

# Physicochemical and Electrochemical Characterization of Cation-Exchange Membranes Modified with Polyethyleneimine for Elucidating Enhanced Monovalent Permselectivity of Pilot-Scale Electrodialysis Testing

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Monovalent permselective cation-exchange membrane (CEM) CR671 was developed by coating polyethyleneimine onto the normal grade CEM CR67. Pilot-scale electrodialysis of brackish groundwater demonstrated excellent monovalent permselectivity of the modified CR671 as compared to the normal grade CR67. Both normal grade and monovalent permselective membranes achieved same desalting efficiency. The monovalent selectivity of the CR671 was demonstrated up to 9 times better than the CR67 during pilot-scale electrodialysis.

Advanced analytical approaches were employed to characterize the physicochemical and electrochemical properties of the CEMs to elucidate the mechanisms of permselectivity. Ion-exchange capacities of the CR671 and CR67 were measured to be 2.0 and 2.1 meq/g dry membrane, respectively. Zeta-potential analysis revealed that the CR671 surface was positively charged because of polyethyleneimine coating. Electrochemical impedance spectroscopy (EIS) data indicated larger impedance for the CR671 and fitted well to the Maxwell-Wagner model, which provided an equivalent electric circuit for the CEMs, as well as indication of the existence of polyethyleneimine layer. The time constants of different ions transporting through polyethyleneimine modification layer were calculated based on the EIS responses. The results revealed the polyethyleneimine modification layer led to longer transport time for  $\text{Ca}^{2+}$  ions through the CR671 than for  $\text{Na}^{+}$  ions, supporting the pilot-scale testing results that the CR671 improved the  $\text{Na}^{+}$  removal by selectively rejecting  $\text{Ca}^{2+}$  ions.

However, the difference in ion transport time became less significant with increasing ionic strength of the feed water. The EIS results suggest the monovalent permselectivity decreased during treatment of higher salinity water, supporting the finding that the CR671 exhibited higher monovalent permselectivity during electrodialysis of brackish groundwater than reverse osmosis concentrate in which the salt concentration was 5.7

times higher than the brackish groundwater. This study demonstrates that ion transport time constant is a better indicator for permselectivity of modified ion-exchange membranes than electrical resistance measured by EIS.