NISHIMURA * and Mitsuru HIGA *

日本海水学会誌　第63巻第6号（通巻364号）
平成21年12月

Bulletin of the Society of Sea Water Science, Japan
Vol. 63. No. 6 (364) December 2009

Bull. Soc. Sea Water Sci., Jpn., 63, 381 − 386 (2009)

Bulletin of the Society of
Sea Water Science, Japan

特集「第60年会：技術交流セクション」
技術交流ポスター賞受賞
（報文）

# Ion Transport Properties of Anion Exchange Membranes Prepared from Poly (Vinyl alcohol) and Poly (Allylamine)

Megumi NISHIMURA * and Mitsuru HIGA *

**Abstract**

Anion exchange membranes with interpenetrating network structures were prepared by blending PVA and a polycation, poly (allylamine). The membranes obtained were physically cross-linked by annealing them and chemically cross-linked by reaction with various concentrations of glutaraldehyde (GA) aqueous solutions. The effect of the cross-linking conditions and polycation content on the ionic transport properties through the membranes was investigated. The water content of the membranes increased with increasing polycation content and with decreasing GA concentration, $C_{GA}$. The effective charge density of the membranes increased with increasing polycation content, $C_{pc}$. The highest value of the effective charge density was 0.78 mol dm$^{-3}$ at the membrane of $C_{pc}$ = 20 wt.% and $C_{GA}$ = 0.10 vol.%. The electric resistance of the membranes also depended on polycation content and GA concentration. The membrane of $C_{pc}$ = 20 wt.% and $C_{GA}$ = 0.01 vol.% had the lowest membrane resistance (1.23 Ωcm$^2$) of all the membranes.

The dynamic transport number of the membranes increased with increasing polycation content and with increasing GA concentration while the membrane resistance also increased with increasing GA concentration. These results indicate that the ion transport properties of the PVA-based anion exchange membranes can be controlled by changing the polycation content and the cross-linking conditions.

**Key Words :** Poly (vinyl alcohol); Anion exchange membrane; Cross-linking conditions; Ionic transport property

## 1. Introduction

Ion exchange membranes for electrodialysis have been applied to various industrial fields1): the separation of environmental polluting metal ions from hard water2), and a separator for electrolysis such as in chlor-alkali production3), the electrodialytic concentration or desalination of electrolyte solutions4), etc. Demands of ion exchange membranes for electrodialysis are high counter ion permselectivity, low membrane resistance, and low cost. Almost all of the commercially-available anion exchange membranes for electrodialysis have styrene-co-divinylbenzene matrices. The drawbacks of this type of membrane are that it is difficult to control the membrane structure because its copolymerization and cross-linking processes occur at the same time, and the high cost of preparing the membranes. Recently, a lot of study on preparation of novel ion exchange membranes has been reported to overcome these problems. For example, Choi et al.5) controlled the fixed charge distribution of an ion exchange membrane by plasma-induced graft polymerization onto glycidylmethacrylate-*g*-polypropylene membranes. Miyazawa et al. prepared on ion exchange membrane with one-step reaction by means of electron-beam induced graft polymerization of sodium styrene sulfonate onto a nylon-6-made film6).

Another method of preparing an ion exchange membrane is to mix water-soluble base polymers and a polyelectrolyte, and then to cross-link the base polymer. The membrane obtained has a semi-interpenetrating network (semi-IPN) structure in which polyelectrolyte chains are immobilized in a polymer cross-linked network matrix. Hence, the ion-exchange capacity of the membranes can be controlled easily by changing the polymer ratio of water-swollen base polymer to polyelectrolyte. Poly (vinyl alcohol) (PVA) is one of the most popular polymers used as a membrane matrix. PVA is a polyhydroxy polymer that has been studied intensively because of its good film forming and physical properties, high hydrophilicity, processability, biocompatibility, and good chemical resistance7-10). Since PVA is a crystalline polymer, its crystalline region becomes a possible physical cross-link point. Hence, self-standing membranes can be easily prepared by casting PVA solution on a glass plate. The degree of cross-linking can be controlled easily by annealing conditions, because the number of cross-link points increase with increasing annealing temperature11). PVA chains can also be chemically cross-linked using cross-linking agents such as glutaraldehyde (GA). Hence, the water content of the membrane, which plays an important role in permselectivity in an ion exchange membrane, can be easily controlled by annealing an as-cast membrane and/or cross-linking it by using cross-linking agents. Cation exchange membranes with a semi-IPN structure have been prepared by blending

