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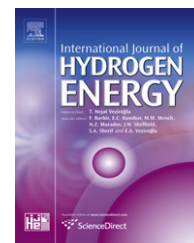
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Characterization of cation-exchange membranes prepared from poly(vinyl alcohol) and poly(vinyl alcohol-*b*-styrene sulfonic acid)

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ABSTRACT

Block-type cation-exchange membranes (CEMs) have been prepared by blending poly(vinyl alcohol) (PVA) and the polyanion poly(vinyl alcohol-*b*-styrene sulfonic acid) at various molar percentages of cation-exchange groups to vinyl alcohol groups, C_{pa}, and by cross-linking the PVA chains with glutaraldehyde (GA) solution at various GA concentrations, C_{GA}. The characteristics of the block-type CEMs were compared with random-type CEMs prepared in a previous study from the random copolymer, poly(vinyl alcohol-co-2-acrylamido-2-methylpropane sulfonic acid). At equal molar percentages of the cation-exchange groups, the water content of the block-type CEMs was less than that of the random-type CEMs. The charge density of the block-type CEMs increased with increasing C_{pa} and reached a maximum value. Further, the maximum value of the charge density increased with increasing C_{GA}. The maximum charge density value of 1.3 mol/dm³ was obtained for the block-type CEM with C_{pa} = 3.1 mol% and C_{GA} = 0.10 vol.%, which is almost two thirds of the value of a commercially available CEM [CMX: ASTOM Corp. Japan]. A comparison of the block-type and random-type CEMs with almost the same membrane resistance showed that the block-type CEMs had higher dynamic transport numbers than the random-type ones. The dynamic transport number and membrane resistance of the block-type CEM with C_{pa} = 4.0 mol% and C_{GA} = 0.10 vol.% were 0.96 and 4.9 Ω cm², respectively.

1. Introduction

Cation-exchange membranes (CEMs) have been used for various industrial purposes [1] such as separation of environmental polluting metal ions from hard water [2], chlor-alkali electrolysis [3], fuel cells [4–8], electrodialytic concentration or desalination of electrolyte solutions [9], and continuous hydrogen production in electro-electrodialysis systems [10–12]. At present, the vast majority of commercially available

CEMs for electrodialysis include styrene-co-divinylbenzene matrices. The drawbacks of this type of membrane are as follows: it is difficult to control the membrane structure because it undergoes copolymerization and cross-linking processes simultaneously, and the cost of membrane preparation is high. Recently, many novel ion exchange membranes have been developed to overcome these problems [13,14]. Ion exchange membranes can be prepared by mixing water-soluble base polymers and a polyelectrolyte and then cross-

linking the base polymer. The membrane thus obtained consists of a semi-interpenetrating network (semi-IPN) structure in which the polyelectrolyte chains are immobilized in the cross-linked network polymer matrix. The ion exchange capacity of the membrane can be easily controlled by changing the ratio of water-swollen base polymer to polyelectrolyte. Poly(vinyl alcohol) (PVA) is one of the most popular water-soluble base polymers. 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 resistance [15−18]. Many PVA-based CEMs have been developed for use in direct methanol fuel cells because of the excellent methanol barrier properties of PVA [19−26]. Various kinds of PVA-based CEMs with a semi-IPN structure have been prepared by blending PVA with a polyanion such as poly(styrene sulfonic acid) [27], poly(acrylic acid) [19], poly(styrene sulfonic acid-co-maleic acid) [20], sulfosuccinic acid [21], sulfonated poly(ether ether ketone) [22], sulfated β-cyclodextrin [23], titanium oxide nanotubes and poly(styrene sulfonic acid) [24], montmorillonite and poly(styrene sulfonic acid) [25]. One of the potential disadvantages of CEMs with a semi-IPN structure is that they show low long-term stability in aqueous solutions owing to the dissolution of the un-crosslinked water-soluble polyelectrolytes from the network into the solution. To overcome this disadvantage, CEMs with an IPN structure have been prepared by blending PVA and PVA-based polyanions such as the random copolymer of vinyl alcohol and 2-methyl-1-propanesulfonic acid (AMPS) groups [26,28−30]. In CEMs with an IPN structure, the chains of PVA and the PVA-based polyanion are cross-linked with each other; hence, these CEMs show higher long-term stability in water than CEMs with a semi-IPN structure. However, the counter-ion selectivity of CEMs with an IPN structure in previous study [30] is much lower than that of commercially available CEMs.

