

## SYNTHESIS OF ORGANIC-INORGANIC COMPOSITE MEMBRANE BY SOL-GEL PROCESS

Han Sung Kim, Jung Woo Han\*, Kyoung Yong Chun, Yong Gun Shul and Yung-il Joe<sup>†</sup>

Department of Chemical Engineering, Yonsei University, Korea

\*Hanhwa Group Research and Engineering Center, Korea

(Received 4 April 1994 • accepted 6 May 1995)

**Abstract**—Silica was successfully incorporated into cation exchange polymer membranes, CL-25T and Nafion 417, utilizing sol-gel process. As dipping time increased, increase in silica uptake in membrane was observed. In Nafion 417 membrane, no relationship was found between the silica uptake and the change in ion exchange capacity. But CL-25T which has larger pores than Nafion 417 shows proportional decrease in ion exchange capacity with increasing silica uptake. It suggests that the pore structure of membrane and the size control of silica sol are important to modify the structure of composite membranes. In CL-25T membranes modified by silica, the transport rate of IPA (isopropyl alcohol) increased with increasing OH<sup>-</sup> concentration on the pore surface.

**Key words:** Sol-gel Method, Composite Membrane, Modification, Pore, Transport Properties

### INTRODUCTION

The ultrastructure control of materials through sol-gel process offers significant implications in the preparation of new glasses, composite materials and advanced functional materials. Because it enables one to have molecular level homogeneity, better control of stoichiometry, high purity, low processing temperatures and flexibility in sol-gel transformation [Brinker and Scherer, 1990; Henry and Urich, 1984]. With these advantages, some studies were performed to prepare organic-inorganic composites materials [Hiroshi et al., 1981; Yoshio et al., 1981]. Conjugated polymers were incorporated into silica materials for the application of nonlinear optical materials [Bloembergen, 1965; Stegeman, 1989]. Hybrid materials incorporating triethoxy silane with poly(tetramethylene oxide) has been successfully prepared for the new glass application [Zeldin et al., 1988].

The modifications on the polymer membranes with inorganic substance have been also studied. But there was no specific study about surface characteristics in organic-inorganic composite membrane [Xiong et al., 1992].

In this study, silica was incorporated in ion exchange polymer membranes by using sol-gel process, and the subsequent changes in properties of the modified membrane were discussed in the light of membrane structure. The transport properties of the modified membranes were examined by electrodialysis of isopropyl alcohol.

### EXPERIMENTAL

#### 1. Preparation of Silica Incorporated Composite Membrane

In order to make sulfonate group to H<sup>+</sup> form, CL-25T (Tokuyama Soda) and Nafion 417 (duPont) membranes (Table 1) were immersed in 2 M and 7 M HCl solution at 60°C for 48 hrs, respectively. And membranes were placed in stirred deionized water at 60°C for 24 hrs to remove HCl [Mauritz et al., 1989].

All the pretreated membranes were swollen in 2 : 1 (mole/mole)

Table 1. Physical properties of CL-25T and Nafion membranes

Grade	CL-25T	Nafion 417
Type	strongly acidic cation permeable	strongly acidic cation permeable
Electric resistance (Ω·cm <sup>2</sup> )	2.2-3.0	1.95
Transport number (total cation)	0.98<	0.98<
Thickness (mm)	0.15-0.17	0.31-0.34
Exchange capacity (meq./g dry membrane)	1.5-1.8	0.91
Water content (H <sub>2</sub> O g/g dry membrane)	0.25-0.35	0.17
Reinforcing	yes	yes

H<sub>2</sub>O/EtOH solution for 5 hrs at 25°C. For making a dipping sol in a specific composition (H<sub>2</sub>O : TEOS : EtOH = 2 : 1 : 2), mixture of H<sub>2</sub>O and EtOH was added and this mixture was placed in ultrasonic atmosphere to promote chemical interaction between silica sol and membranes.

After dipping into silica sol, all membranes were rinsed with deionized water at 60°C for 24 hrs to complete reaction.

#### 2. Characterization of Composite Membrane

Ion exchange capacity, water content and specific conductivity were measured to evaluate the changes of composite membrane properties [Helfferich, 1962; Yawatawa, 1982]. And morphological change was investigated by micrographs of SEM. Tensile strength was measured to examine the mechanical property and chemical structure of composite membrane was confirmed by FT-IR (ATR).