---

* Applied Fine Chemistry, Graduate School of Science and Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

PVA and a polyanion such as poly (styrene sulfonic acid)[12], poly (acrylic acid)[13], poly- (styrene sulfonic acid-co-maleic acid)[14], poly (vinyl alcohol-co-2-acrylamido-2-methylpropane sulfonic acid)[15-16], and by using PVA and sulfosuccinic acid[17], etc.

In this paper, anion exchange membranes with a semi-IPN structure have been prepared by blending PVA and poly (allylamine) PAA with changing polycation content, and by cross-linking PVA chains under various conditions with GA. We have investigated the effect of the cross-linking conditions and polycation content on the membrane ion transport properties: the effective charge density, membrane resistance and the transport number.

## 2. Experimental

### 2.1 Preparation of anion exchange membranes

An aqueous solution of a mixture of PVA (Kuraray Co., Ltd.) and PAAm (Nittobo Industries Inc.) was cast on a plastic plate and dried on a hot stage (NISSIN, NH-45N) at 50 ℃ overnight to produce self-standing membrane (thickness ca. 0.1 mm). The weight percentage of PAAm to PVA in the resulting dried membranes, $C_{pc}$, was modified to control the ion-exchange capacity of the membranes. The membranes were annealed at 160 ℃ for 30 min in a vacuum to induce physical cross-linking between PVA chains. The membranes were chemically cross-linked by immersing them in a mixed solution of various concentrations of GA, $C_{GA}$, 0.05 mol $dm^{-3}$ $H_2SO_4$ (pH = 1), and 2.0 mol $dm^{-3}$ $Na_2SO_4$ at 25℃ for 24 h.

### 2.2 Measurement of membrane water content

The water content was measured as follows. Membranes were weighed in the dry state after the annealing treatment, and cross-linked chemically. The cross-linked membranes were immersed in deionized water at 25 ℃ for 7 days. The membranes were removed from the water, dabbed with filter paper to remove excess water on the membrane surfaces, and weighed in the wet state. The water content is calculated from the weights in the wet state, $W_w$, and in the dry state, $W_d$, as:

$$H = (W_w - W_d)/1.0/((W_w - W_d)/1.0 + W_d/1.3) \tag{1}$$

where 1.0 and 1.3 are the densities of water and PVA, respectively.

### 2.3 Determination of effective membrane charge density

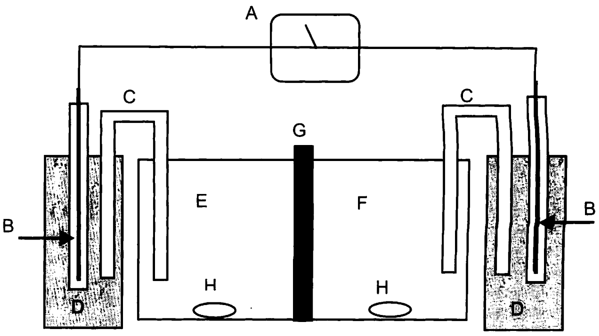

**Fig.1** Apparatus for membrane potential measurement. A, voltmeter; B, Ag/AgCl electrode; C, KCl salt bridge; D, 3.0 mol $dm^{-3}$ KCl solution; E, high concentration of KCl solution; F, low concentration of KCl solution; G, sample membrane; H, magnetic stirrer tip. The effective area of the cell is 7.06 $cm^2$.

