Investigation and Thin Film Formation of a Non-Swelling Vinyl Polymer Membrane for Recovering High-Concentration Mg²⁺ from Brackish Water

Hidenori Ohashi

Tokyo University of Agriculture and Technology

Summary

As one of the most valuable resources and the lightest among practical metals, the demand for Mg is expected to increase significantly. A promising source of MgCl₂, which is a major ingredient for Mg, is the wastewater produced during electrodialysis for salt production. To obtain MgCl₂ at high concentrations, an efficient separation membrane for Mg^{2+} and Na^+ is required. For this purpose, fabrication of a membrane with high content of immobilized anions that can strongly interact with cations is necessary. In the present study, a membrane with a high density of immobilized anions was prepared using atmospheric pressure induced plasma graft polymerization; a polymer with sulfonic acid side groups (immobilized anions) was grafted onto the pores of a mechanically strong polyimide porous membrane. The resultant membrane did not swell, maintaining its anion concentration inside even in water.

To separate Mg^{2+} and Na^+ , Na^+ should permeate through the membrane selectively. With the cooperation of The Salt Industry Center of Japan, the membrane resistance and NaCl electrodialysis performance were measured. The resistance of the fabricated membrane was around $0.2-0.4 \ \Omega \cdot cm^2$, which was lower than conventional membranes. However, the NaCl electrodialysis performance was found to be low. It suggested that, Cl⁻ ion was permeating along with Na⁺, which was not desirable. To verify this hypothesis, the transport numbers of Na⁺ and Cl⁻ were measured. It was confirmed that the transport number of Na⁺ was lower than that of conventional membranes, indicating that the current grafting rate was insufficient to fully fill the pores with sulfonic groups. Increment of the grafting rate is expected to enhance the Na⁺ transport number and lead to an efficient separation of Mg²⁺ and Na⁺.

Another critical issue for increasing the processing rate is the "thinning of the separation membrane." A typical thickness of conventional membranes are tens of µm. Ultralong carbon nanotubes (CNTs) with high tensile strength was fabricated. By dispersing ultralong CNTs using electrochemical oxidation and fabricating membranes through filtration, self-standing membranes with a thickness of less than 2 µm were fabricated. These membranes exhibited a permeability of approximately 2400 LMH/bar, indicating sufficiently porous structure of the membranes.