#### 3. Electrodialysis

To investigate change of transport properties of modified membranes, transport test of IPA (isopropyl alcohol) were carried as shown in Fig. 1. The anode solution was 100 mL of 20 wt% isopropyl alcohol. The cathode solution was 100 mL of distilled water. 15 mL of aqueous of 0.25 N NaOH as an electrolyte was added and electrodialysis carried out under current density of 150 mA at 25°C for 3 hr.

<sup>†</sup>To whom all correspondences should be addressed.

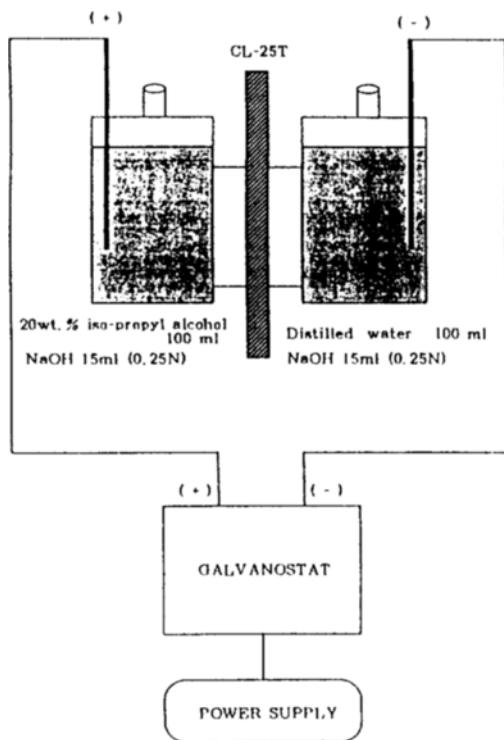


Fig. 1. Schematic apparatus for electrodialysis.

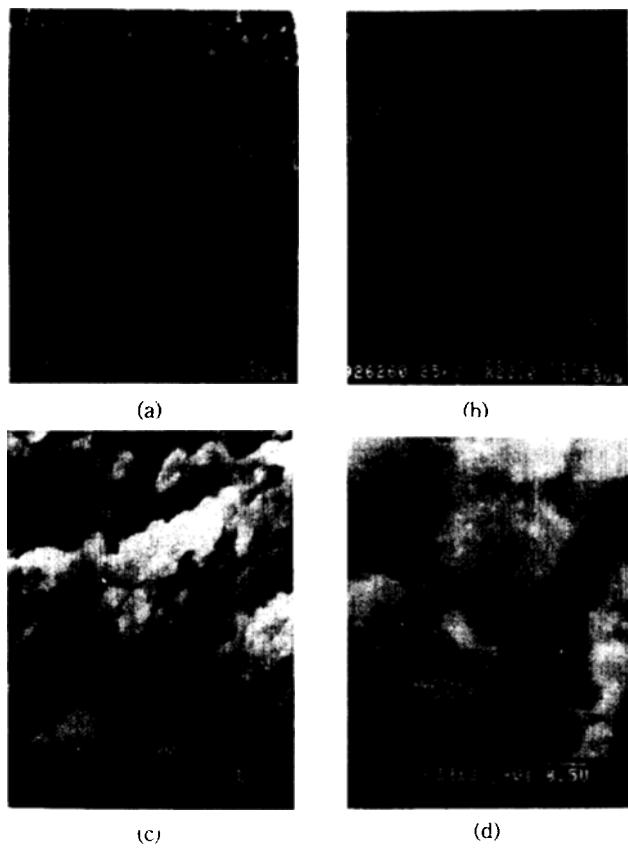


Fig. 2. Micrographs of SEM on the CL-25T membrane.

- (a) Surface: Dipping time 0 min.
- (b) Surface: Dipping time 30 min.
- (c) Cross section: Dipping time 0 min.
- (d) Cross section: Dipping time 30 min.

