Anti-organic Fouling Properties of Composite Membranes Prepared from Anion Exchange Membranes and Polypyrrole

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The composite membrane prepared from commercial anion exchange membranes and polypyrrole showed excellent anti-organic fouling properties in electrodialysis.

One unsolved problem in electrodialysis is organic fouling of ion exchange membranes, especially anion exchange membranes. Namely, when electrodialysis is carried out in the presence of large organic ions, the electric resistance of the membrane increased markedly during the electrodialysis. There have been various attempts to solve this problem: formation of a layer of opposite charge to that of the ion exchange groups of the membrane on the membrane surface to prevent permeation of the foulant ions;[1] making the structure of the membrane loose so that ions could permeate through easily;[2] use of a neutral membrane instead of an anionic membrane.[3] Although these methods solved some of the problems, new methods are needed because various large organic ions are harmful to ion exchange membranes.

Conducting polymers such as polypyrrole, polyaniline, polythiophene *etc.* have recently been examined as materials for separation membranes. For example, the composite membranes prepared from anion exchange membranes and polypyrrole showed properties with high acid retention in electrodialysis;[4] the composite membranes from ion exchange membranes and polypyrrole were effective for the dehydration of alcohol–water mixture by the pervaporation method;[5] such membranes have been studied as switchable gate membranes.[6] In this work, anti-organic fouling properties of the composite membrane prepared from an anion exchange membrane and polypyrrole in electrodialysis are reported.

The anion exchange membrane used was NEOSEPTA AM-1 [thickness: 0.13 mm; electric resistance: 1.7 Ω cm^2; ion exchange capacity: 1.86 mequiv. g^{-1} dry membrane; water content: 0.25; reinforced by poly(vinyl chloride) fabric], made by Tokuyama Soda Co., Ltd. The membrane is a styrene–divinylbenzene copolymer having quaternary ammonium groups as anion exchange groups. Pyrrole was used as the monomer to prepare the composite membrane, and was polymerized by use of Fe^{3+}. In this work, after the anion exchange membrane (Cl^- form) had been equilibrated with concentrated $FeCl_3$ solution, the membrane was immersed in an aqueous solution of pyrrole to polymerize the pyrrole by Fe^{3+} absorbed in the membrane. When the anion exchange membrane equilibrated with the pyrrole solution is immersed in the $FeCl_3$ solution, polypyrrole exists on the membrane surface as layers.[7] When pyrrole is polymerized by Fe^{3+} absorbed in the membrane, polypyrrole is present homogeneously in the membrane phase and the amount of polypyrrole in the membrane can be controlled by the amount of absorbed Fe^{3+} ions. The composite membrane obtained had sufficient mechanical strength.

The composite membrane was prepared as follows: after the anion exchange membrane (Cl^- form; 7.0 × 7.0 cm) had been equilibrated with aqueous $FeCl_3$ (2.09 mol l^{-1}), the membrane was immersed in aqueous pyrrole (0.745 mol l^{-1}) without washing and stirred for 16 h. Various concentrations of $FeCl_3$ solution were examined: 0.74, 1.85 and 2.09 mol l^{-1}. When the concentration of $FeCl_3$ in the solution in which the anion exchange membrane had been equilibrated was lower than 2.09 mol l^{-1}, protection from organic fouling was not sufficient for this NEOSEPTA AM-1 membrane. The membrane and solution turned black immediately on immersion of the membrane in the pyrrole solution. After polymerization, the membrane was removed, washed with pure water, equilibrated alternately in 1.0 mol l^{-1} hydrochloric acid and aqueous 0.5 mol l^{-1} ammonia, and stored in 0.0833 mol l^{-1} aqueous sodium chloride.

Anti-organic fouling properties of the composite membrane were studied from the change in voltage drop across the membrane during electrodialysis. Electrodialysis was carried out in a two-compartment cell (effective membrane area: 2.0 × 2.0 cm) with silver–silver chloride electrodes. The anode compartment was filled with 120 cm^3 of 0.0833 mol l^{-1} aqueous sodium chloride and the cathode compartment with a mixture of 0.0833 mol l^{-1} sodium chloride and 1.67 × 10^{-3} mol l^{-1} sodium n-dodecyl sulfate. Electrodialysis was carried out at a current density of 5 mA cm^{-2} at 25.0 °C with vigorous agitation immediately after both compartments had been filled with the solutions. The cell had two silver–silver chloride wire probe electrodes close to the membrane (about 2 mm apart) connected to an *X–t* recorder (internal resistance: 2 MΩ). The change in the voltage drop across the membrane was recorded during electrodialysis. After electrodialysis, the concentration of chloride ions in the anode compartment was analysed by the Mohr method, and the current efficiency was calculated from the change in concentration of chloride ions and the amount of electricity as measured by a digital coulometer.

