# High power density of reverse electrodialysis with porefilling ion exchange membranes and high-open-area spacer

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# Nomenclature

 $R_i$ : Internal resistance $R_{ohmic}$ : Ohmic resistance $R_{dc}$ : Bulk layer resistance $R_{BL}$ : Boundary layer resistance $R_{BL}$ : Boundary layer resistance of AEM and CEM, respectivelyN: Number of cell pairsA: Effective aread: Thickness of compartment, subscripts c and d denote concentrated and diluted, respectively $\kappa$ : Conductivity $\alpha$ : PermselectivityJ: Current density (A/m<sup>2</sup>)F: Faraday constant (96485 C/mol)R: Universal gas constant (8.314 J/mol\_K)T: Absolute temperature (K) $\Delta a$ : Dimensionless concentration at the outflow,  $1+((J \cdot L)/(F \cdot q \cdot c))$ . Subscripts c and d denote

concentrated and diluted, respectively

*c*: Concentration (mol/m<sup>3</sup>)

q: Flow rate ( $m^3/s$ )

P: Power from RED stack (W)

Pgross: Gross power density (W/m<sup>2</sup>)

*I*: Electric current (A)

 $R_u$ : Resistance of external load ( $\Omega$ )

V<sub>0</sub>: Open circuit voltage (V)

#### Materials of ion exchange membrane

The host microporous substrate that consisted of polyolefin and was to be used for the preparation of pore-filling cation exchange membranes (CEMs) and anion exchange membranes (AEMs) was purchased from Asahi Kasei. According to the manufacturer's information provided by Asahi Kasei, the pores made up 45% of the volume of the substrate. The mean pore diameter and thickness of the substrate were 70 nm and 22  $\mu$ m, respectively. For KIER-AEM1, (vinylbenzyl)trimethyl-ammonium chloride and *N*,*N*'-bis(acryloyl)piperazine were purchased from Aldrich. For KIER-CEM1, *N*,*N*' ethylenebis(acrylamide) and vinyl sulphonic acid were purchased from Aldrich and Asahi Kasei, respectively. For KIER-CEM2, *N*,*N*'-ethylenebis(acrylamide) and acrylamido-2-methyl-1-propanesulphonic acid were purchased from Aldrich and TCI, respectively. Sodium dodecyl sulphate purchased from TCI was used as a surfactant. All reagents were used without further purification.

## Fabrication of ion exchange membrane

The monomers for KIER-AEM1, which included (vinylbenzyl) trimethylammonium chloride with functionalized ammonium groups and N,N'-bis(acryloyl)piperazine as the cross-linker, were dissolved in water to prepare a homogenous solution. The porous substrate was treated with a surfactant to make it hydrophilic. The substrate was then immersed in the aqueous monomer solution to allow the monomer to be filled into the pores. The monomer-impregnated substrate was then sandwiched between two polyethylene terephthalate (PET) films. To polymerize the monomers, the assembly was placed in a UV reactor with a power density of 30–150 mJ cm<sup>-2</sup>. The by-products that accumulated on the surface of the membrane were removed to make the surface uniform. Finally, the membrane was washed thoroughly with deionized water several times to remove any water-soluble compounds. For KIER-CEM1 and KIER-CEM2, N,N' ethylenebis(acrylamide) was used as the cross-linker, and vinyl sulphonic acid monomer and acrylamido-2-methyl-1-propanesulphonic acid were used as cationic electrolytes. The CEMs were fabricated by the same process as that used typically for AEM1. Scheme 1 illustrates all the prepared polymer structures without the substrate.



Scheme 1. Chemical structures of polymers prepared in this study: (a) AEM1, (b) CEM1, and (c) CEM2

## Membrane thickness

The thickness of the dry and wet membranes was measured using a micrometer (Mitutoyo, Japan). Before measuring the thickness of the wet membranes, the membranes were soaked in 0.5 M NaCl solution for 24 h. The thickness measurement was performed several times, and then, the average thickness was obtained.