The effective charge density of the membrane is one of the most important factors for estimating the permselectivity between ions with different sign and valence through an ion exchange membrane. In order to estimate the effective charge density, the membrane potentials $\Delta\phi$ were measured by using an acrylic plastic cell of two parts separated by a membrane, as shown in **Fig.1**. One chamber of the cell was filled with KCl solution of various concentrations, $C_o$, while the other chamber was filled with KCl solutions with concentration, $C_d$, which is 5 times higher than those in the first chamber ($r = C_d / C_o = 5$). The membrane potential between the solutions in the two chambers was measured at 25.0 ± 0.5℃ using Ag/AgCl electrodes (TOA HS-205C) with a salt bridge (3.0 mol $dm^{-3}$ KCl) and a voltmeter. The effective charge density, $C_x$, was calculated from the measured membrane potential using the following equation[18, 19]:

$$\begin{aligned}\Delta\phi = &-\frac{RT}{F}\ln\left(r\cdot\frac{\sqrt{C_x^2+(2C_0)^2}-C_x}{\sqrt{C_x^2+(2rC_0)^2}-C_x}\right)\\ &-\frac{RT}{F}W\ln\left(\frac{\sqrt{C_x^2+(2rC_0)^2}-C_xW}{\sqrt{C_x^2+(2C_0)^2}-C_xW}\right)\end{aligned} \tag{2}$$

where $W = (\omega_K - \omega_{Cl})/(\omega_K + \omega_{Cl})$; $\omega_K$ and $\omega_{Cl}$ are the $K^+$ and $Cl^-$ ion mobilities in a membrane, respectively; $F$, $R$ and $T$ are the Faraday constant, the gas constant and the absolute temperature, respectively. Parameters $W$ and $C_x$ were adjusted so that the left-hand side of Eq. (2) fits the experimental data of $\Delta\phi$ at various KCl concentrations.

### 2.4 Measurement of membrane resistance

The electric resistance through the membranes was measured by using a hand-made acrylic plastic cell of two parts separated by a membrane, as shown in **Fig.2**, with a LCR meter at 10 KHz AC (A&D corp. Ltd. AD-5827). After 0.5 mol $dm^{-3}$ NaCl solution was poured into the two cell compartments, the electrical resistance, $R_0$, was measured at 25.0 ± 0.5 ℃ with a water bath. And then, after a sample membrane was set in the cell, the resistance, $R_s$, was measured again under the same conditions. The difference between $R_s$ and $R_0$ gives the membrane resistance, $R_m$.

### 2.5 Measurement of transport number

To determine the dynamic state transport number, $t_{d-}$, of the membrane, electrodialysis was carried out by using a hand-made acrylic plastic cell in two parts separated by a membrane, as shown in **Fig.3** at a current density of 10 mA cm$^{-1}$ at 25 ℃ for 75 min. (360 C). The amount of transported ions that passed through the membrane during the electrodialysis was measured using a conductivity meter (HORIBA 3552-10D). The dynamic state transport number was obtained in terms of the following equation:

$$t_{d-} = 1 - (\Delta CVF/Q) \tag{3}$$

where $\Delta C$, $V$, $Q$ are the concentration change of transported ions, the volume of the measurement solution and the amount of electricity passed through the membrane during the electrodialysis, respectively.

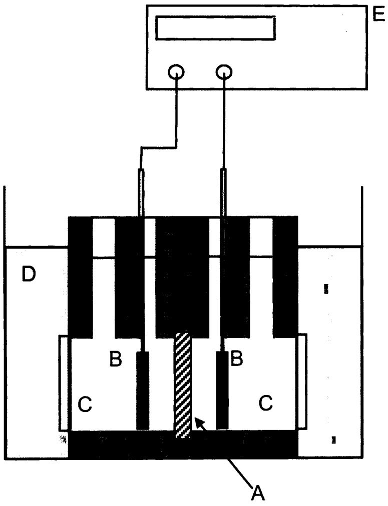

**Fig.2** Apparatus for membrane resistance. A, sample membrane; B, Pt electrodes; C, NaCl solution; D, water bath; E, LCR meter. The effective area of the cell is 1.0 cm$^2$.

