Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2018

Supporting Information

Multiscale-pore ion exchange membrane for better energy efficiency

*Hyukjin J. Kwon, Bumjoo Kim, Geunbae Lim† and Jongyoon Han**

S01. Thermodynamic analysis and desalination performance measurement

Various terms were used for evaluating desalination performance to compare the MP-IEM with a conventional IEM. Based on the first and second law of thermodynamics, irreversible thermodynamics is applicable approximately in transport phenomena at the ion exchange membrane. The equation is introduced from second law of thermodynamics [1]:

$$\frac{TdS}{dt} = -J_V \cdot R \cdot T \cdot \Delta C + J_i \cdot R \cdot T \cdot \ln\left(\frac{C_{desalted}}{C_{concentrated}}\right) + I \cdot V, \quad \text{(S1)}$$

$$\Delta C = (C_{concentrated} - C_{desalted}), \quad \text{(S2)}$$

in which, J_V and J_i are the volume and ionic flux through the membrane respectively. R is the gas constant and T is the temperature in Kelvin scale. $C_{desalted}$ and $C_{concentrated}$ are the concentration of desalted and concentrated stream respectively. I and V are the input electrical current and voltage.

Current efficiency (*CE*) is the ratio of 'the amount of ionic current induced by transport salt ions across the membrane' to 'applied current'[2]. It allows to understand how effectively remove the salt ion using applied current. *CE* can be introduced as follow:

$$CE = \frac{z_i \cdot F \cdot J_i}{I}, \quad \text{(S3)}$$

where z_i is the charge of ion and F is the faraday constant. In ideal condition, *CE* would be 1 indicating every current is used to remove the salt ions. From the Equation (S1) and some phenomenological coefficients related to inefficiency of an ion exchange membrane J_i can be described as follow:

$$J_i = \frac{L_P \cdot (\sigma_i - 1) \cdot R \cdot T(\Delta C)^2}{\ln\left(\frac{C_{desalted}}{C_{Concentrated}}\right)} + \omega_i \cdot R \cdot T \cdot (\Delta C) + \frac{tI}{F}.$$

(S4)

The coefficients in Equation (S4) are termed as follow: L_p is the hydraulic conductivity, σ_i is the reflection coefficient, ω_i is the solute permeability and t is the transport number. In order to calculate current efficiency in the experiment directly, J_i is obtained experimentally by measuring conductivities of each stream:

$$CE = \frac{z_i \cdot F \cdot Q_{desalted} \cdot \Delta C}{I},$$

(S5)

where $Q_{desalted}$ is flow rate of desalted water. CE is shown in Figure 4 for the comparison. The conductivities of each stream, measured by an inflow-type conductivity electrode (Microelectrodes, USA), represents the concentration of solution as follows:

$$C\ [mol/l] = \frac{\sigma}{\Lambda_{+,i} + \Lambda_{-,i}} [\frac{S/m}{S \cdot m^2/mol}], \quad \text{(S6)}$$

where C is the concentration of stream. $\Lambda_{+,i}$ and $\Lambda_{-,i}$ are the molar conductivity of cation and anion, respectively and σ is electrochemical conductivity. The concentration drop between the desalted stream and feed stream can be described as the salt removal ratio (SRR):

$$SRR = \frac{(C_0 - C_{desalted})}{C_0}, \quad \text{(S7)}$$

where C_0 is the concentration of feed stream.

Energy consumption (P) has been widely investigated to compare desalination energy efficiency. In electrochemical desalination systems, energy consumption is evaluated by the electrical power consumption (product of current, I and voltage, V) divided by the flow rate of desalted water, $Q_{desalted}$:

$$P = \frac{I \cdot V}{Q_{\text{desalted}}} [Wh/l] \quad . \tag{S8}$$

Calculating the efficiency of energy conversion, which is thermodynamics efficiency, allow to understand how effectively energy inputs are being used by a desalination process and how far from the thermodynamic limit[2–4]. From Equation (S1), efficiency of energy conversion (η) can be described approximately as the ratio of 'the thermodynamic minimum energy to remove salt ion (P_{Th})' to 'input energy (P)' as follow:

$$\eta = \frac{P_{Th}}{P} , \tag{S9}$$

$$P_{Th} = z_i RT\left(\frac{C_0}{\emptyset}\ln\left(\gamma_0\right) - C_{desalted}\ln\left(\gamma_{desalted}\right) - \frac{(1-\emptyset)C_{concentrated}}{\emptyset}\ln\left(\gamma_{concentrated}\right)\right) , \tag{S10}$$

where $\emptyset$ is a recovery ratio which is ratio of the desalted flow rate to the feed flow rate. γ is salt activity coefficient of each stream. As shown in **Figure S1**, the thermodynamic minimum energy was calculated. From the experiment of seawater desalination with our MP-CEM, efficiency of energy conversion (thermodynamic efficiency, η) were around 4.7% at 10mM and 0.68% at 500mM.