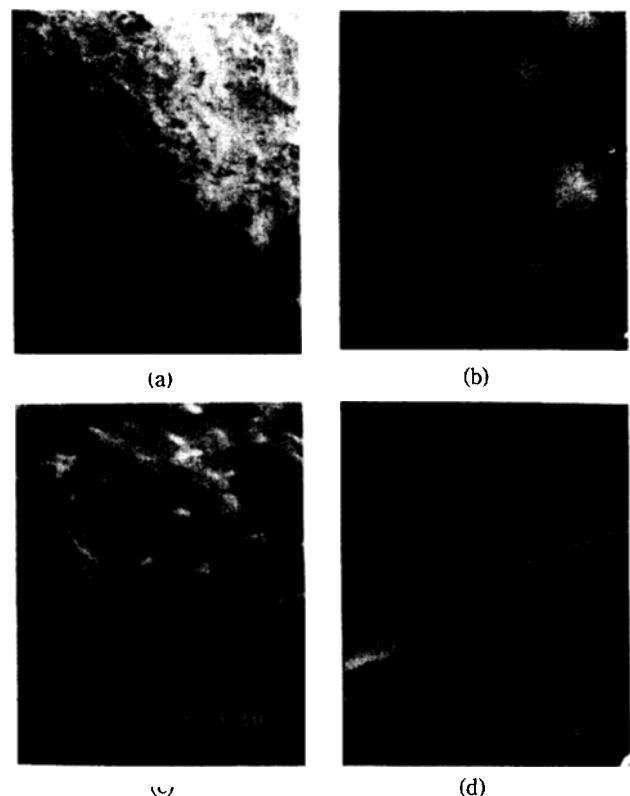


Fig. 3. Micrographs of SEM on the Nafion 417 membrane.

- (a) Surface: Dipping time 0 min.
- (b) Surface: Dipping time 30 min.
- (c) Cross section: Dipping time 0 min.
- (d) Cross section: Dipping time 30 min.

## RESULT AND DISCUSSION

### 1. Morphology of Composite Membrane

To observe the changes of membrane surface, micrographs of SEM were taken as shown in Fig. 2 and 3. For both samples, modified membrane surface by deposited silica could be easily recognized. From the cross sectional view of CL-25T, modified surface by silica particles in the range of 0.01-0.2  $\mu\text{m}$  were found. It is noteworthy that the order of magnitude of silica particle size in cross section was almost same as that in the surface. But corresponding changes were not observed in Nafion 417 as in CL-25T. Instead, larger silica particles were found on the surface of Nafion 417 and no deposited silica particle was observed in inside of cross section. This should come from the pore structure difference between two membrane: in CL-25T membrane, silica sol can penetrate into the membrane through the open pore on membrane but in Nafion 417 membrane, silica sol couldn't be accessible to the inside of membrane due to dense structure. It is known that Nafion has a open pore in the range of 10  $\text{\AA}$ -50  $\text{\AA}$  and CL-25T has much larger open pores (200  $\text{\AA}$ -350  $\text{\AA}$ ). It means that the size of silica sol in this experiments must be in the range of several 10  $\text{\AA}$ -100  $\text{\AA}$ .

In Fig. 4, Si analysis was carried out using EDS. The result show that Si peak can be observed on the cross section of CL-25T. But in case of Nafion, Si peak can't be observed on the cross section. In CL-25T, the deposited silica ratio of cross section vs. surface was 0.075/5.575. Therefore, we can see that silica al-

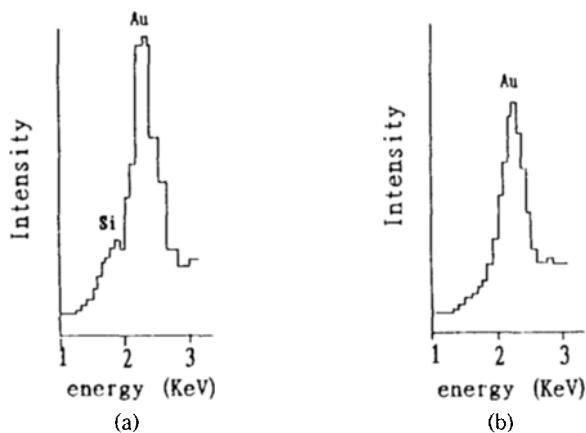


Fig. 4. EDS data sheet of cross section (dipping time : 30 min).  
(a) CL-25T, (b) Nafion