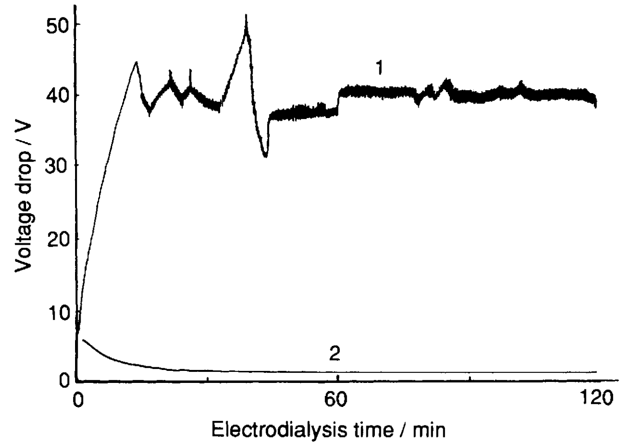

Fig. 1 Change in voltage drop across (1) the anion exchange membrane NEOSEPTA AM-1, and (2) the composite membrane prepared from NEOSEPTA AM-1 and polypyrrole during electrodialysis (in the presence of sodium n-dodecyl sulfate)

Fig. 1 shows the change in the voltage drop during electrodialysis using the anion exchange membrane NEOSEPTA AM-1, and the composite membrane from NEOSEPTA AM-1 and polypyrrole when a mixed solution containing 0.0833 mol l^{-1} sodium chloride and 1.67 × 10^{-3} mol l^{-1} sodium n-dodecyl sulfate was electrodialysed at a current density of 5 mA cm^{-2}. The voltage drop with NEOSEPTA AM-1 increased immediately after the electrodialysis had started, and was then unstable, oscillating with a short cycle. The electric resistance of the membrane increased from 1.7 Ω cm^2 to about 8000 Ω cm^2. In contrast, the voltage drop across the composite membrane decreased gradually in the initial stage of electrodialysis, possibly as a result of polypyrrole of low molecular mass being removed from the membrane. However, the voltage across the membrane never increased during the electrodialysis. The concentration of sodium n-dodecyl sulfate increased tenfold to 1.67 × 10^{-2} mol l^{-1}. The voltage drop across the membrane increased slightly during 240 electrodialyses. Similar experiments using sodium n-dodecyl benzenesulfonate under the same measuring conditions (1.67 × 10^{-3} mol l^{-1}) also showed no increase in voltage drop across the composite membrane, although that for NEOSEPTA AM-1 alone increased markedly.

After electrodialysis, the anolyte was analysed and the current efficiency calculated. The current efficiency for all the composite membranes was >98% and did not decrease compared with that for NEOSEPTA AM-1.

In general, anionic surface-active agents are absorbed selectively on anion exchange membranes. Since the composite membrane is covered with polypyrrole, which is a weakly basic polymer, selective absorption of the agents on the membrane will be depressed. Also, pyrrole leads to a rigid and tight polymer, polypyrrole, through which n-dodecyl sulfate ions cannot cross whereas chloride ions can. In order to prepare a similar composite membrane, *m*-phenylenediamine was impregnated in the same anion exchange membrane and condensed with formaldehyde in the presence of hydrochloric acid. The voltage drop across the composite membrane increased greatly in spite of the formation of a weakly basic anion-exchangeable polymer network of the membrane surface and of a crosslinked network in the membrane matrix. Although the mechanism of anti-organic fouling is not clear, permeation of large organic ions through the composite membrane would be depressed by sieving of the ions by the membrane network or by induced charges in the membrane during electrodialysis.

Finally, composite membranes were prepared by use of other NEOSEPTA anion exchange membranes: NEOSEPTA AM-2, AM-3 and AFN, and a similar protection from organic fouling was confirmed.

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