The aim of this study is to obtain a PVA-based CEM with higher counter-ion selectivity than that of previously reported PVA-based CEMs. To this end, CEMs with an IPN structure (hereafter referred to as PVA-*b*-PSS) have been prepared by blending PVA with the PVA-based polyanion, poly(vinyl alcohol-*b*-styrene sulfonic acid), which is a block copolymer of vinyl alcohol and sodium p-styrenesulfonate groups. The chemical structure of PVA-*b*-PSS is shown in Fig. 1. Because PVA is a semi-crystalline polymer, the crystalline region acts as a physical cross-link point, and hence, the water content of the CEM, which considerably influences the counter-ion selectivity, electrical resistance, and mechanical properties of the membrane, depends on the degree of crystallinity. The crystallinity of the PVA region within a CEM prepared from the
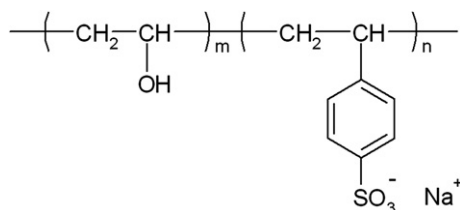
block copolymer is higher than that of a CEM prepared from the random copolymer, because the cation-exchange groups of the random copolymer chains disturb the formation of the crystal. Thus, the former has a higher counter-ion permselectivity than the latter. We have investigated the differences in the following ionic transport properties between PVA-based CEMs prepared from the two different copolymers: charge density, membrane resistance, and transport number.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA, 100% hydrolyzed, average Mw = 198,000) and poly(vinyl alcohol-*b*-styrene sulfonic acid) (PVA-*b*-PSS, 100% hydrolyzed) were obtained from Kuraray Co., Ltd. Glutaraldehyde (GA) (25 wt.% solution in water) was of analytical grade and was obtained from Wako Pure Chemical Industries. Sulfuric acid and sodium sulfate were of analytical grade and were obtained from Nakarai Tesque.

2.2. Preparation of block-type CEMs

Self-standing base membranes, BP-X (X = 1−6), for block-type CEMs were prepared by casting an aqueous solution of a mixture of PVA and PVA-*b*-PSS on a plastic plate and then drying the mixture over a hot stage (NISSIN, NH-45N) overnight at 50 °C. The thickness of the base membranes was ca. 0.1 mm. The weight percentage of PVA-*b*-PSS to PVA in the mixture solution was varied to control the molar percentage of cation-exchange groups to vinyl alcohol groups (C_{pa}) in BP-X, as shown in Table 1. The block-type CEMs were prepared by annealing BP-X at 180 °C for 30 min under vacuum to induce physical cross-linking between the PVA chains. Chemical cross-linking was induced by immersing the membranes in an aqueous solution of various concentrations of GA, 0.05 mol/dm³ of H_2SO_4 (pH = 1), and 2.0 mol/dm³ of Na_2SO_4 at 25 °C for

Fig. 1 − Chemical structure of polyanion, PVA-*b*-PSS: poly(vinyl alcohol-*b*-styrene sulfonic acid).

Table 1 − Molar percentage of cation-exchange groups, C_{pa}, and ion-exchange capacity, IEC, of base membrane: membranes prepared from block copolymers, BP-X (X = 1−6); and membrane prepared from random copolymer, RP-1.

Sample	C_{pa} (mol%)	IEC (meq/g-dry CEM)
BP-1	1.8	0.28 (0.36[a])
BP-2	2.2	0.39 (0.44)
BP-3	2.6	0.48 (0.51)
BP-4	3.1	0.54 (0.58)
BP-5	3.5	0.58(0.65)
BP-6	4.0	0.59 (0.65)
RP-1[b]	3.2	0.62 (0.78)
CMX[c]	−	2.0

a Results calculated from the molar percentage of the cation-exchange groups.
b One of the random copolymers used in Ref. [30].
c A commercially available CEM [Neosepta CMX, ASTOM Corp. Japan].