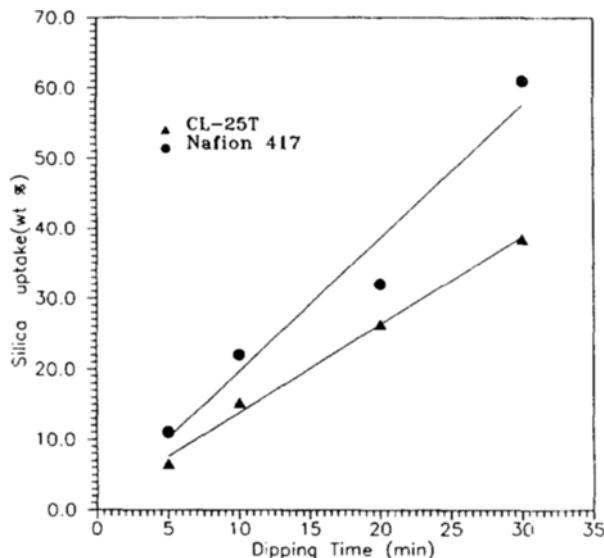


Fig. 5. The effect of dipping time on the silica uptake in the membrane.

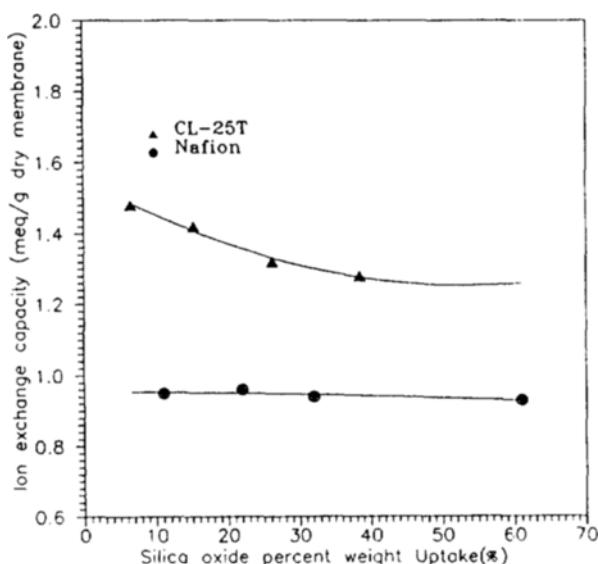


Fig. 6. Silica oxide percent weight uptake (%) vs. ion exchange capacity Nafion 417 and CL-25T membranes in indicated TEOS/alcohol/H<sub>2</sub>O solution.

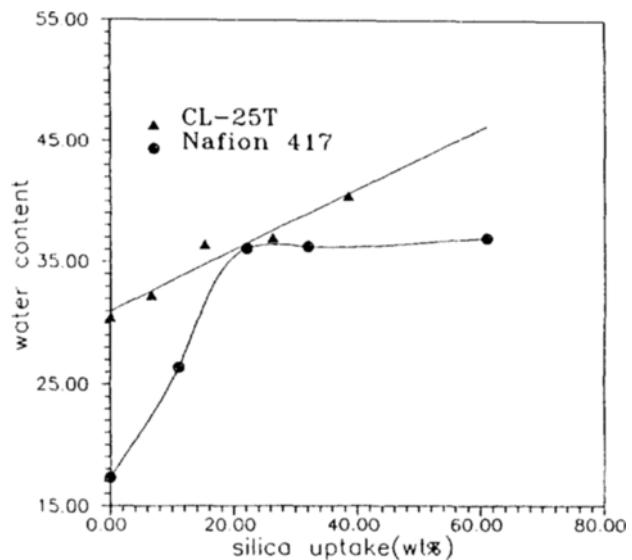


Fig. 7. Relationship between water and silica in membrane.

