Korean J. Chem. Eng., **25**(5), 1151-1153 (2008)

SHORT COMMUNICATION

Electrochemical characterization of phosphonic acid cation exchange membrane prepared by plasma-induced graft polymerization

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(*Received 11 April 2007 • accepted 27 January 2008*)

Abstract−The phosphonic acid cation exchange membrane (CEM) was prepared by plasma-induced grafting of phosphonated glycidyl methacrylate, and its properties were compared with those of sulfonated acid CEM. Although ion exchange capacity and water content of the phosphonic and sulfonic acid CEMs are almost same, the electrical resistance of the phosphonic acid CEM was higher and the transport number was slightly lower compared to the sulfonic acid CEM due to weakly acidic fixed ionic charges. However, those properties of the phosphonic acid CEM were comparable with those of the membranes reported in literature. Current-voltage curves of the membranes showed that the strong fixed charge of sulfonic acid CEM induced more electroconvection of electrolyte near the surface over the limiting current density than phosphonic acid CEM with weaker fixed charge.

Key words: Cation Exchange Membrane, Phosphonic Acid, Sulfonic Acid, Plasma-induced Graft Polymerization, Current-voltage Relation

INTRODUCTION

Ion-exchange membranes have been extensively used in various separation and chemical processes such as diffusion dialysis, electrodialysis, electrolysis, and fuel cells [1]. Although various preparation methods for ion exchange membranes have been developed, the sulfonic acid (SO_3^-) and carboxylic acid (COO^-) cation-exchange membranes (CEMs) for the cation-exchange have been mainly used, but phosphonic acid (PO_3^{2-}) CEMs has been not widely used [2]. However, as concern on the CEM for selective permeation of monovalent ions has increased, the preparation of a phosphonic acid CEM has drawn attention [2-4]. For example, Sata et al. [2] prepared phosphonic acid CEMs from copolymers of chloromethylstyrene and divinylbenzene or styrene and divinylbenzene. Lee et al. [5] prepared phosphonic acid CEMs by grafting glycidyl methacrylate (GMA) onto base membrane with radiation-induced graft polymerization and introducing phosphate groups.

Plasma-induced graft polymerization (PIGP) is a method for the surface modification of polymers since only the outer surface of a polymer is activated while the bulk properties remain unchanged. When a porous membrane is used as a substrate, PIGP occurs both on the outer surface of the substrate and on the surface of the pores in the substrate [6,7]. In spite of potential of PIGP for ion exchange membrane preparation, only a few studies on preparation of ion exchange membrane with PIGP have been reported [8-10] and preparation of phosphonic acid CEMs with PIGP has been not reported. In particular, since PIGP easily occurs on thin substrate, PIGP can offer an effective method to prepare a thin ion exchange membrane with low electrical resistance. Therefore, in this paper, the preparation of phosphonic acid CEM by using PIGP is described and its properties are compared with those of sulfonic acid CEM. The phosphonic and sulfonic acid CEMs were prepared by plasma-induced grafting of phosphonated and sulfonated GMA, respectively. The prepared membranes were characterized in terms of chemical structure, ion-exchange capacity, electrical resistance, water content, transport number and current-voltage (I-V) relation.

EXPERIMENTAL

Microporous polypropylene membrane (PP, Celgard® 2500, Hoechst Celanese, Germany) was used for a substrate. Its porosity was 47%, the oval pore size 0.05 μm×0.21 μm, and the thickness 20 μm. GMA was used as a monomer to introduce a cation-exchangeable group to the PP membrane surface. The preparation method of GMA-g-PP membrane is described in a previous report [11]. The GMA-g-PP membranes were phosphonated and sulfonated by immersing into phosphonic acid and a mixture of sodium sulfite, isopropyl alcohol and water (10/15/75 wt%, respectively) at 80 °C. The preparation scheme of the phosphonated GMA-g-PP membranes (phosphonic acid CEM) and sulfonic acid GMA-g-PP membrane (sulfonic acid CEM) is illustrated in Fig. 1.

The chemical structure of the prepared membranes was confirmed by an attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, FT-IR, 460 Plus, Jasco, Japan). The electrochemical properties of the prepared membranes such as water content, ion exchange capacity, electrical resistance, transport number and I-V were determined according to a procedure described in a previous report [12].

