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Effects of Silica Sol on Ion Exchange Membranes: Electrochemical Characterization of Anion Exchange Membranes in Electrodialysis of Silica Sol Containing-Solutions

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Abstract−The fouling potential of the negatively charged silica sol in electrodialysis (ED) by adsorption on the surface of an anion exchange membrane was investigated. Since the fouling potential is related to the physical and electrochemical properties of the silica sol and anion exchange membranes, it is important to characterize the properties of silica sol and membranes. The surface charge of silica sol was investigated by the electrophoretic mobility and its isoelectric point was determined as pH 3. The commercial anion exchange membranes were characterized in terms of exchange capacity, water content, the zeta potential and the electrochemical properties of the membranes using impedance spectroscopy to predict the effects on the electrodialysis performances. Among the characterized properties, exchange capacity and some electrochemical properties of the anion exchange membranes were rather improved after ED experiments. In the electrodialysis of solution containing silica sol, deposition of the silica sol did not decrease the desalting performance of the anion exchange membranes because of loosely packed cake layer on the membrane surface.

Key words: Characterization, Silica Sol, Electrodialysis, Impedance Spectroscopy, Fouling

INTRODUCTION

Electrodialysis (ED) is an electrochemical separation process using electrically charged ion exchange membranes and an electrical potential difference as a driving force. Applications of ED can be found in environmental and biochemical industries as well as in the production of table salt and the desalination of seawater [Strathmann, 1990; Choi and Jeong, 2002; Kang et al., 2002]. Despite the expanding applications of ED, fouling of ion exchange membranes is one of the most important limitations in the design and operation of electrodialysis processes [Lee et al., 2002a; Lindstrand et al., 2000].

Among common foulants, colloidal particles exist in natural waters and many effluent streams in forms of clay minerals, colloidal silica, iron oxide, aluminum oxide, manganese oxide and organic colloids. Colloidal fouling is caused by accumulation of particles on the membrane surface and/or a cake layer formation [Zhu and Elimelech, 1997; Vladisavljević et al., 1992]. Particularly, silica sol is often found in wastewater streams generated in semiconductor industries. Negatively charged silica particles move toward an anion exchange membrane in the electric field and deposit on the membrane surface due to their electrostatic attraction to the membrane surface [Schoeman and Thompson, 1996]. Deposition of colloids on the membrane surface in electrodialysis depends on the properties of the colloids such as the zeta potential and the critical coagulation concentration. It is also related to the properties of the anion exchange membrane, such as hydrophobicity, exchange capacity, surface charge and electrochemical properties [Lee et al., 2002b].

Electrochemical impedance is known as a non-destructive characterization method for conducting membranes [Coster et al., 1992]. The impedance method has been employed since it allows investigation of electrochemical properties, such as resistance and capacitance, as a function of frequency [Coster et al., 1996]. Measurement of the amplitude and phase difference in the impedance spectroscopy permits studies on corrosion, conducting polymers including membrane characterization as well as analysis of the electrode process related to diffusion, kinetics and the electrical double layer near the membrane surface [Benavente et al., 2000; Lee et al., 1998].

In this study, the properties of silica sol and anion exchange membranes were characterized to predict performances of electrodialysis of silica sol-containing solution. Further, the effects of silica sol deposition on the desalting performances were investigated through the ED experiments.

EXPERIMENTAL

Negatively charged silica sol, Ludox HS-40® (Dupont, USA) with a diameter of 12 nm was used as colloidal particles. The characteristics of the silica sol are shown in Table 1 [Dupont, 1999]. The electrophoretic mobilities of the silica sol were measured in an electrophoretic apparatus (ELS-8000, Ostuka Electronics, Japan) and the zeta potentials as a function of pH were estimated with the Smoluchowski equation [Ricq et al., 1998; Shim et al., 2002].

Commercial anion exchange membranes, NEOSEPTA® AMX, AM-1 and ACM (Tokuyama Corp., Japan), were used in this study. The exchange capacity, expressed as meq/g-dried membrane, was determined by an automatic titrator (702 SM Titrion, Metrom, Switzerland) after the anion exchange membranes were pre-soaked in 0.1 N NaOH solution to exchange counterion from Cl^- to OH^- [Yo-

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Table 1. Characteristics of the silica sol (Ludox HS 40) [Dupont, 1999]

Hydrophilicity	Hydrophilic
Stabilizing counterion	Sodium
Particle charge	Negative
pH (at 25 °C)	9.7
Specific surface area	200 m^2/g
Silica (as SiO_2) wt%	40 wt%
pI	3.5
Molecular weight	1,340 KDa
Specific gravity	1.31
Particle size	12 nm

shida et al., 1998]. For the water content measurement, membranes were equilibrated for 2 days in deionzed water. The wet weight of the swollen membrane (W_{wet}) was determined after the surface water was removed, and the membranes were dried at room temperature for 2 days until a constant weight (W_{dry}) was attained [Strathmann, 1990]. Then, the water content was calculated from the difference between the wet and dry weights divided by the dry weight. Zeta potentials of the anion exchange membranes were determined in 0.01 M KCl solution at pH 5.8-6.0 using a streaming potential measurement cell (BI-EKA, Brookhaven Instruments Corp., USA) [Möckel et al., 1998; Lee et al., 2002b].