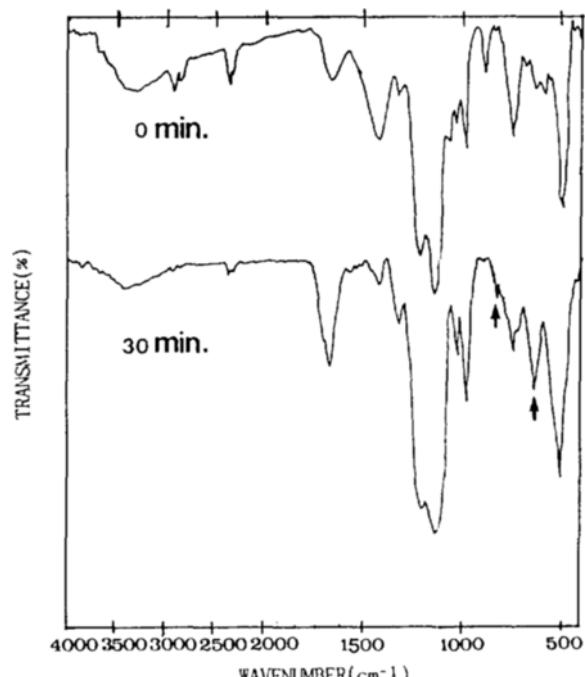


Fig. 8. FT-IR (ATR) spectra modified Nafion and Nafion membrane.

most deposited on the surface than pore both CL-25T membrane and Nafion. This result well coincide with SEM photographs.

In Fig. 5, silica uptake in membrane was linearly increased with dipping time. The uptake of inorganic material in Nafion 417 was much greater than that of CL-25T. We assume that this fact results from the strong acidity of Nafion and the difference of polycondensation environment. That is, in the case of Nafion, its pore is not large enough for silica sol to permeate into the membrane. Silica sols polycondensate on the acid sites of surface to form the big particles of silica. But for the case of CL-25T membrane, pore is so large that silica sols permeate and disperse into the membrane to make silica particles deposited in pore. It means that the size of silica is limited by pore structures of

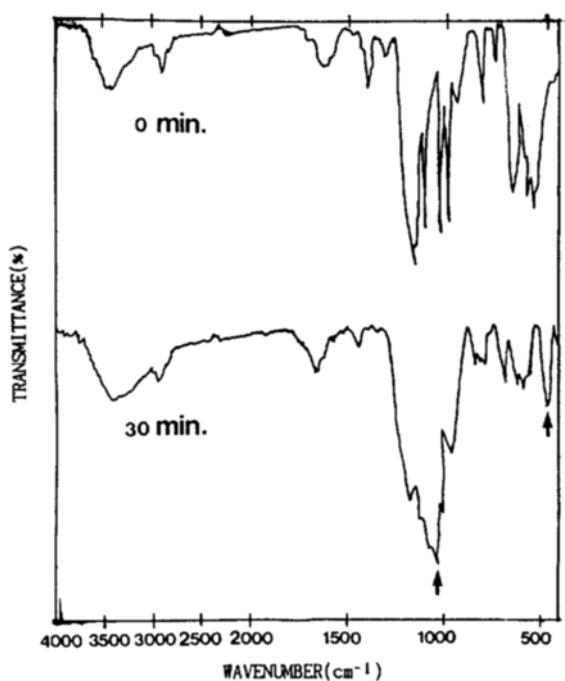


Fig. 9. FT-IR (ATR) spectra modified CL-25T and CL-25T membrane.

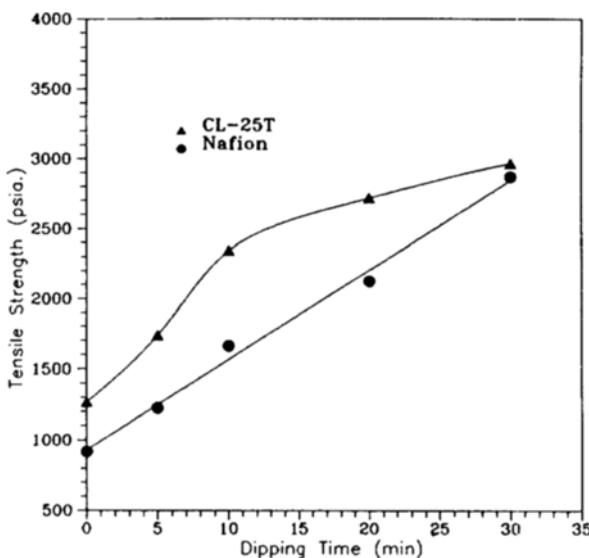


Fig. 10. The effect of dipping time on the tensile strength of membrane.

membrane as observed in metal supported on zeolite [Breck, 1974].