## 3. Results and Discussion

### 3.1 Water content as a function of polycation content

The water content is an important property of an ion exchange membrane because the effective charge density and membrane resistance depend on the water content. **Figure 4** shows the water content of the anion exchange membranes as a function of polycaion content. The water content increased with increasing polycaion content because the osmotic pressure in the membranes increases with an increasing number of charged groups in the membranes. The water content decreased with increasing GA concentration, because the membrane has much dense structure after cross-linked with high concentration of GA solution.

### 3.2 The effective charge density as a function of polycation content

The effective charge density is also one of the important properties of an ion exchange membrane. The higher effective charge density a membrane had, the higher counter ion

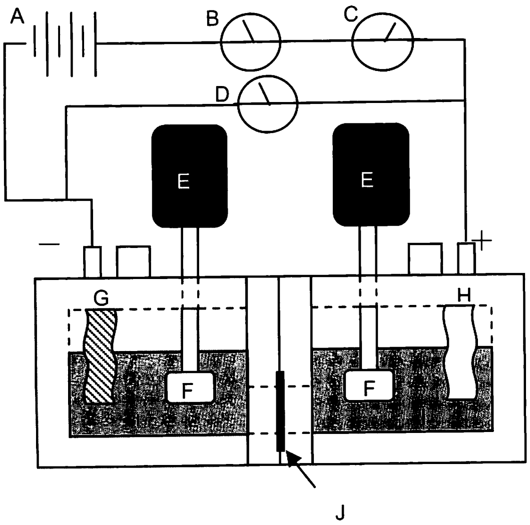

**Fig.3** Apparatus for measuring dynamic state transport number. A, power supply; B, ampere meter; C, coulomb meter; D, voltmeter; E, motor; F, stirrer; G, cathode electrode; H, anode electrode; I, 0.5 mol dm$^{-3}$ NaCl solution; J, sample membrane. The effective area of the cell is 8.0 cm$^2$.

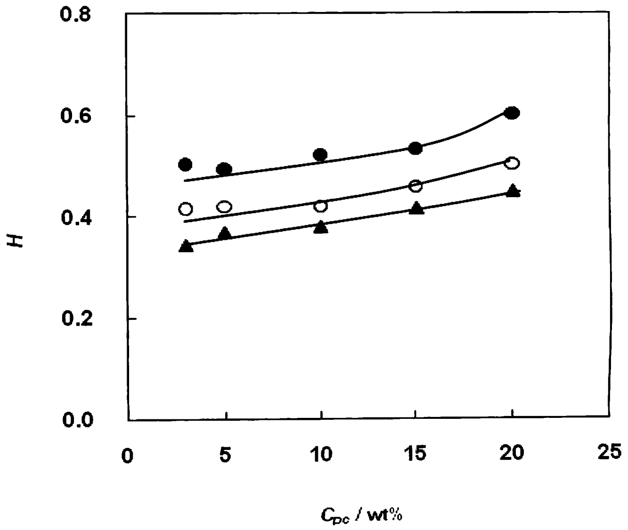

**Fig.4** Water content, $H$, of the anion-exchange membranes as a function of polycation content, $C_{pc}$. Annealing temperature: 160 ℃. Concentration of GA solution: o closed circles, 0.01 vol.%; open circles, 0.05 vol.%, and closed triangles, 0.10 vol.%, respectively.

permselectivity it had. **Figure 5** shows the effective charge density as a function polycaion content. The effective charge density increased with increasing polycaion content. The effective charge density is proportional to the division of ion exchange capacity, *IEC*, by the water content, *H*:

$$C_x \propto IEC/H \qquad (4)$$

*IEC* is proportional to polycaion content. Hence, the effective charge density increases with increasing polycaion content. The highest value of the effective charge density was 0.78 mol dm$^{-3}$ at the membrane of $C_{pc}$ = 20 wt. % and $C_{GA}$ = 0.10 vol.%.

