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A Novel Thin Film of Anion Exchanger Prepared by Plasma Polymerization

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A novel ultra-thin film of an anion exchanger has been prepared by plasma-polymerization of 4-vinylpyridine followed by quaternarization. The resulting anion exchange film exhibits a chloride ion transference number of higher than 0.8 in the aqueous KCl system.

Ion-exchange membranes have been used in a variety of electrochemical applications, including, among others, water electrolyzers,[1] sensors,[2] redox-flow batteries,[3] and fuel cells.[4] Perm-selectivity of the ion exchange membrane is governed by Donnan equilibrium at a very thin interface region between ion-exchange membrane and solution.[5] Therefore, the thinner the ion-exchange membrane, the lower the membrane resistance of the ion-exchange membrane keeping the ion selectivity unchanged. However, it is not easy to prepare thin pinhole-free ion-exchange membranes by a conventional technique. Plasma polymerization is a useful method for preparing such thin films. We have modified a surface of cation exchange membrane, Nafion®,[6] using plasma polymerization technique.[7,8] This paper reports on the preparation of an ultra-thin (~0.2 μm) anion exchanger film on a substrate by plasma-polymerized 4-vinylpyridine (4-VP) followed by quaternarization ; the resulting anion exchange membrane exhibits of a chloride transference number of greater than 0.8 in an aqueous KCl system.

The system for plasma polymerization consisted of a glass reactor equipped with capacitively coupled inner disk electrodes connected to an RF supply (13.56 MHz), a monomer inlet, a Pirani gauge, and a vacuum pump.[8] Substrates were placed at 2 cm downstream from the bottom edge of the electrodes. 4-VP was selected as a monomer. The monomer vapor and a plasma assist gas (Ar, 10 cm^3 (STP)/min) were introduced separately. While keeping gas flow constant, the reactor was maintained at desired pressure. Then plasma polymerization was initiated by applying RF power of 50 W between the electrodes. Glass plate deposited with gold and porous poly(propylene) film, Duragard®[9] 2400 (average pore size: 0.02x0.2 μm), were used as substrates.

The plasma membranes were characterized by FT-IR spectrometry using a reflection method. The transference number of Cl^- was measured by the concentration cell in the aqueous KCl system.

IR spectra of plasma polymers showed that the absorption peaks of N-H vibration and C≡N vibration and that the peaks were broadened. These facts indicate the cleavage of pyridine ring of the 4-VP during the plasma polymerization process. On the scale of scanning electron micrograph (resolution: ~50nm), the plasma polymer film was free from pinholes and of uniform thickness.

The amino and pyridine groups of the plasma polymer were quaternarized by using 1-bromopropane (1-BP). The polymer films were soaked in 1% 1-BP/propylene carbonate (PC) solution at 50 °C for 48 h. After soaking, the films were washed with PC to remove excess 1-BP from the films. These films treated thus were then dried under reduced pressure (10^{-1} Pa) in order to evaporate PC.

The transference number of Cl^- in the aqueous KCl system through quaternarized plasma polymer is summarized in Fig.1, together with the transference number of Duragard® used as a substrate. Cl^- transference number of the untreated Duragard® was 0.51. On the other hand, the quaternarized plasma polymer exhibited the value over 0.8 at low polymerization pressure. The transference number decreases with increasing pressure. Since decreasing the pressure enhances electron temperature, the cross-linking process becomes significant at low pressure.[10] The cross-linking decreases water content of quaternarized plasma polymer. Therefore, the film prepared at a low pressure is lower in water content than that prepared at a high pressure. The low water content leads to a high Cl^- transference number.

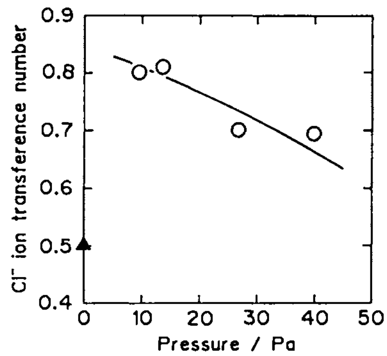

Fig.1. Variation of Cl^- transference number in the K^+-Cl^- system with preparation pressure for quaternarized plasma-polymerized 4-VP deposited on Duragard®.
RF power: 50 W
Ar flow rate: 10 cm^3(STP)/min
4-VP flow rate: 5 cm^3(STP)/min
▲ : Duragard®

The anion exchanger film by plasma polymerization was strongly adherent on various substrates, and was pinhole-free and of uniform thickness. Therefore, the film is promising for a wide range of electrochemical applications.

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