RESULTS AND DISCUSSION

Fig. 2 shows the FTIR spectra of the base PP membrane, the GMA-g-PP membrane and the phosphonic and sulfonic acid CEMs measured by the ATR mode. In the GMA-g-PP membrane, the IR peaks corresponding to C=O and C-O of the ester bond and epoxide group

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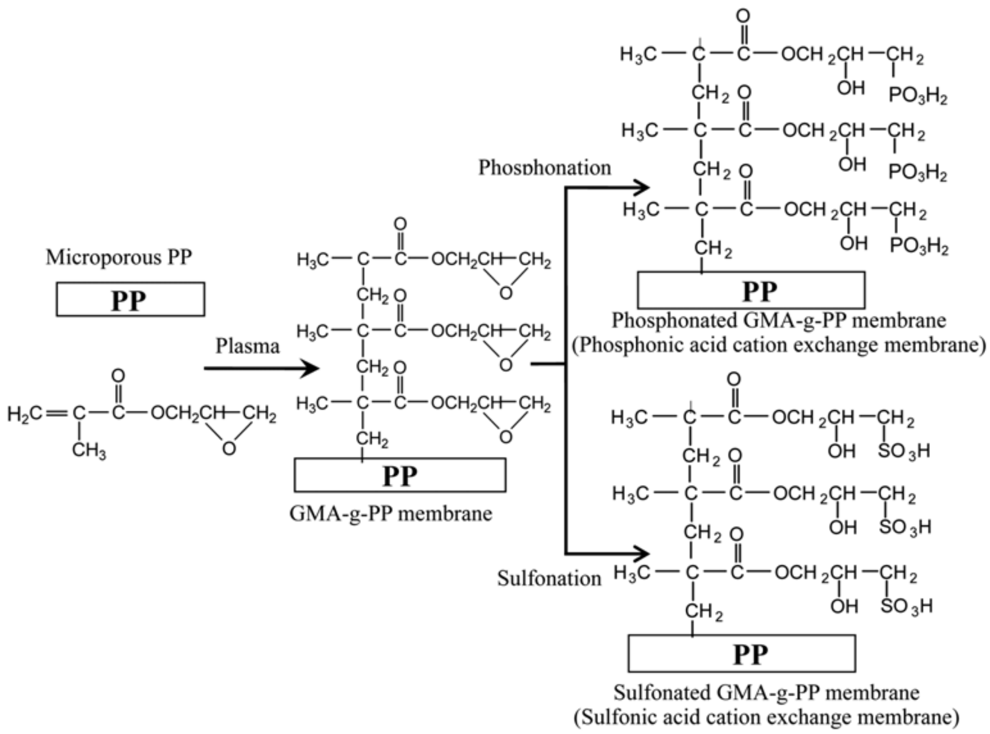

Fig. 1. Preparation scheme of phosphonic and sulfonic acid CEMs .

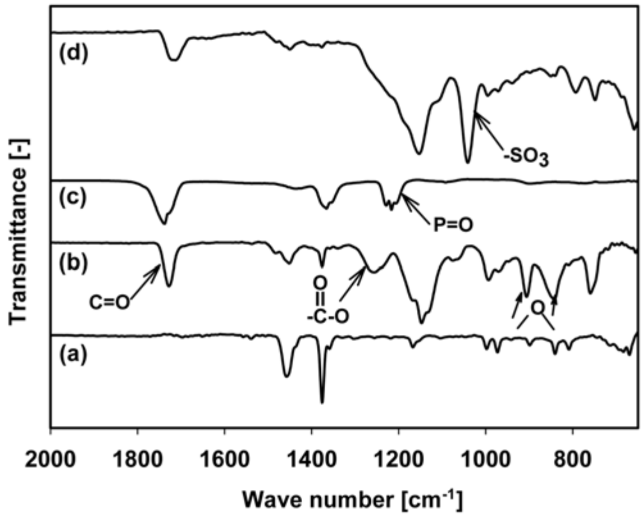

Fig. 2. ATR-FTIR spectra: (a) original PP, (b) GMA-g-PP membrane, (c) phosphonic acid CEM (d) sulfonic acid CEM.

stretching mode were observed at 1,721 cm^{-1}, at 1,272 cm^{-1}, and at 910 and 845 cm^{-1}, respectively. In the phosphonic acid CEM IR peak corresponding to P=O was observed at 1,250 cm^{-1}. In the sulfonic acid CEM, sulfonic acid groups were detected at 1,030 cm^{-1}. All ATR-FTIR peaks show that the phosphonic and sulfonic acid CEM were successfully prepared by using plasma-induced graft polymerization.

