

Supporting Information

Controlled metal loading on poly(2-acrylamido-2-methyl-propane-sulfonic acid) membrane by ion-exchange process to improve electro-dialytic separation performance for mono/bi-valent ions

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Section S1. Instrumental analysis

FT-IR spectra of dried sample were recorded by KBr technique with a spectrum GX series 49387 spectrometer in the range of 4000-400 cm⁻¹ in the range.

Thermal degradation and stability of the membranes were investigated using a thermogravimetric analyzer (TGA) (Mettler Toledo TGA/SDTA851 with star software) under a nitrogen atmosphere at a heating rate of 10 °C/min from 30 to 600 °C. Differential scanning calorimetry (DSC) measurements were carried out in a temperature range of 30 to 300 °C. The samples of about 10-20 mg were loaded into aluminium pans and then heated to the desired temperature at a heating rate of 5 °C/min. The empty aluminum pan was used as a reference during the course of the experiment. The dynamic mechanical stability (DMA) of the composite membranes was evaluated by using a dynamic mechanical analyzer (Mettler Toledo; DMA) 861c instrument with star^c software under a nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 400 °C.

Surface morphology of membranes were studied by scanning electron microscopy (SEM) using a LEO Instruments (Kowloon, Hong Kong) microscope after the gold sputter coatings on desired membrane samples.

Section S2. Membrane water uptake, contact angle measurements and ion exchange capacity

The membrane samples were soaked in the deionized water at room temperature for 24 h. The hydrated polymer membranes were taken out, and the excess water on the surface was removed by wiping with a tissue paper and weighed immediately (denoted by the variable W_{wet}). The wet membrane then was dried under vacuum at a fixed temperature of 80 °C until a constant dry weight was obtained (W_{dry}). The water uptake WU was calculated with the following equation:

$$\text{water uptake } (\varphi_w \%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

where W_{wet} and

W_{dry} are the mass of the membrane under wet and dry conditions.

The contact angle with water for the prepared membranes was measured using a contact angle goniometer at 25 °C. The contact angle θ , was estimated from the following equation:

$$\theta = \cos^{-1}[(\cos \theta_a + \cos \theta_r/2)] \quad (2)$$

The ion exchange capacity (IEC) of the membranes was measured by the classical titration method. Pieces of the membrane samples with known dry weight were equilibrated in 1.0 M HCl for converting all charge sites into the H⁺ form. The membranes were then washed thoroughly with deionized water to remove the last trace of acid. Then, they were equilibrated in a known volume of 1.0 M NaCl for 24 h to replace the H⁺ by Na⁺ ions. The remaining solution was titrated against 0.1 M NaOH solution using phenolphthalein as an indicator.

The IEC value (mequiv/g) is obtained from following equation:

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}} \quad (3)$$

where V_{NaOH} is the volume of NaOH solution, C_{NaOH} is the concentration of the NaOH solution and W_{dry} is the weight of dry membrane.

S3. Counter-ion transport numbers and membrane permselectivity.

For the estimation of membrane permselectivity (P_s), membrane potential measurement was carried out in equilibrium with NaCl solutions of 0.10 and 0.01 M concentration. For membrane potential measurements, the ratio of salt concentrations on the higher to lower side (C_1/C_2) was kept constant at 10.0 while $\Delta C/C_s = 1.60$, where C_1 and C_2 are the electrolyte concentrations, $\Delta C = C_1 - C_2$, and $C_s = (C_1 + C_2)/2$. Counter-ion transport number (t_-^m) across the membranes was estimated by membrane potential according to following Eq.

$$E^m = (2t_+^m - 1) \frac{RT}{nF} \ln \frac{a_1}{a_2} \quad (4)$$

where a_1 and a_2 are the activities of electrolyte solutions contacting two surfaces of the membrane, R is the gas constant, T is the absolute temperature, n is the electro-valance of counter-ion and F is the Faraday constant. The membrane permselectivity towards the anions are estimated with the help of transport number using following equation.

$$P_s = \frac{t_-^m - t_-}{1 - t_-} \quad (5)$$

Where t_- is the counter-ion transport number in the solution.

