



Development of selective electro dialysis membranes for water reuse and desalination

Energy and resource recovery



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Background

Selective separation of monovalent ions *versus* multivalent ions is important for desalination, agricultural irrigation, and industrial salt production. However, the selective membranes currently in the market are costly and challenged during desalination of unconventional waters with high fouling and scaling potential. The project goal is to develop low-cost monovalent permselective membranes for improved water reuse and desalination. This study is focused on characterization of the membrane and coating lay to investigate the mechanisms and the factors affecting the separation performance using different types of synthetic and real waters.

Approach

Innovative monovalent permselective cation exchange membrane (CEM) - CR671 was developed by coating a polyethyleneimine layer onto the normal grade membrane CR67 manufactured by the Suez (previously General Electric Water & Process Technologies), which is an homogeneous negatively charged CEM.

During membrane coating, the CR67 membranes with pre-fixed glycidyl methacrylate were submerged in 500 mg/L polyethyleneimine solution at 40 °C for 24 hours, which allowed a reaction between amines groups of polyethyleneimine and epoxy groups on the surface of CR67 membranes to generate the desired coating layer (Figure 1).

Advanced analytical approaches were employed to characterize the physicochemical and electrochemical properties of the CEMs to elucidate the mechanisms of permselectivity, including zeta-potential analysis and electrochemical impedance spectroscopy (EIS).

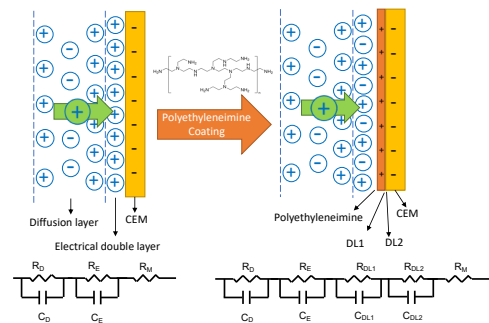


Figure 1. Modification of CR67 with polyethyleneimine (PEI) coating to create CR671. Representation of the two parts of the depletion layer, the electrical double-layer, the diffusion boundary layer, and the CEM.

Results

Membrane surface charge

- As a CEM, the CR67 surface initially carried negative charge (Figure 2a), e.g., -4.9 mV at neutral pH.
- Zeta-potential of the membrane became less negative with the increasing pH of the electrolyte solution (curve CR67-1 in Figure 2a).
- Membrane surface reached isoelectric point at pH 9.0.
- During the titration from pH 12 back to neutral using HCl solution, the zeta-potential of the CR67 (curve CR67-2 in Figure 2a) was more negative than the previous titration.
- The CR671 was positively charged (7.9 mV) at neutral pH due to the cationic polyethyleneimine coating.
- Zeta-potential of the membrane increased with the increasing pH of the electrolyte solution (curve CR671-1 in Figure 2b).
- When the pH of the electrolyte solution was reduced from pH 12 to neutral, the zeta-potential of the CR671 became negative at pH lower than 10 (curve CR671-2 in Figure 2b).

The latter curve of the CR671 (curve CR671-2 in Figure 2b) approached close to that of the CR67 with IEP of 9.9 (CR67-2 curve in Figure 2a), suggesting the disappearance or the bond breakage of the polyethyleneimine coating on the CR671 membrane surface.

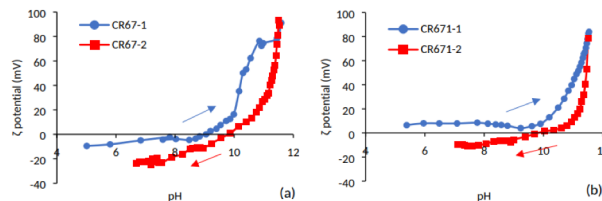


Figure 2. Zeta-potential of (a) the normal grade CR67 and (b) the selective CR671 membranes. - 1 refers the membrane zeta-potential measured with pH increase from neutral to 12 titrated using 0.1 M NaOH solution; -2 refers the zeta-potential measured after the pH of the electrolyte solution achieved 12, then gradually titrated to neutral using 0.1 M HCl solution.

EIS Analysis

For the CR67, the impedance barely changed over the entire frequency range of 0.1 Hz to 378 2,000 Hz (Figure 3a), while the phase shift and capacitance changed slightly at low frequency (0.1 379 Hz -1 Hz) (Figure 3b and 3c).

The impedance and capacitance increased significantly at low to medium frequency (0.1Hz-10 Hz), the phase shift of the CR671 started to increase from 100 Hz. The EIS result suggests that there is a sub-structure within the system, thus, the polyethyleneimine layer changed the electrical behavior of the CR671 membrane from an electrical homogeneous mono-layered system to a multi-layered system.

Results, cont.

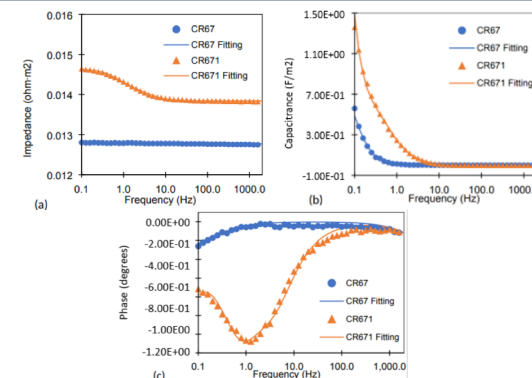


Figure 3. Responses of (a) impedance, (b) capacitance, and (c) phase with the function of frequency for the selective CR671 and the normal grade CR67.

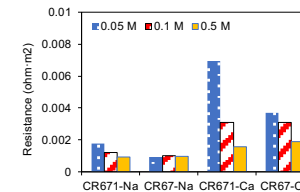


Figure 4. The membrane resistance of Maxwell-Wagner model fitting for the CEMs in solutions with different electrolytes and ionic strength.

Conclusions

- The enhanced monovalent permselectivity due to polyethyleneimine coating on the CEMs was investigated and characterized.
- Zeta-potential analysis revealed the positively charged CR671 surface and the impact of solution pH on the chemical stability of polyethyleneimine coating.
- EIS indicated larger impedance for the CR671, corresponding to lower total cation flux during electro dialysis.
- Different electrolytes and ionic strength on EIS revealed the CR671 presented higher resistance to Ca²⁺ than Na⁺, supporting the pilot testing results that the CR671 improved the Na⁺ removal by selectively rejecting divalent cations. However, the difference became less significant with increasing ionic strength, suggesting the monovalent permselectivity may decrease during treatment of higher salinity water.

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