For the electrochemical properties such as the charge transfer resistance and the electrical double layer capacitance, differences of the phase angle and amplitude as a function of frequency were measured in an electrochemical cell consisting of two half-cells separated by a membrane [Lee et al., 1998]. The two Pt electrodes with effective area of 0.783 cm^2 were connected to a potentiostat/galvanostat (AUTOLAB 30, Eco Chemie, The Netherlands) having a frequency response analyzer. Measurements were made with 50 different frequencies in the range of 50 mHz to 1 MHz with a voltage of 0.1 V in a 10^{-4} M NaCl solution.

The influence of deposition of silica sol on the functional groups of anion exchange membranes was investigated by using an attenuated total refractive-Fourier transform infrared (ATR-FTIR) spectrophotometer (Jasco 460 Plus, Japan) with a ZnSe crystal at an incident angle of 45°. Spectral scanning range was between 500 and 2,000 cm^{-1} at a resolution of ±2 cm^{-1}. Prior to FTIR measurements, membrane samples were completely dried in a desiccator for more than 3 days. In addition, the deposited silica sol on the anion exchange membrane surface was analyzed by using an energy dispersive X-ray (EDX) analytical spectrometer (Kevex Sigma Gold, USA) connected to a field emission scanning electron microscope (S-4700, Hitachi, Japan).

The two-cell pair unit in TS-1 (Tokuyama Corp., Japan) with effective area of 100 cm^2 was prepared with CMX as a cation exchange membrane and each of three membranes (AMX, AM-1, ACM) as an anion exchange membrane. As dilute (feed) and concentrate solutions, five liters of 0.1 M NaCl solution containing 0.4 wt% of the silica sol and 0.05 M NaCl were circulated at flow rates of 0.2 and 0.3 L/min, respectively. For an electrode rinse solution, 800 mL of 3.0 wt% Na_2SO_4 was used. A constant direct current was kept at 0.6 A (current density: 6.0 mA/cm^2) throughout the electrodialysis experiment. Electrodialysis experiments were performed within the pH values of 6-8 for the dilute and the concentrate solutions. For chemical cleaning after electrodialysis experiments, 500 mL of 1.0 wt% NaOH and the deionized water were circulated through dilute and concentrate compartments for 15 min. The electrodialysis performances were compared in terms of the cell resistance and the conductivity change. In addition, concentration of the silica sol was determined based on the Si concentration measured at a wavelength of 251.611 nm in an ICP-AES (Jovin Yvon 38 Plus, France).

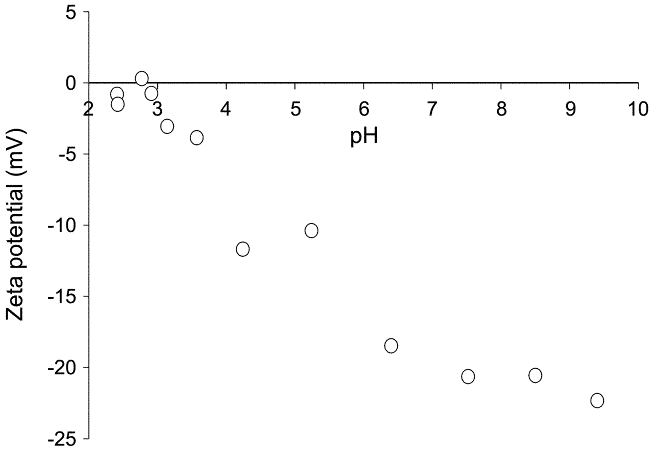


Fig. 1. Zeta potential of the silica sol in 0.01 M KCl as function of pH based on electrophoretic mobilities.

RESULTS AND DISCUSSION

1. Characteristics of Silica Sol and Anion Exchange Membranes

The zeta potential was determined by the electrophoretic mobility of the silica sol as a function of solution pH in 0.01 M KCl as shown in Fig. 1. The isoelectric point of the colloidal silica was observed approximately at pH 3, which is consistent with the previous study [Jönsson and Jönsson, 1996]. The surface potentials indicated by the zeta potential of silica sol were highly negative at high pH values. With decreasing pH values, the surface potential became positive. Since commercial anion exchange membranes have negatively charged functional groups, it was expected that the silica sol deposited on the surfaces of anion exchange membranes in the pH range of 6-8 where the electrodialysis experiments were performed.