## 2. Characteristics of Composite Membrane

As shown in Fig. 6, ion exchange capacity of CL-25T was decreased with increasing silica uptake, and it can be explained as surface interaction between fixed carrier ( $\text{SO}_3^-$ ) and silica sol. But in Nafion 417, there was no remarkable change in ion exchange capacity even though silica uptake increased up to 60 wt%.

Fig. 7 shows the relationship between water content and silica uptake in modified membrane. In CL-25T water content increased linearly with increasing silica uptake but there was no relationship in Nafion. It suggests that the silica modification enhances the hydrophilic properties of CL-25T membrane.

Fig. 8 and 9 are the spectra of FT-IR to confirm the chemical

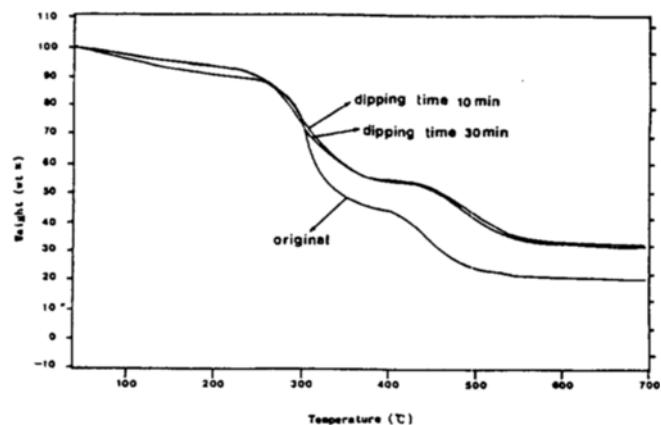


Fig. 11. TGA of CL-25T and modified CL-25T membrane.

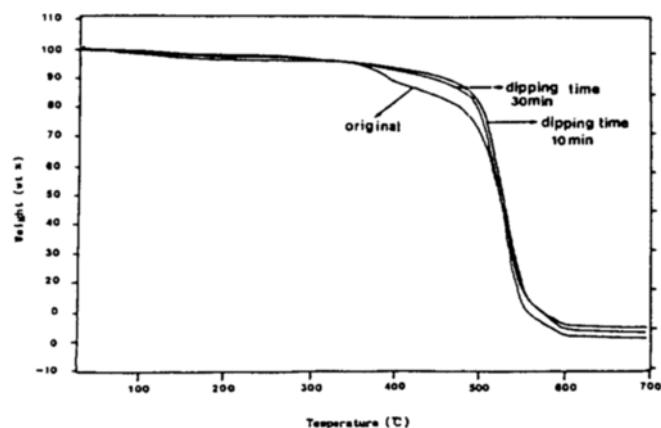


Fig. 12. TGA of Nafion and modified Nafion membrane.

state of silica in composite membranes. In modified CL-25T membrane, two peaks at around  $1070\text{ cm}^{-1}$  and  $440\text{ cm}^{-1}$  were increased with dipping time which were assigned to Si-O-Si asymmetric stretching vibration and Si-O-Si stretching bending vibration. In modified Nafion membranes peaks at around  $625\text{ cm}^{-1}$  corresponding to 4-fold rings of silica was observed. The 4-fold rings of silica should be originated from bulk silica itself and agrees well with the results from the SEM micrographs and the changes of ion exchange capacity. It means that chemically interacted structure between ion exchangeable site and silica sol was more easily obtained in pore surface of CL-25T than in Nafion [Michael, 1982].

As shown in Fig. 10, tensile strength was proportionally increased with dipping time irrespective of silica state on membrane surface. From this result we can presume that the membrane gained non-ductile property of inorganic polymer.

In the result of TGA which is air on nitrogen, membranes of both type show changes improved in decomposition rate (Fig. 11, 12). Which means that enhancement in thermal stability by making composite membranes in this condition. And uniform modification in membrane could be promising future work for improving mechanical and thermal properties.