S4. Chronopotentiometric studies

The chronopotentiometric responses for PMPS-3 membrane in equilibrium with electrolyte solutions (NaCl, NiSO₄ and ZnSO₄) of were recorded in of known concentrations using Perspex cell. The cell contained two compartments separated by the ion exchange membrane (25.0 cm²). A constant current was applied across the membrane using two dimensionally stable titanium electrodes coated with precious metal oxide, with the help of

potentiostat/galvanostat (Auto Lab, Model PGSTAT 30 (EcoChemie, B.V. Utrecht, The Netherlands)). Electrolyte solutions of known concentrations (50 and 150 cm³, respectively) were continuously recirculated in two compartments with the help of peristaltic pumps. Variation in potential with time under static conditions was recorded. In all these studies, the direction of the current was set in such a way that the counter-ion should move vertically upward from the outer to the inner compartment with minimal perturbations caused by natural convection. Two saturated calomel electrodes were used for the measurement of the potential difference across the ion-exchange membrane under static conditions. The solutions of both the compartments were vigorously recirculated between two successive experiments to ensure the return of equilibrium conditions in two solution-membrane interfacial zones.

Detailed analysis of chronopotentiograms

If an ion-exchange membrane separates two identical monovalent electrolytic solution of concentration C , then according to Fick's second law of linear diffusion, at the membrane-solution interfacial zone, the variation in counter-ion (i) concentration (C_i) with time (t), may be given as follows:

$$\frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} \quad (6)$$

where D is the diffusion coefficient of the electrolyte. Passage of constant electric current I (mA cm⁻²) across the membrane cause migration of counter-ion from one of membrane-solution interfacial zone towards the membrane surface, while away from the membrane surface in the other zone. Under concentration polarization, the incoming flux through the ion-exchange membrane (J_m) and outgoing flux from membrane surface (J_s) eventually becomes equal as counter-ion concentration is constant within the membrane phase ($J_m = J_s$).

Considering contribution of electro-osmotic transport of H₂O along with I to change the potential is negligible, concentration and electric current are related as:

$$\left(\frac{\partial C_i}{\partial x}\right) = \frac{I}{z_i F D} (t_i^m - t_i) \quad (7)$$

t_i^m and t_i are counter-ion transport number in the membrane and solution phase, respectively. At the transition time (τ) (concentration polarization), $C_i \rightarrow 0$ at the membrane surface ($x = 0$). Thus, under boundary conditions ($C_i = 0$ at $x = 0$ and $t = \tau$), following equation express the relationship between $I\tau^{1/2}$ and membrane permselectivity (P_s).

$$I\tau^{1/2} = \frac{z_i F (\Pi D)^{1/2}}{2(1-t_i)P_s} C_i \quad (8)$$

Eq. 8 indicates inversely relation between $I\tau^{1/2}$ and P_s of the IEM.

S5. Ionic flux, energy consumption and current efficiency of electro dialysis

Electro-transport flux for ions (J) obtained from DC considering negligible mass (water) transport across the membrane using following relation.

$$J = \frac{V_a C_i - C_0}{A \Delta t} \quad (9)$$

Where C_i and C_0 are the initial and final concentration in CC (mol m^{-3}); where ΔC is the concentration of metal changes in initial and final (mol m^{-3}), Δt is the time allowed for electro-transport (s), V_a is the total volume for of solution in each compartment ($0.50 \times 10^{-3} \text{ m}^3$); and A is the effective membrane area ($6.6 \times 10^{-3} \text{ m}^2$).

The energy consumption (W, kWh/kg of salt recovered) can be obtained by the following estimated by following equation:

$$W(\text{kWh}/\text{kg}) = \int_0^t \frac{V I dt}{m} \quad (10)$$

where V is the applied voltage, I the current, t the time allowed for ED process, and m is the weight of salt separated. Current efficiency (CE) was estimated by:

$$CE(\%) = \frac{m n F}{MQ} \times 100 \quad (11)$$

where F is the Faraday constant, M the molecular weight of metal salt, n the stoichiometric number and Q is the electric quantity passed (Coulombs; A s).

Table S1. Physicochemical and electrochemical properties of AEM (ASV, supplied by Selemion, Japan).