Characteristics of the virgin (before ED experiments) and tested anion exchange membranes (after ED experiments) were compared to investigate influence of the silica sol deposition on the properties of anion exchange membranes. Table 2 shows the characteristic values such as exchange capacities, water contents, contact angles and the zeta potentials. The exchange capacity of membranes is considered as one of the most significant factors to predict the performances of electrodialysis process. It is generally accepted that fouling due to foulant deposition on the membrane surface increases electrical resistance, thus decreasing an ion exchange capacity [Schoeman and Thompson, 1996]. Unexpected increase in the exchange capacity of the tested anion exchange membranes in Table 2 can be explained by the fact that deposited hydrophilic silica sol within the anion exchange membranes attracted more water molecules.

Table 2. Characteristics of the virgin and tested membranes [Tokuyama Corp., 1993]

Mem	Status	Exchange capacity (meq/g-dried membrane)		Water content (%)		Zeta potential (mV) Measured
		Referred	Measured	Referred	Measured	
AMX	Virgin	1.5-1.8	1.7	25-30	21	−4.9
	Tested		2.4			−3.7
AM-1	Virgin	1.8-2.2	2.7	25-35	37	−5.4
	Tested		5.1			−5.0
ACM	Virgin	1.4-1.7	3.9	13-18	22	−5.6
	Tested		3.8			−5.4

Especially, the AM-1 membrane showed an 87% increase in its exchange capacity after the experiment. The water content, depending on the nature of the polymeric material, the cross-linking density and the homogeneity, increased exchange capacity then decreased electric resistance as shown in Table 2 [Lee et al., 2002b]. The highest water content of the AM-1 membrane implies that its structure provides more volume or space for electromigration of ions. During ED experiments, the silica sol deposited more easily on the AM-1 membrane surface, and resulted in a significant increase in exchange capacity. Considering contact angle in the previous study [Lee et al., 2002b], the ACM membrane showed the highest hydrophobic property among the three anion exchange membranes since little amount of hydrophilic silica sol may deposit on the hydrophobic surface. Therefore, the hydrophobic surface of the ACM membrane did not change the exchange capacity as shown in Table 2.

The electrodialysis performance may be affected by the charge interaction between the membranes and colloidal particles, which can be determined by the zeta potential as a function of the pH value of the electrolyte. The zeta potential by streaming potential measurement provides a quantitative measure for the electrical surface charges interacting with their surroundings, although this potential is somewhat different from the actual surface potential [Childress and Elimelech, 1996; McDonogh et al., 1989]. Estimated zeta potentials for the virgin and tested membranes are presented in Table 2. The zeta potential became more positive after electrodialysis experiments for all the anion exchange membranes. It is suggested that coverage of the silica sol reduced cationic functionality and then decreased the amount of adsorbed anions, thus reducing the zeta potentials [Lee et al., 2002b]. The least change in the zeta potential of the ACM membrane might be due to its hydrophobic property. In overall, deposit of silica colloidal particles on the anion exchange membrane surface influenced the characteristics depending on the membrane surface property.

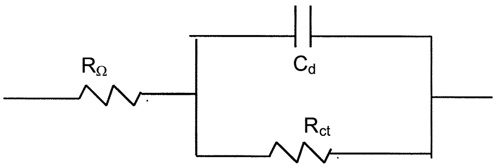
2. Consideration of an Impedance Spectroscopy and Electrochemical Properties

An electrochemical impedance spectroscopy consists of a resistance (Z') and a reactance (Z") in the complex plane. An important feature of the impedance spectroscopy is that it enables developing direct correlations between the response of a real system and an idealized electrical equivalent circuit consisting of discrete electrical components, such as resistances and a capacitance. Influences of the electrical double layer and diffusion at the surface of electrode are minimized since the concentration of ions at an interface is changed periodically at a high frequency region [Coster et al., 1996; Lee et al., 1998].

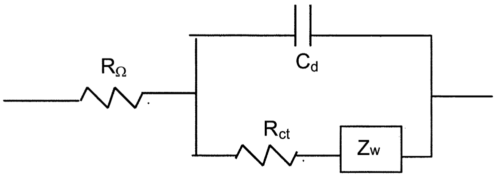
In the impedance plot of Z' and Z" consisting of resistances and a capacitance, a semi-circle appears, which has the center at $Z'=R_\Omega+R_{ct}/2$ and $Z''=0$ and a radius of $R_{ct}/2$. It can be expressed by the following equation for the kinetic controlled region:

$$\left(Z' - R_\Omega - \frac{R_{ct}}{2}\right)^2 + Z''^2 = \left(\frac{R_{ct}}{2}\right)^2. \tag{1}$$