## 3. The Effect of Surface Modification on Transport Properties of Membrane

The result of electrodialysis of isopropyl alcohol using modified membrane operation was showed in Fig. 13. In modified CL-25T membranes, transport rate of isopropyl alcohol increased with the

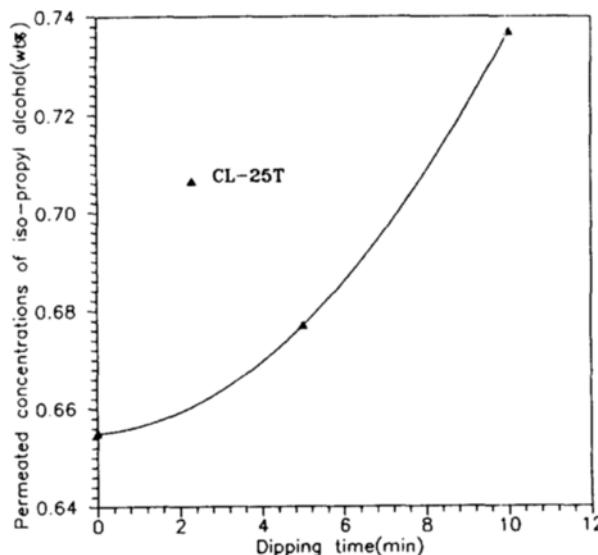


Fig. 13. Permeated concentration of iso-propyl alcohol after 2 hours in various dipping time.

dipping time. This fact is explained by increase of  $\text{OH}^-$  by the surface modification of hydrophilic silica. That is, the increase in  $\text{OH}^-$  concentration on the membrane pore surface improved isopropyl alcohol's mobility under eletrodialysis condition. So the transport rate of isopropyl alcohol was increased. Therefore, despite of slightly reduction of ion exchange of capacity, we can see improved transport properties of membrane.

## CONCLUSION

By using TEOS as starting material in sol-gel process and fixed carrier of ion exchange membrane as acid site, silica incorporated composite membrane was successfully obtained. Chemical state of deposited silica was different by the types of membrane. In CL-25T which has large pore, deposited silica particles were found in the pore as well as on the surface. But in Nafion 417 which has small pore, no deposited silica particles were observed inside of pore surface. In modified CL-25T membranes, the transport rate

of iso-propyl alcohol increased with increasing  $\text{OH}^-$  concentrations on the pore surface and tensile strength was found.

## ACKNOWLEDGMENT

This research was supported financially Korea Sanhak Foundation.

## NOMENCLATURE

TEOS : Tetraethoxysilane  
EtOH : Ethyl alcohol

## REFERENCES

- Bloembergen, N., "Nonlinear Optics", Benjamin, New York, 1965.
- Breck, D. W., "Zeolite Molecular Sieves", John Wiley & Sons, New York, 1974.
- Brinker, C. J. and Scherer, G. W., "Sol-Gel Science", Academic Press, New York, 1990.
- Helfferich, F., "Ion Exchange", McGraw-Hill, New York, 1962.
- Henry, L. L. and Urich, D. R., "Ultrastructure Processing of Ceramic Glass and Composites", Wiley, New York, 1984.
- Hiroshi, A., Takayuki, S. and Toshiki, G., European Patent Application 0031660, 1981.
- Mauritz, K. A., Storey, R. F. and Jones, C. K., "Perfluorinated-Inomer-Membrane-Based Microcomposites", ACS. Symp., Washington DC., 395 (1989).
- Michael, F., "Infrared Spectra of Perfluoro Sulfonated Polymer Membranes", ACS. Symp., Washington DC., 139 (1982).
- Stegeman, G. I., "Wave-Guides and Fibers for Nonlinear Optics", *J. Opt. Soc. Am. Bull.*, **6**, 652 (1989).
- Xiong, Y., Jialing, L. and Hong, S., "Bubble Effect on Ion-Exchange Membranes-An Electrochemical Study", *J. Appl. Electrochem.*, **22** (1992).
- Yawatawa, D., "Ion Exchange Membrane", Tokyo, 1982.
- Yoshio, O., Takeasi, M. and Kohji, S., UK Patent Application GB 2064586 A, 1981.
- Zeldin, W. and Allcock, "Inorganic and Organic Polymers", ACS Symp., Washington DC., 360 (1988).