Table 1. Characteristics of phosphonic and sulfonic acid CEMs

Properties	Phosphonic acid membrane	Sulfonic acid membrane
Ion exchange capacity[a] [mmol/g]	2.8	2.9
Electrical resistance[b] [Ω cm^2]	0.68	0.45
Transport number[c] [-]	0.97	0.99
Water content[d] [%]	92	95

[a] Determined by measuring the number of ion-exchange groups in the membrane by a titration method.

[b] Measured using a clip cell and LCZ meter at 100 kHz with membranes conditioned in 0.5 M NaCl solution for 24 h.

[c] Measured by the *emf* method using a two-compartment diffusion cell and a pair of Ag/AgCl reference electrodes.

[d] Determined by measuring the weight of the wet (W_{wet}) and dry membrane (W_{dry}) (Water content=($W_{wet}-W_{dry}$)×100/ W_d

The properties of the phosphonic and sulfonic acid CEMs are listed in Table 1. The low electrical resistance of the prepared CEM was caused by the use of the thin substrate and high water content. The high water content of the membranes is due to water molecules remaining in the pores in the bulk of the substrate which still exist even after grafting reaction. Although their ion exchange capacity and water content are almost same, the electrical resistance of the phosphonic acid CEM was higher and the transport number was slightly lower compared to the sulfonic acid CEM. The high electrical resistance and the low transport number of the phosphonic acid CEM relative to the sulfonic acid CEM might be due to weakly acidic fixed ionic charges. However, the phosphonic acid CEM had the properties as good or even better as those of the membranes reported in literature [2,5]. The I-V curves of the phosphonic and sulfonic acid CEMs are presented in Fig. 3. Both curves show the typical characteristics consisting of three regions (the first region of approximately ohmic behavior, the second region showing a pla-

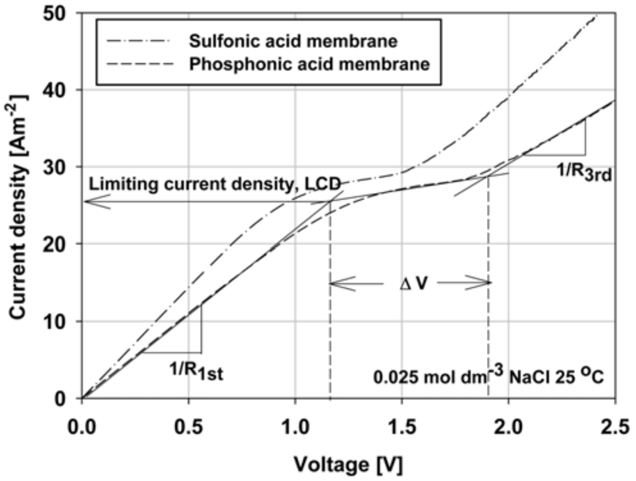

Fig. 3. I-V curves of phosphonic and sulfonic acid CEMs.

Table 2. Characteristic values of I-V curves

Characteristic value	Phosphonic acid membrane	Sulfonic acid membrane
R_{1st} [$\Omega\cdot cm^2$]	454.3	346.6
R_{3rd} [$\Omega\cdot cm^2$]	525.5	388.4
R_{3rd}/R_{1st} [-]	1.157	1.121
ΔV [V]	0.850	0.762
Limiting current density [A/m^2]	25.6	25.8