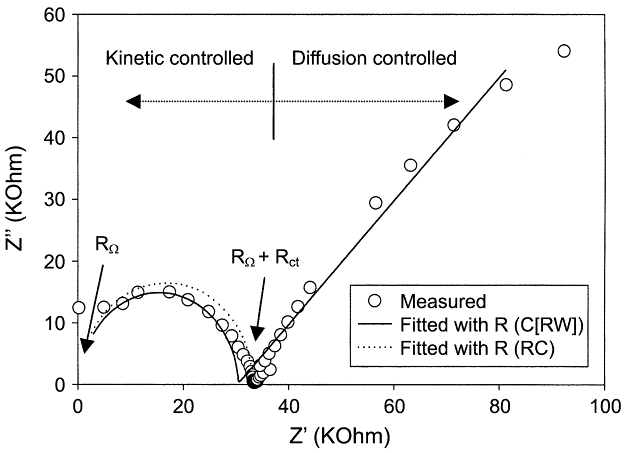
where R_Ω is the resistance of solution and R_{ct} is the resistance of



(a) An equivalent circuit of R(RC) with resistors and a capacitor



(b) An equivalent circuit of R(C[RW]) with the Warburg impedance



(c) Representation of the impedance plot for the AMX membrane

Fig. 2. Equivalent circuits of an electrochemical cell and its impedance plot (R_Ω, the solution resistance; R_{ct}, the charge transfer resistance; C_d, the double layer capacitance; Z_w, the Warbug impedance).

charge transfer. As the frequency decreases, the capacitance in the electrical double layer becomes more significant as given in Eq. (2):

$$Z''=Z'-R_\Omega-R_{ct}+2\sigma^2C_d \tag{2}$$

where σ is a constant related to charge density and C_d is the capacitance in an electrical double layer. Therefore, a line with the unit slope and an intercept of $R_\Omega+R_{ct}-2\sigma^2C_d$ appears in the plot of Z' and Z" as a diffusion-controlled region.

In the impedance spectroscopy of anion exchange membranes, the solution resistance (R_Ω), the charge transfer resistance (R_{ct}) and the electrical double layer capacitance (C_d) were considered in an electrical equivalent circuit of R(RC) in Fig. 2(a) for the kinetic controlled region. In addition, the electrical equivalent circuit of R(C[RW]) in Fig. 2(b) illustrates the membrane system including the diffusion controlled region using the Warburg impedance (Zw). The impedance plot in the complex plane in Fig. 2(c) combines the features of both cases [Bard and Faulkner, 1980]. The slopes in the diffusion-controlled region showed similar values in the range of 1.2-1.4 for three anion exchange membranes. The unit slope in an impedance plot represents that the transport of ions depends on diffusion only. Therefore, the slope greater than the unit implies that the transport rate of anions increases by ion exchange due to charged functional groups in the anion exchange membrane structures as an additional driving force [Kim et al., 1996; Eco Chemie, 1998]. In addition, the similar values of the slope suggest that three anion exchange membranes have the similar surface charge property.

The impedance plot of the AMX membrane in Fig. 2 enabled us to estimate the value of each component by using a non-linear least square method [Park et al., 1999]. The solution resistance was determined as 0.4 KOhm, the charge transfer resistance as 31.2 KOhm and the double layer capacitance as 17.2 pF for the equivalent circuit of R(RC). In the case of the circuit of R(C[RW]), R_{ct} was estimated as 30.2 KOhm, C_d as 17.1 pF, and Z_w as 2.47×10^{-5} Ohm. The estimated values of R_{ct} and C_d were almost same for the two equivalent circuits. In addition, the value of Z_w in the equivalent circuit of R(C[RW]) is considered to be negligible compared to the charge transfer resistance. Therefore, the electrochemical properties in the impedance spectroscopy were determined in the equivalent circuit, R(RC). Fig. 3 illustrates the impedance plots for the anion exchange membranes. It is worth noting that the ACM membrane showed the highest value for the charge transfer resistance while the AMX membrane showed the lowest. It is known that the ACM membrane was developed to minimize the proton leakage by a surface modification, thus increasing the electric resistance [Strathmann, 1990; Tokuyama Corp., 1993].

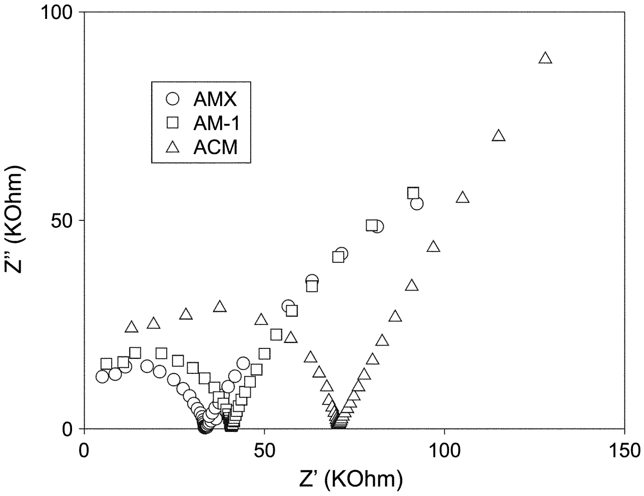


Fig. 3. Impedance plots for three anion exchange membranes (electrolyte: 10^{-4} M NaCl; potential: 0.1 V).

