CHEMISTRY LETTERS, pp. 953-954, 1990.

A Novel Ultra-thin Cation-exchange Membrane Prepared by Plasma Polymerization

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An ultra-thin membrane containing sulfonic ester group was prepared by plasma polymerization of methyl benzenesulfonate and 1,3-butadiene. The sulfonic ester group of the plasma polymer was transformed to lithium sulfonate group by treatment with lithium iodide. The resultant ultra-thin cation exchange membrane was about 0.2 μm thick and pinhole-free, and showed high K^+ ion transference number of 0.92 in the aqueous KCl system and resistance of 1.3 $\Omega\,cm^2$.

Ion-exchange membranes have received considerable attention owing to their wide application in electrochemistry. Since perm-selectivity of the ion-exchange membrane is governed by Donnan equilibrium at the interface layer between the ion-exchange membrane and a contacting solution, the thinner the ion-exchange membrane, the lower the membrane resistance of the ion-exchange membrane without changing the perm-selectivity is. Plasma polymerization is a useful method to deposit a uniform, ultra-thin polymer film on various substrates. This paper reports the preparation of an ultra-thin cation-exchange membrane containing sulfonic acid group by plasma polymerization of 1,3-butadiene and methyl benzenesulfonate, followed by the hydrolysis of the resulting sulfonic ester to sulfonic acid.

The apparatus for the plasma polymerization has been described elsewhere.[1] The system consists of a glass reactor equipped with inner disk electrodes connected to an RF supply (13.56 MHz). Substrates were placed between the electrodes. Glass plates deposited with gold and porous poly(propylene) films, Duragard®[2] 2400 (average pore size: 0.02x0.2 μm), were used as substrates.

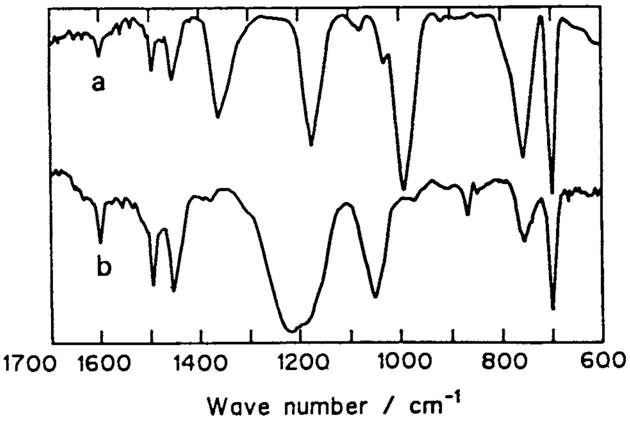

Fig. 1. IR spectra of plasma polymer (a) before and (b) after treatment of LiI.

Argon [10 cm^3(STP)/min], 1,3-butadiene [8 cm^3(STP)/min], and methyl benzenesulfonate [0.16 cm^3(STP)/min] were introduced into the glass reactor. The pressure in the reactor was maintained at 0.07 Torr. Under these conditions, RF power of 30 W was turned on.

Table 1. Electrochemical properties of plasma polymer and Nafion 117

	t_K a)	t_K b)	Ionic conductivity $S\ cm^{-1}$	Resistance $\Omega\ cm^2$
Plasma polymer	0.92	0.88	1.5×10^{-5}	1.3
Nafion 117	0.97	0.93	4.6×10^{-3}	3.9

a) t_K estimated by 0.01 mol dm^{-3}/0.005 mol dm^{-3} KCl concentration cell.
b) t_K estimated by 0.01 mol dm^{-3}/0.1 mol dm^{-3} KCl concentration cell.

The resultant plasma polymer layer containing sulfonic ester group was about 0.2 μm thick.

The plasma polymer films were soaked in saturated LiI/ butanol solution at 40 °C for 2 h in order to hydrolyze sulfonic ester into lithium sulfonate.

Figure 1 illustrates IR spectra of the plasma polymer before [Fig. 1a] and after [Fig. 1b] LiI treatment. The two absorption peaks at 1360 ,1175, and one at 990 cm^{-1} in Fig. 1a, which were assigned, respectively, to asymmetrical and symmetrical S=O stretching vibration modes and S-O-C stretching vibration mode of the sulfonic ester group,$^{3)}$ completely disappeared in Fig. 1b. Furthermore, two new peaks of 1210 and 1050 cm^{-1} appearing in Fig. 1b were attributed to the lithium sulfonate group. These facts suggest that the sulfonic ester groups in the plasma polymer reacted with LiI to yield lithium sulfonate.

SEM observation revealed that the plasma polymer was pinhole-free and uniform in film thickness. The transference number of K^+ of the plasma polymer layer deposited on Duragard after LiI treatment was measured by the concentration cell in the aqueous KCl system. Since Duragard is hydrophobic, the membrane resistance and ionic conductivity were measured in 0.5 mol dm^{-3} H_2SO_4 (H_2O/ethanol = 1/1) solution by a DC current method.$^{4)}$

The K^+ ion transference number (t_K), ionic conductivity, and membrane resistance of the plasma polymer after LiI treatment and commercially available cation-exchange membrane, Nafion® 117 $^{5)}$ (thickness: 180 μm) are summarized in Table 1. The t_K value of Duragard was 0.49. On the other hand, the plasma polymer exhibited the t_K as high as 0.92, which is slightly lower than that of commercially available cation exchange membrane, Nafion® 117. The specific ionic conductivity of the plasma polymer film is still lower than Nafion® 117. However, the practical membrane resistance of the plasma polymer film is lower than that of Nafion® 117 because of its low thickness.

References

1) Z. Ogumi, Y. Uchimoto, and Z. Takehara, J. Electrochem. Soc., 136, 625(1989).
2) "Duragard" is a registered trade mark of the Polyplastics Co., Inc.
3) R.M. Silverstein, G.C. Bassler, and T.C. Morril, "Spectrometric Identification of Organic Compounds," 4th ed., John Wiley & Sons, N.Y. (1981).
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5) "Nafion" is a registered trade mark of the Du Pont de Nemours and Co., Inc.

(Received February 9, 1990)