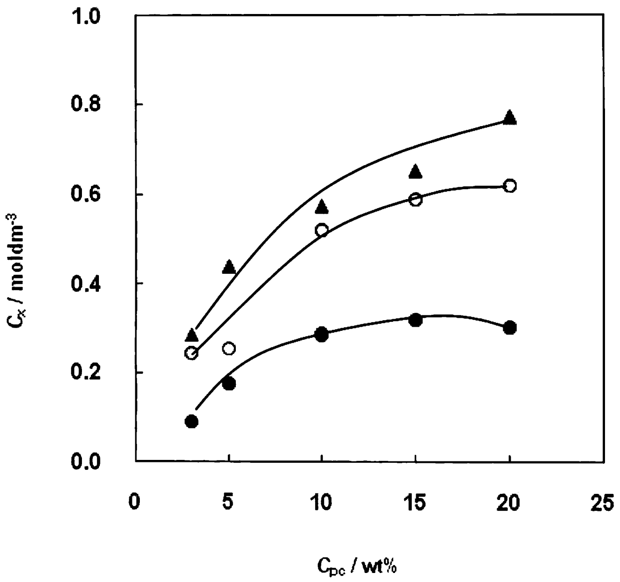

Fig.5 Charge density, $C_x$, of the anion-exchange membranes as a function of polycation content, $C_{pc}$. Markers in this figure are the same as those in Fig.4.

### 3.3 Membrane resistance as a function of water content

The membrane resistance is an important parameter for an energy-saving electrodialysis process. **Figure 6** shows the membrane resistance as a function of water content, *H*. The membrane resistance decreased with increasing *H*, because the ion channel of the membrane increased with increasing *H*. The membrane resistance increased with increasing of GA concentration because of the decreased in the water content. This means that the membrane resistance in this study can be controlled by changing the water content of the membrane. The membrane of $C_{pc}$ = 20 wt.% and $C_{GA}$ = 0.01 vol.% had the lowest membrane resistance (1.23 Ωcm$^2$) of all the membranes. This value has almost the same performance as that of the commercially available anion exchange membrane, AM-1 (2.0 Ωcm$^2$, Astom Corp.).

### 3.4 Relationship between dynamic state transport number and polycation content

The dynamic state transport number relates to the counter ion permselectivity of an ion exchange membrane in a practical electrodialysis process. A membrane with a 1.0 transport number can permeate only the counter ions in an electrodialysis system. **Figure 7** shows the dynamic state transport number of the anion exchange membranes as a function of polycaion content. The transport number increased with increasing polycaion content, and then de-

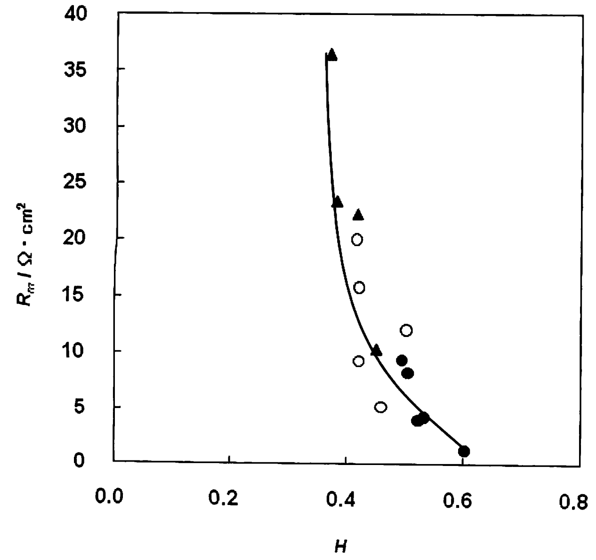

Fig.6 Membrane resistance, $R_m$, of the anion-exchange membranes as a function of polycation content, $C_{pc}$. Markers in this figure are the same as those in Fig.4.