It is believed that deposition of the silica sol with negative charges affects the electrochemical properties of anion exchange membranes including resistance and capacitance during electrodialysis. The impedance plots of the virgin and tested AMX membranes are shown in Fig. 4. The charge transfer resistance of the membrane decreased even after electrodialysis of the silica sol. The values of R_{ct} and C_d in the equivalent circuit of R(RC) were estimated for the virgin and tested AMX membranes as shown in Table 3. Decrease in the charge transfer resistance is due to the increased exchange capacity by the adsorption of the silica sol to the functional groups of the membranes. Also, the adsorption of the silica sol increased the double layer capacitances for all anion exchange membranes after electrodialysis. It is interesting that the AM-1 membrane showed the largest increase in the capacitance as 58% even after electrodialysis, indicating that silica sol improved the characteristic properties

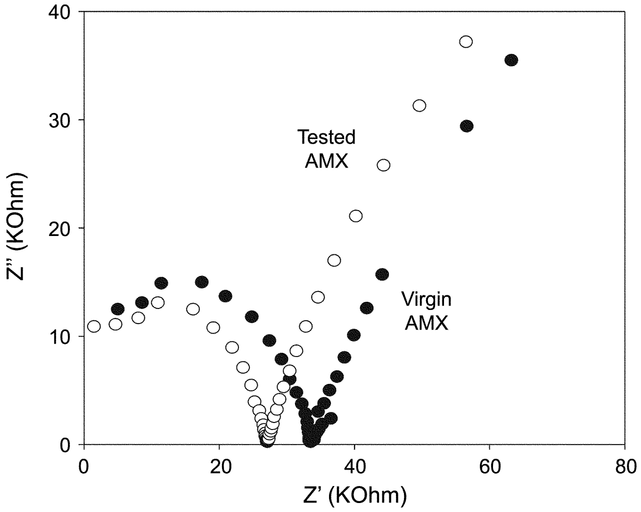


Fig. 4. Impedance plots of the virgin and tested AMX membranes (electrolyte: 10^{-4} M NaCl; potential: 0.1 V).

Table 3. Influence of the silica sol on electrochemical values determined in impedance plots

Membrane	Fouling status	Fitted values in the impedance plot	
		R_{ct} (KΩ)	C_d (pF)
AMX	Virgin	31.2	17.2
	Tested	28.5	18.2
AM-1	Virgin	42.5	14.0
	Tested	27.5	22.1
ACM	Virgin	70.6	16.9
	Tested	25.0	20.3

of the AM-1 membrane structure. The properties in Table 2 and Table 3 indicate that even the deposition of the silica sol did not decrease the performance of electrodialysis of solution containing the silica sol, especially for the AM-1 membrane.

3. Effects of Silica Sol on Electrodialysis Performance

The electrodialysis performance of three anion exchange membranes was compared in terms of the conductivity change in the dilute solution and the cell resistances. It is generally accepted that fouling mainly occurs due to deposition on the membrane surface during electrodialysis of charged foulants [Lee et al., 2002c]. The deposition of organic foulants, such as humate [Lee et al., 2002b], bovine serum albumin [Lee et al., 2002e], fermentation broth [Lee et al., 2002d] and fermentation waste [Lee et al., 2003], decreased electrodialysis performances by increasing electric resistances and decreasing flux of mobile ions (sodium chloride or sodium lactate). Those foulants were considered to form a fouling layer on anion exchange membrane surfaces. However, electrodialysis performances of the membranes did not change even in the presence of silica sols, considered as inorganic foulant. The flux and the current efficiency of NaCl did not show significant differences in the cell structures of different membranes after electrodialysis experiments with NaCl flux of 2.1 mol/m^{2}hr and the current efficiency of 95-96%. The results suggest that the ionic transport rate may not be decreased by the loosely packed cake layer of deposited silica sol on the membrane surface during electrodialysis [Lee, 2002].

Fig. 5 shows the amount of transported silica sol to the concentrate compartment with the elapsed time. The largest transported amount through the AM-1 membrane may be related to high water content compared to the other membranes as shown in Table 2. Also, the amount of the deposited colloidal silica sol increased until 400 min and then reached a steady state as shown in Fig. 6. It is considered that colloidal particles with negative charges accumulated and deposited on the surface of anion exchange membranes up to a critical concentration with accumulated electrical charges [Zhu and Elimech, 1997].