## Ion exchange capacity

The resulting AEM (or CEMs) was soaked in 2 M NaOH (or 2 M HCl) solution for 24 h to exchange the chloride ions (or impurities such as sodium ions) with the hydroxide ions (or protons). The OH-formed AEM (or the H<sup>+</sup>-formed CEMs) was immersed in 50 mL of 3 M NaCl for 24 h. Subsequently, each solution obtained from the AEM or CEMs was titrated with 0.01 M HCl or 0.01 M NaOH solution by using 848 Titrino plus (Metrohom auto-titrator). The IEC of the membranes was calculated using the following equation:

# IEC = $(C_{\text{NaOH or HCl}} \times V_{\text{NaOH or HCl}})/M_{dry}$

where IEC is the ion exchange capacity of the membrane (meq.  $g^{-1}$ ),  $C_{NaOH \text{ or }HCl}$  is the molar concentration of the titrant,  $V_{NaOH \text{ or }HCl}$  is the volume of the titrant added at the equivalent point (ml), and  $M_{dry}$  is the weight of the dry membrane.

## Swelling degree

The swelling degree (SD) was determined by measuring the volume change between the dried membrane and the fully swollen membrane. Before determining the volume of the dry membrane, it was dried at 80°C for 24 h. The volume of the dry membrane was calculated by the measured thickness and area. The dry membrane was then immersed and equilibrated in 0.5 M NaCl solution for 24 h. The change in its volume was determined by measuring the thickness and area of the swollen membrane. Subsequently, the SD for the membrane swollen in 0.5 M NaCl solution was calculated using the following equation.

 $SD_{normalized} = (V_{wet mem} - V_{dry mem})/V_{dry mem}$ 

The SD is normalized as a dimensionless unit.

## Fixed charge density

The fixed  $CD_{fix}$  was determined in the IEC per normalized SD with respect to the swollen membrane in 0.5 M NaCl solution.

 $CD_{fix} = IEC/SD_{normalized}$ 

## Area resistance

The membranes equilibrated in 0.5 M NaCl solution for 24 h were placed between a two-compartment cell with each chamber equipped with a 1 cm<sup>2</sup> platinum electrode. The resistance of each membrane was measured by impedance spectroscopy (IS) using an LCR meter (Delta United Instrument, DU-6011) in the frequency range of 1 kHz. The electrical resistance was measured in the presence of the membrane ( $R_1$ ). In the next step, the electrical resistance was measured after removing the membrane ( $R_2$ ). The electric resistance ( $R_m$ ) of a membrane can be obtained by employing the specific resistance calculated from the difference between ( $R_1$ ) and ( $R_2$ ) and the effective membrane area (S).

 $\mathbf{R}_{\mathrm{m}} = (\mathbf{R}_{1} - \mathbf{R}_{2}) \times \mathbf{S}$ 

## Membrane potential and permselectivity

To equilibrate the membranes under investigation, the membranes were soaked in 0.5 M NaCl solution for 24 h prior to the measurement. The equilibrated membranes with the salt solution were placed between a two-compartment cell filled with 0.507 M and 0.017 M NaCl solution. Both compartments

were stirred during the measurements to minimize the effect of the boundary layer on the potential. The membrane potential was measured using two Ag/AgCl reference electrodes and a digital multimeter ( $E_m$ ). The transport number of counter-ions through the membrane was calculated from the measured membrane potential.

$$E_m = (2t_- - 1)\frac{R.T}{z.F}\ln(\frac{a_1}{a_2})$$

where t., T, R, F, z,  $a_1$ , and  $a_2$  are the transport number of anions (or cations) through the membrane, temperature, gas constant, Faraday constant, electrovalence of counter-ion, and activities of the 0.507 M and 0.017 M solution, respectively.

The permselectivity of each membrane ( $\alpha$ ) can also be defined in terms of the transport number.

$$\alpha = \frac{t_{\rm M}^{\rm m} - t_{\rm M}^{\rm s}}{t_{\rm X}^{\rm s}}$$

where t is the transport number obtained from the membrane potential. M and X are counter-ions and co-ions in the membrane or the solution phase, respectively. m and s refer to the membrane and the solution phase, respectively.

#### Internal resistance of RED stack



Fig. S1 Internal resistance of RED stack at various flow rates of feed solutions.