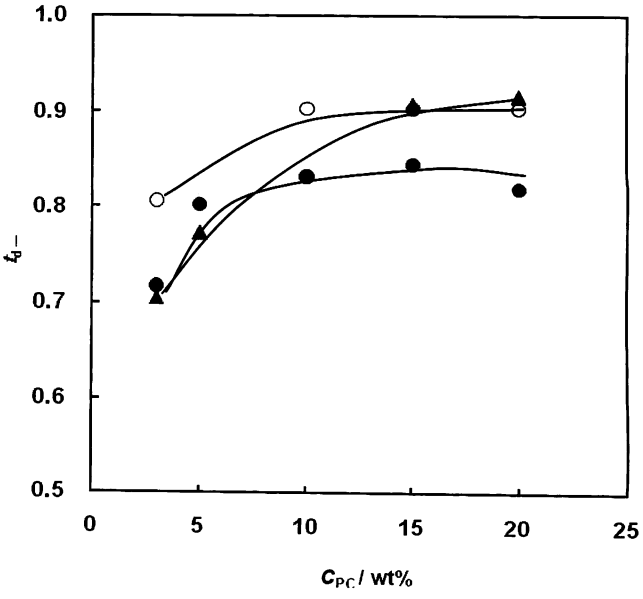

Fig.7 Dynamic state transport number, $t_{d-}$, of anion exchange membranes as a function of polycation content, $C_{pc}$. Markers in this figure are the same as those in Fig.4.

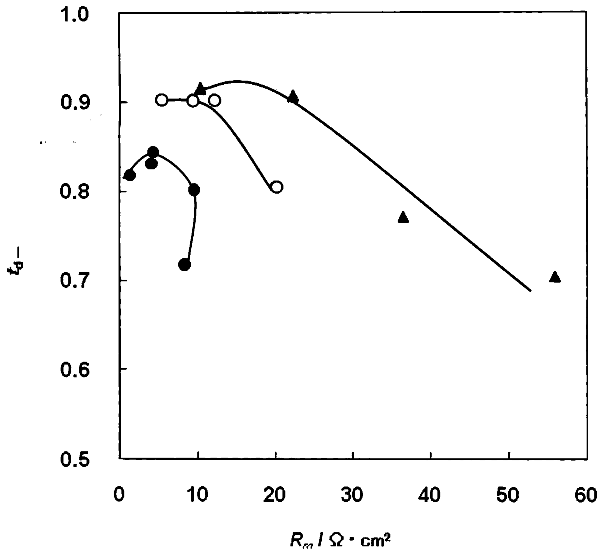

**Fig.8** Dynamic state transport number, $t_{d-}$ of the cation-exchange membranes as a function of membrane resistance, $R_m$. Markers in this figure are the same as those in Fig.4.

creased after it had reached a maximum value when polycaion content was almost equal to 20 wt.%. As mentioned above, it is because the effective charge density has a maximum value at the same value of polycaion content. These results indicate that the transport number of the membranes can be controlled by changing the cross-linking conditions.

### 3.5 Relationship between membrane resistance and dynamic state transport number

An ion exchange membrane having both high ion permselectivity and low membrane resistance is desirable in electrodialysis processes. **Figure 8** shows the relationship between the membrane resistance and the dynamic state transport number of the membranes. A membrane located on the upper left-hand side has high performance for electrodialysis processes. The membrane resistance decreased and the dynamic state transport number increased with increasing polycaion content. The transport number of the membrane increased with increasing GA concentration. These data show that the PVA based anion exchange membranes has potential applications in desalination of salt water.

## 4. Conclusions

In this paper, anion exchange membranes with a semi-interpenetrating network structure are prepared by blending PVA and poly (allylamine) with changing PAAm content, and by cross-linking them under various concentrations of GA.