In order to analyze deposited chemical species on the membrane surface after electrodialysis experiment of silica sol-containing solution, the AMX membrane surface was washed with distilled water and was coated with Pt. It was confirmed in the image of SEM-EDX with x-axis as energy level and y-axis as logarithm of intensity in Fig. 7. The spectrum showed that silica sol chemically adsorbed on the membrane surface after deposition of silica sol. In the ATR-FTIR spectroscopy, the functional groups of the AMX membrane were identified to investigate the effects of the deposited silica sol on the functional groups in the membrane surface. The transmittances for the virgin and tested AMX membranes are presented in Fig. 8. The silica functional groups were found in the spectrum of the tested AMX membrane after electrodialysis experiment, implying that silica sol chemically bond to the functional groups of the anion exchange membranes.

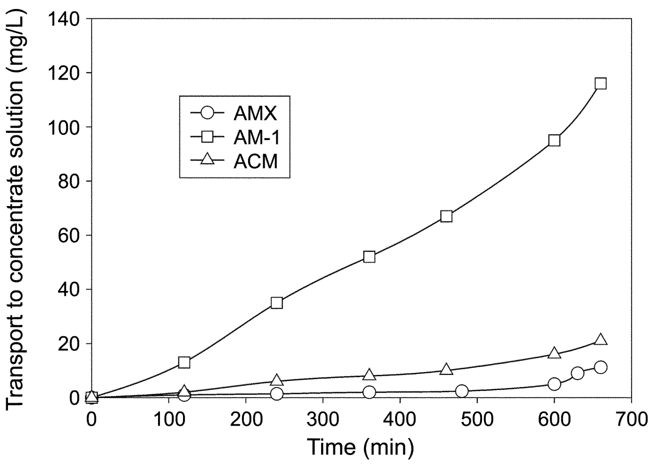


Fig. 5. Time courses of transported into concentrate solution in different cell pairs (silica sol: 0.4 wt% in 0.1 M NaCl).

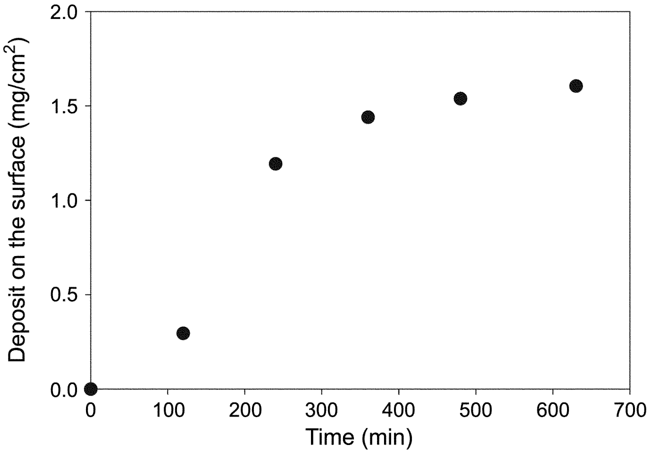


Fig. 6. Deposited Si per cm^2 on the AMX membrane surface (silica sol: 0.4 wt% in 0.1 M NaCl in 2 cell pairs of CMX and AMX).

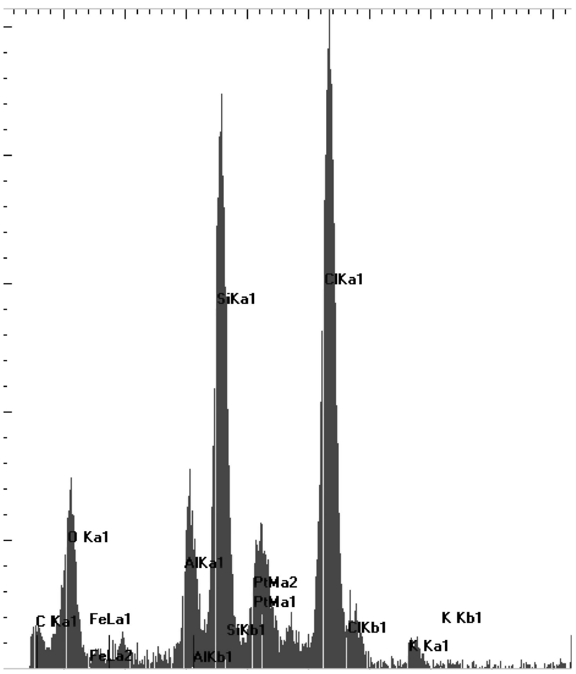


Fig. 7. Surface analysis of tested AMX membrane by EDX connected to SEM.