Properties	ASV membrane
Characteristic	Mono-valent anion selective
Thickness (μm)	130
Brust strength (MPa)	0.40
Ion-exchange capacity (mequiv./g)	1.13
Transport number for Cl^- ^a	0.97
Resistance ($\Omega \text{ cm}^2$) ^b	3.2

^ameasured in equilibration with 0.055 M NaCl solution.

^bmeasured in equilibration with 0.5 M NaCl solution.

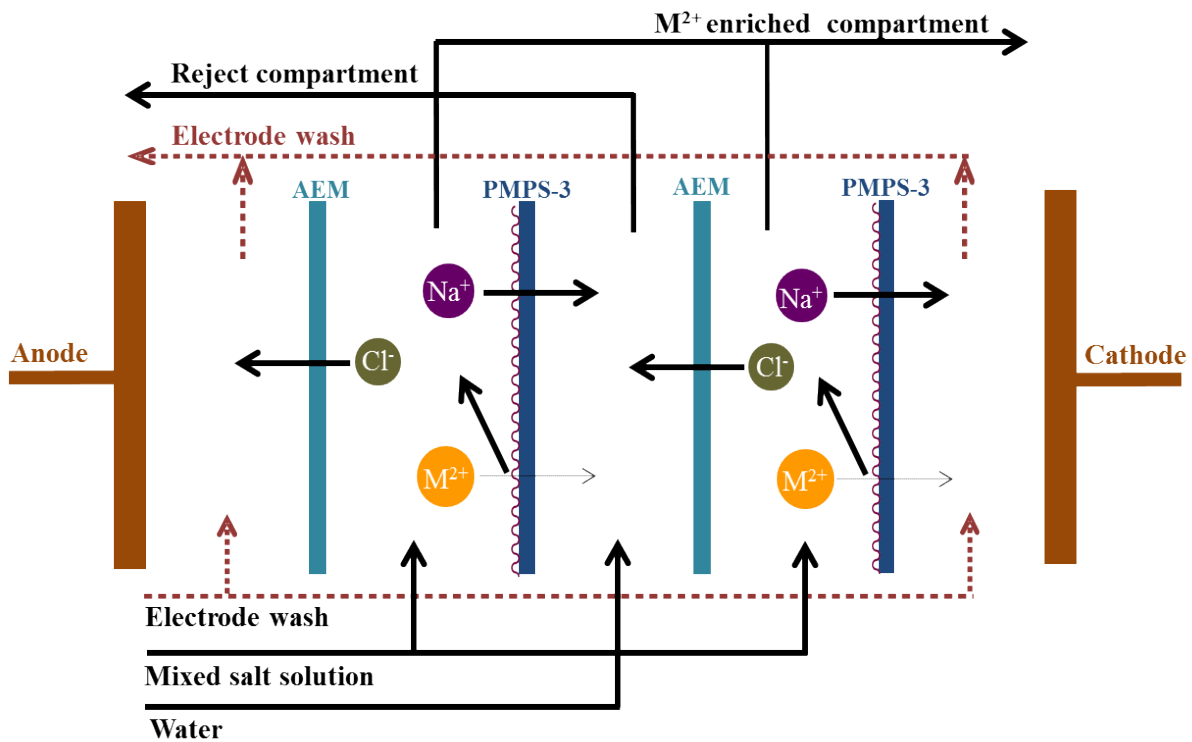


Fig. S1. Schematic diagram of ED cell used for selective electro-separation of Na^+ from other bi-valent ions.