teau, and the third region of a rapid current increase governed by electroconvection) [13,14]. The characteristic values obtained from the curves of the membranes are listed in Table 2. The electrical resistances of the first region (R_{1st}) are strongly affected by the conductivity of the membrane and its ion exchange capacities [12,15]. The R_{1st} value of the phosphonic acid CEM was higher than that of the sulfonic acid, which is consistent with the measured results of the electrical resistance listed in Table 1. The limiting current density of phosphonic acid CEM was slightly lower than that of sulfonic acid CEM, indicating that in the sulfonic acid CEM higher current density can pass through the membrane area without inducing high electrical resistance or low current utilization. The resistance ratio (R_{3rd}/R_{1st}) and plateau length ΔV of I-V curves are important parameters for information on electrochemical properties of ion exchange membrane because they directly affect the power consumption and the over-limiting current density. As shown in Fig. 3 and Table 2, the R_{3rd}/R_{1st} ratio and ΔV plateau length of the phosphonic acid CEM are higher than those of the sulfonic acid CEM. The over-limiting current is explained with help of electroconvection theory proposed by Rubinstein [14,16-18]. Electroconvection is a non-gravitational free convection that is observed in macroscopic domains of the electrolyte solutions, resulting from the interactions of a self-consisting electric field with the corresponding space charge under the local electroneutrality condition. This phenomenon leads to convective mixing that could lead to an over-limiting current. In general, electroconvective effect of the ion exchange membrane causes lower R_{3rd}/R_{1st} ratios and shorter ΔV plateau length of its I-V relation. The higher R_{3rd}/R_{1st} ratios and longer ΔV plateau length of phosphonic acid CEM can be understood by the result of weakly acidic fixed ionic charges. In spite of the similar ion exchange capacity of the phosphonic and sulfonic acid CEMs, the strong charges of sulfonic acid CEM induced the stronger convection of electrolyte near the membrane surface compared to the phosphonic acid CEM. It implies that the intensity of fixed charge of CEM affects the transport phenomena of electrolyte and energy requirement for an electrically driven process.

In conclusion, the phosphonic acid CEM was successfully prepared by plasma-induced graft polymerization. The properties of the phosphonic acid CEM were comparable with those of the membranes reported in literature [2,5]. In particular, its electrical conductance may be enhanced significantly because of the use of the thin substrate. The I-V curve suggested that the prepared phosphonic acid CEM should be properly used by considering the current density of an electrically driven process because its use at a very high current density can increase the energy requirement.

REFERENCES

1. H. Strathmann, *Ion-exchange membrane separation processes*, Elsevier (2004).
2. T. Sata, T. Yoshida and K. Matsusaki, *J. Memb. Sci.*, **120,** 101 (1996).
3. T. Sata, T. Sata and W. Yang, *J. Memb. Sci.*, **206**, 31 (2002).
4. W. A. Trochimczuk, *Eur. Polym. J.*, **35**, 1457 (1999).
5. K.-P. Lee, S.-H. Choi and H.-D. Kang, *J. Chromatogr. A*, **948**, 129 (2002).
6. T. Yamaguchi, S. Nakao and S. Kimura, *Macromolecules*, **24**, 5522 (1991).
7. T. Yamaguchi, S. Nakao and S. Kimura, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 1203 (1996).
8. Y. Yokoyama, A. Tanioka and K. Miyasaka, *J. Membr. Sci.*, **43**, 165 (1989).
9. A. Tanioka, Y. Yokoyama, M. Higa and K. Miyasaka, *Colloids and Surfaces B: Biointerfaces*, **9**, 1 (1997).
10. B. Bae and D. Kim, *J. Membr. Sci.*, **220**, 75 (2003).
11. E.-Y. Choi, H. Strathmann, J.-M. Park and S.-H. Moon, *J. Membr. Sci.*, **268**, 168 (2005).
12. M.-S. Kang, Y.-J. Choi, I.-J. Choi, T.-H. Yoon and S.-H. Moon, *J. Membr. Sci.*, **216**, 39 (2003).
13. V. M. Barragan and C. Ruiz-Bauza, *J. Colloid Interf. Sci.*, **205**, 365 (1998).
14. I. Rubinstein, *Phys. Fluids*, **3**, 2301 (1991).
15. J.-H. Choi, H.-J. Lee and S.-H. Moon, *J. Colloid Interf. Sci.*, **238**, 188 (2001).
16. I. Rubinstein and L. Shtilman, *J. Chem. Soc., Faraday Trans.*, **75**, 231 (1979).
17. I. Rubinstein, *J. Chem. Soc., Faraday Trans.*, **77**, 1595 (1981).
18. I. Rubinstein, E. Staude and O. Kedem, *Desalination*, **69**, 101 (1988).