Table 4 presents the silica sol behaviors after electrodialysis in

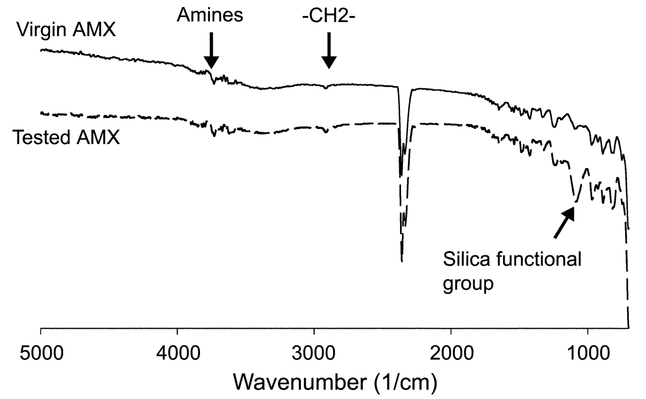


Fig. 8. ATR-FTIR spectra of the virgin and tested AMX membranes.

Table 4. Distribution of silica sol after electrodialysis experiments

(Unit: %)

	AMX	AM-1	ACM
Recovered in the dilute solution	93.3	93.2	95.8
Transported into the concentrate solution	0.4	4.6	0.4
Recovered by cleaning	0.7	0.5	0.2
Irreversibly bound on the membrane[a]	5.5	1.7	3.6

[a]Estimated from the mass balance.

cell structures of three different anion exchange membranes. The recovery in each cell structure was obtained through analysis of the drained dilute solution at the end of experiment. The amount of reversible fouling indicates silica sol recovered in the cleaning solutions, listed in the third row of Table 4, while the degree of irreversible fouling in the fourth row was estimated from the mass balance. The silica sol transported into the concentrate solution in the cell of the AM-1 membrane showed the highest value of 4.6%, while three other cells were below 0.4%. As a result, the least irrversible fouling was observed in AM-1 due to the membrane structure having the least water content as shown in Table 2. The reaults revealed that silica sol reversibly fouled anion exchange membranes by formation of the loosely cake layer on the surface during ED experiments. Aslo, little fouling potential between silica particles and membrane surfaces was observed through characterization of membrane and foulant in this study.

CONCLUSION

Through characterization of the silica sol and the anion exchange membranes, effects of the negatively charged silica sol on the electrodialysis performance were predicted and confirmed by electrodialysis of the silica sol-containing solution. The characterized electrochemical properties of silica sol and anion exchange membranes indicate that the membrane properties were changed by deposition, followed by chemical adsorption on the membrane surface.

The effects of the silica sol on the electrodialysis performances were further examined in terms of the cell resistances, NaCl flux and the current efficiency. The results showed that the silica sol did not decease electrodialysis performances for the three anion exchange membranes due to formation of the reversible cake layer on the membrane surface. In the electrodialysis experiments, adsorption of the silica sol on the anion exchange membrane rather improved the membrane characteristics due to increasing hydrophilic property under the experimental conditions.

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NOMENCLATURE

C_d : capacitance in an electrical double layer [F]
R_Ω : resistance of solution [Ohm]
R_{ct} : resistance of charge transfer [Ohm]
Z' : resistance [Ohm]
Z" : reactance [Ohm]
Zw : Warburg impedance [Ohm]
σ : constant related to charge density [C/m^3]

REFERENCES

Bard, A. J. and Faulkner, L. R., "Electrochemical Methods-Fundamentals and Applications," John Wiley & Sons, New York (1980).

Benavente, J., García, J. M., Riley, R., Lozano, A. E. and de Abajo, J., "Sulfonated Poly(etherether sulfones) Characterization and Study of Dielectric Properties by Impedance Spectroscopy," *J. Membr. Sci.*, **175**, 43 (2000).

Childress, A. E. and Elimelech, M., "Effect of Solution Chemistry on the Surfce Charge of Polymeric Reverse Osmosis and Nanofiltration Membranes," *J. Membr. Sci.*, **119**, 253 (1996).

Choi, K. H. and Jeong, T. Y., "Removal of Zinc Ions in Wastewater by Electrodialysis," *Korean J. Chem. Eng.*, **19**(1), 107 (2002).

Coster, H. G. L., Chilcott, T. C. and Coster, A. C. F., "Impedance Spectroscopy of Interfaces, Membranes and Ultrastructures-Review," *Bioelectrochemistry and Bioenergetics*, **40**, 79 (1996).

Coster, H. G. L., Kim, K. J., Dahlan, K., Smith, J. R. and Fell, C. J. D., "Characterization of Ultrafiltration Membranes by Impedance Spectroscopy. I. Determination of the Separate Electrical Parameters and Porosity of the Skin and Sublayers," *J. Membr. Sci.*, **66**, 19 (1992).

Dupont, http://www.dupont.com/silica (1999).

Eco Chemie, "AUTOLAB-User's Manual for Frequency Response Analysis (FRA)," The Netherlands (1998).

Jönsson, A. and Jönsson, B., "Colloidal Fouling During Ultrafiltration," *Sep. Sci. Tech.*, **31**, 2611 (1996).

Kang, M. S., Tanioka, A. and Moon, S. H., "Effects of Interface Hydrophilicity and Metallic Compounds on Water-Splitting in Bipolar Membranes," *Korean J. Chem. Eng.*, **19**(1), 99 (2002).