The water content of the membranes increased with increasing polycation content and with decreasing GA concentrations. The effective charge density of the membranes increased with increasing polycation content of the membranes, and had a maximum value. This means the effective charge density in this study can be controlled by changing the cross-linking conditions.

The membrane resistances of all the membranes decreased in almost the same trend with increasing water content, which means that the membrane resistance will be estimated from the value of the water content.

The dynamic state transport number increased with increasing polycation content, and had a maximum value.

The PVA-based anion exchange membranes can be prepared more cheaply and has a higher mechanical strength than commercially-available anion exchange membranes. Although their ionic selectivity at high salt concentrations is slightly inferior to commercial ion exchange membranes, the membranes will have potential application in the desalination of salt water.

## Acknowledgements

This work was partly supported by Electric Technology Research Foundation of Chugoku, the Mazda Foundation, the UBE Foundation, Kurita Water and Environmental Foundation (No. 20320), and the Salt Science Research Foundation (No. 0612, No. 0709 and No. 0810).

## References

1) T. Sata, "Ion Exchange Membranes, Preparation, Characterization, Modification and Application", The Royal Society of Chemistry, Cambridge (2004)
2) P. Ray, "Performance Studies of Heterogeneous Ion exchange membranes in the Removal of Bivalent Metal Ions in an Electrodialysis Stack", *Journal of Applied Polymer Science*, **113**, pp. 1155–1164 (2009)
3) T. Sata, "Recent trends in Ion Exchange Membrane Research", *Pure & Appl. Chem.*, **58**, pp. 1613-1626 (1986)
4) L. Melnik, O. Vysotskaja and B. Kornilovich, "Boron Behavior During Desalination of Sea and Underground Water by Electrodialysis", *Desalination*, **124**, pp. 125-130 (1999)
5) E.-Y. Choi, B. Bae and S.-H. Moon, "Control of the Fixed Charge Distribution in an Ion-Exchange Membrane via Diffusion and the Reaction Rate of the Monomer", *J. Phys. Chem. B*, **111**, pp. 6383-6390 (2007)
6) T. miyazawa, Y. Asari, K. Miyoshi, T. Umeno, K. Saito, T. Nagatani and N. Naohito, "Development of Novel Ion-Exchange Membranes for Electrodialysis of Seawater by Electron-Beam-Induced Graft Polymerization (II) Graft Polymerization of Vinyl Benzyltrimethylammonium Chloride and Sodium Styrenesulfonate onto Nylon-6 Film", *Bull., Sea Water Sci. Jpn.*, **63**, pp. 175-183 (2009) (Japanese)
7) E. Yang, X. Qin and S. Wang, "Control of the Fixed Charge Distribution in an Ion-Exchange Membrane via Diffusion and the Reaction Rate of the Monomer", *Mater. Lett.*, **62**, pp. 3555-3557 (2008)

8) C. L. Shao, H. Y. Kim, J. Gong, B. Ding, D. R. Lee and S. J. Park, "Fiber Mats of Poly (Vinyl alcohol) / Silica Composite via Electrospinning", *Mater. Lett.*, **57**, pp. 1579–1584 (2003)

9) X. H. Qin and S. Y. Wang, "Filtration Properties of Electrospinning Nanofibers", *J. Appl. Polym. Sci.*, **102**, pp. 1285-1290 (2006)

10) X. S. Dai and S. Shivkumar, "Electrospinning of hydroxyapatite fibrous mats", *Mater. Lett.*, **61**, pp. 2735-2738 (2007)

11) M. Nishimura, M. Higa, K. Akamine and S. Masudaya, "Preparation and Characterization of Anion-Exchange Membranes with a Semi-Interpenetrating Network Structure of Poly (Vinyl alcohol) and Poly (Allyl amine)", *Desalination*, **233**, pp. 157-165 (2008)

12) T. Uragami, R. Nakamua and M. Sugihara, "Studeies on Syntheses and Permeabilities of Special Polymer Membranes, 45. Active and Selective Transport of Alkali Metal Ions Through Crosslinked Poly (Styrenesulfonic Acid) Membrane", *Makromol. Chem. Rapid Commun.*, **3**, pp. 467-470 (1982)

