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

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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 (SO3−) and carboxylic acid (COO−) cation-exchange membranes (CEMs) for the cation-exchange have been mainly used, but phosphonic acid (PO32−) CEMs have 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 not been 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.

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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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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.

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...
Table 2. Characteristic values of I-V curves

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<tr>
<th>Characteristic value</th>
<th>Phosphonic acid membrane</th>
<th>Sulfonic acid membrane</th>
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<tbody>
<tr>
<td>$R_{1st}$ [Ω·cm²⁻¹]</td>
<td>525.5</td>
<td>388.4</td>
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<tr>
<td>$R_{3rd}$ [Ω·cm²⁻¹]</td>
<td>1.157</td>
<td>1.121</td>
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<tr>
<td>$\Delta V$ [V]</td>
<td>0.850</td>
<td>0.762</td>
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<tr>
<td>Limiting current density [A/m²]</td>
<td>25.6</td>
<td>25.8</td>
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