Kim, H. T., Park, J. K. and Lee, K. H., "Impedance Spectroscopic Study on Ion Transport in a pH Sensitive Membrane," *J. Membr. Sci.*, **115**, 207 (1996).

Lee, D. J., Choi, Y. K., Lee, S. B., Ahn, K. H. and Min, B. R., "The Analysis of Electric Properties of Thin Film Composite Reverse Osmosis Membrane with Wet Impedance Method," *J. Membr. Sci.*, **150**, 9 (1998).

Lee, H. J., "Studies on Fouling of Anion Exchange Membranes and Fouling Mitigation in Electrodialysis," PhD Dissertation, Kwangju Institute of Science and Technology (2002).

Lee, H. J., Moon, S. H. and Tsai, S. P., "Effects of Pulsed Electric Fields on Membrane Fouling in Electrodialysis of NaCl Solution Containing Humate," *Sep. Purif. Tech.*, **27**, 89 (2002a).

Lee, H. J., Choi, J. H., Cho, J. and Moon, S. H., "Characterization of Anion Exchange Membranes Fouled with Humate During Electrodialysis," *J. Membr. Sci.*, **203**, 115 (2002b).

Lee, H. J. and Moon, S. H., "Fouling of Ion Exchange Membranes and Their Fouling Mitigation," *Membrane Journal*, **12**(2), 55 (2002c).

Lee, H. J., Oh, S. J. and Moon, S. H., "Recovery of Ammonium Sulfate From Fermentation Waste by Electrodialysis," *Wat. Res.*, **37**, 1091 (2003).

Lee, H. J., Oh, S. J. and Moon, S. H., "Removal of Hardness in Fermentation Broth by Electrodialysis," *J. Chem. Tech. Biotech.*, **77**(9), 1005 (2002d).

Lee, H. J., Park, J. S. and Moon, S. H., "A Study on Fouling Mitigation Using Pulsed Electric Power in Electrodialysis of Lactate Containing BSA," *Korean J. Chem. Eng.*, **19**(5), 880 (2002f).

Lindstrand, V., Sundström, G. and Jönsson, G. A., "Fouling of Electrodialysis Membranes by Organic Substances," *Desalination*, **128**, 91 (2000).

McDonogh, R. M., Fane, A. G. and Fell, C. J. D., "Charge Effects in the Cross-Flow Filtration of Colloids and Particles," *J. Membr. Sci.*, **43**, 69 (1989).

Möckel, D., Staude, E., Dal-Cin, M., Darcovich, K. and Guiver, M., "Tangential Flow Streaming Potential Measurements: Hydrodynamic Cell Characterization and Zeta Potentials of Carbonylated Polysulfone Membranes," *J. Membr. Sci.*, **145**, 11 (1998).

Park, S. Y., Lee, J. W., Jang, S. H., Kim, L. H. and Choi, D. K., "Impedance Characteristics of a Rotating Disc Electrode Coated with a Sulfonated Polysulfone Cation-Exchange Membrane," *J. Power Source*, **83**, 217 (1999).

Ricq, L., Pierre, A., Reggiani, J., Pagetti, J. and Foissy, A., "Use of Electrophoretic Mobility and Streaming Potential Measurements to Characterize Electrokinetic Properties of Ultrafiltration and Microfiltration Membranes," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **138**, 301 (1998).

Schoeman, J. J. and Thompson, M. A., Electrodialysis, in J. Mallevialle, P. E. Odendaal, and M. R. Wiesner (Eds.), "Water Treatment Membrane Processes," McGraw-Hill (1996).

Shim, Y., Lee, H. J., Lee, S., Moon, S. H. and Cho, J., "Effects of Natural Organic Matter and Ionic Species on Membrane Surface Charge," *Environ. Sci. Technol.*, **36**, 3864 (2002).

Strathmann, H., Electrodialysis, in W. S. Winston Ho and K. K. Sirkar, (Eds.) "Membrane Handbook," Van Nostrand Reinhold, New York (1990).

Tokuyama Corp., "Bulletin-NEOSEPTA Ion Exchange Membranes," (1993).

Vladisavljević, G. T., Milonjić, S. K., Nikolić, D. and Pavasović, V. L., "Influence of Temperature on the Ultrafiltration of Silica Sol in a Stirred Cell," *J. Membr. Sci.*, **66**, 9 (1992).

Yoshida, N., Ishisaki, T., Watakabe, A. and Yoshitake, M., "Characterization of Flemion Membranes for PEFC," *Electrochimica Acta*, **43**(24), 3749 (1998).

Zhu, X. and Elimelech, M., "Colloidal Fouling of Reverse Osmosis: Measurements and Fouling Mechanisms," *Environ. Sci. Technol.*, **31**, 3654 (1997).