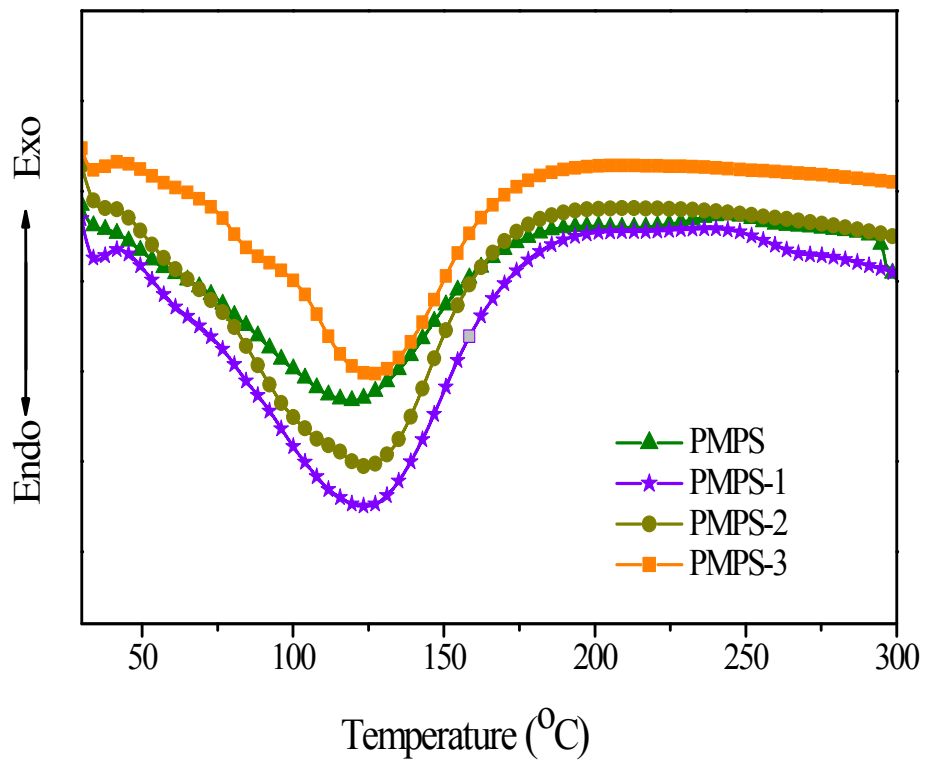


Fig. S2. DSC curves for different CEMs.

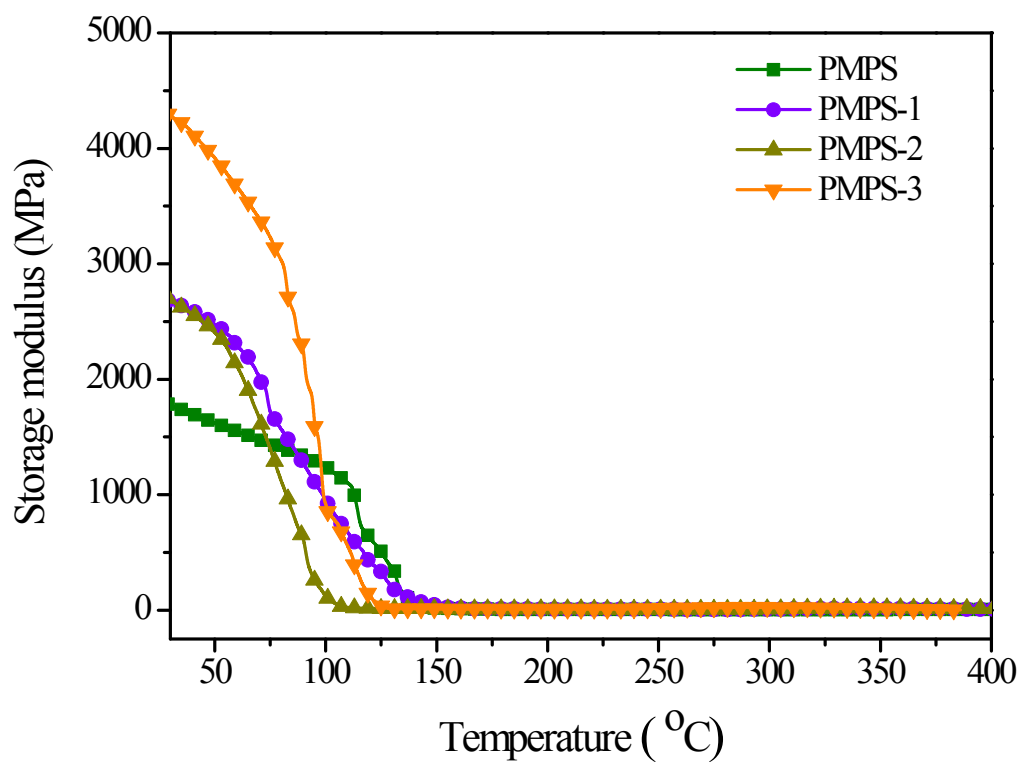


Fig. S3. DMA analysis of different CEMs.