13) D. S. Kim, H. B. Park, J. W. Rhim and Y. M. Lee, "Proton Conductivity and Methanol Transport Behavior of Cross-Linked PVA/PAA/Silica Hybrid Membranes", *Solid State Ionics*, **176**, pp. 117-126 (2005)

14) D. S. Kim, T. I. Yun, M. Y. Seo, H. I. Cho, Y. M. Lee, S. Y. Nam and J. W. Rhim, "Preparation of Ion-Exchange Membranes for Fuel Cell Based on Crosslinked PVA/PSSA_MA/Silica Hybrid", *Desalination*, **200**, pp. 634-635 (2006)

15) M. Higa and T. Yamakawa, "Design and Preparation of a Novel Temperature-Responsive Ionic Gel. 1. A Fast and Reversible Temperature Response in the Charge Density" *J. Phys. Chem. B*, **108**, pp. 16703-16707 (2004)

16) T. Yamakawa, S. Ishida and M. Higa, "Transport Properties of Ions Through Temperature-Responsive ChargedMembranes Prepared Using Poly (Vinyl Alcohol) / Poly (N-Isopropylacrylamide) / Poly (Vinyl Alcohol-co-2-acrylamido-2-methylpropane Sulfonic Acid)", *J. Membr. Sci.*, **250**, pp. 61-68 (2005)

17) D. S. Kim, H. B. Park, J. W. Rhim and Y. M. Lee, "Preparation and Characterization of Crosslinked PVA/SiO2 Hybrid Membranes Containing Sulfonic Acid Groups for Direct Methanol Fuel Cell Applications", *J. Membr. Sci.*, **240**, pp. 37-48 (2004)

18) T. Teorell, "Transport process in ionic membranes", *Prog. Biophys. Biophys. Chem.*, **3**, pp. 305-369 (1953)

19) K. H. Meyer and J. -F. Sievers, "Permeability of membranes I. Theory of ionic permeability" *Helv. Chim. Acta.*, **19**, pp. 649-664 (1936)

(平成 21 年 9 月 2 日受付，平成 21 年 11 月 9 日採用決定
Received September 2, 2009, Accepted November 9, 2009)

# ポリビニルアルコールとポリアリルアミンを用いたアニオン交換膜のイオン輸送特性

西村　恵美*，比嘉　充*

## 要　旨

PVA とポリカチオンであるポリアリルアミン塩酸塩をブレンドさせ，キャスト成形した後に種々の条件下で架橋を行うことで，様々な膜構造を有する親水性マトリクスアニオン交換膜を作製した．得られた膜の基礎特性評価を測定し，ポリカチオン含有量と架橋条件がイオン輸送特性に与える影響について検討した．架橋剤濃度の増加とともに膜含水率は減少した．また，ポリカチオン含有量の増加とともに膜荷電密度は増加し，ポリカチオン含有量が 20 wt.%，架橋剤濃度が 0.1 vol.% の際に最大値 0.78 $\mathrm{moldm^{-3}}$ を示した．膜抵抗もまたポリカチオン含有量と架橋剤濃度に依存しており，ポリカチオン含有量が 20 wt.% でかつ架橋剤濃度が 0.01 vol% の際に最小値 1.23 $\Omega \mathrm{cm^2}$ を示した．膜の動的輸率はポリカチオン含有量の増加，架橋剤濃度の増加に伴い増加したが，一方で架橋剤濃度の増加とともに膜抵抗も増加した．これらの結果はポリカチオン含有量および架橋剤濃度を変えることで PVA ベースアニオン交換膜のイオン輸送特性を制御できることを示している．

キーワード：ポリビニルアルコール，アニオン交換膜，架橋条件，イオン輸送特性

---

* 山口大学大学院理工学研究科（〒 755-8611 山口県宇部市常盤台 2-16-1）