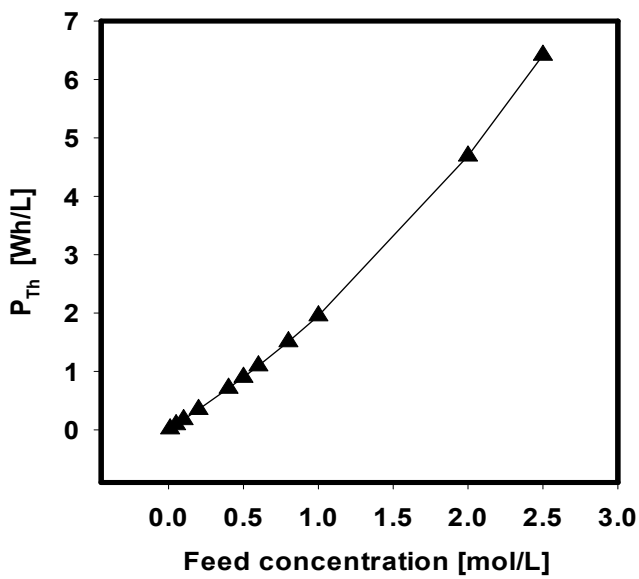

Figure S1. The thermodynamic minimum energy to separate pure water from feed as function of concentration of feed NaCl solution with fixed recovery of 0.5.

S02. Energy consumption of pumping fluid into MP-IEM device

Because the desalted stream flows through the microporous structure in MP-CEM, required energy consumption for pumping (P_H) should be considered. The power can be easily calculated by product of pressure drop (Δp), and flow rate (Q), therefore energy consumption can be introduced as follow;

$$P_H\,[\frac{Wh}{L}] = \frac{W}{Q} = \frac{\Delta p \cdot Q}{Q}. \tag{S11}$$

The flow rate is determined by pump, therefore, in order to calculate the pressure drop for certain flow rate, we adopt Darcy's Law:

$$Q = \frac{k \cdot A_C \cdot \Delta p}{\mu \cdot L}, \tag{S12}$$

where k is permeability of porous medium, A_C is cross-sectional area of MP-CEM membrane, μ is fluid viscosity and L is length of MP-CEM. Although permeability can be calculated with few simplified equations, it is more accurate with experiment of head test method. We measured the flow rate for the MP-CEM (length: 10 mm, width: 20 mm and thickness: 800 um) with 0.01 m differences of total heads which is 97.9 Pa in pressure. Measured flow rate was approximately 819 mL/min. Therefore, based on the Equation (S11) and (S12), pressure drop thus energy consumption can be calculated as function of flow rate:

$$\Delta p = P_H = \frac{\mu \cdot L}{k \cdot A_C} Q. \tag{S13}$$

The calculated power consumption for the 0.104 mL/min is 0.00560 Wh/L indicating the energy consumption needed for fluid delivery is almost negligible.

S03. Limiting current density at various feed solution concentration

Limiting current value is critical property for the ED process because it determines the optimal operation current density. Although the limiting current for the IEM is affected by various factor such as flow velocity and roughness of membrane, it is mainly determined by bulk solution concentration. As shown in Figure S2 limiting current density is almost linearly proportional to feed concentration.

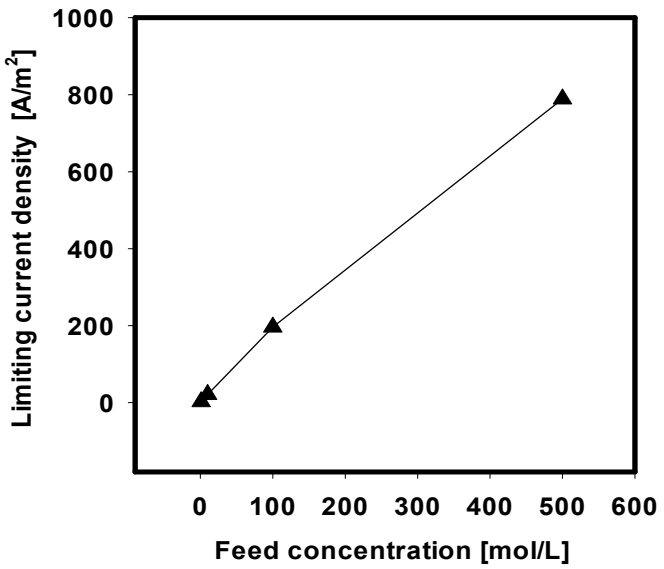

Figure S2. The experimentally measured limiting current density as function of concentration of feed NaCl solution with flow velocity of 2 mm/sec

S04. Mechanism of ICP desalination

Previously, our group has conducted many researches on the desalination using ICP[5,6]. As shown in Figure 1, ICP uses identical IEM to generate the concentration and depletion stream in the same channel without physical barrier between the concentrated and desalted stream. In bulk solution, neutrality is always maintained except near the charged surface (electrical double layer)[7]. In case of the CEM-ICP, the only cations are driven to penetrate CEM by electric field, generating cation-depleted and cation-concentrated region simultaneously. Subsequently, anions are repelled where the cation is depleted while anions are attracted where the cation is concentrated, in order to maintain electroneutrality. Therefore, both cations and anions were concentrated in the concentrated stream and depleted in the desalted stream.

Since typical polluted water contains considerable quantities of suspended solids as well as salts. Yet, as most desalination technologies (Reverse Osmosis, Electrodialysis, Membrane Distillation, etc.) mainly utilizing membrane separation suffer from severe membrane fouling, they should engage additional pre / post treatment to remove suspended solids, thereby bearing more cost. However, ICP desalination can tactfully eliminate them from the dilute stream producing real purified water. In some particular situation, ICP might have certain advantage over conventional ED[6] but there are severe energy efficiency loss and salt removal efficiency loss due to the mixing between the concentrated and the desalted stream by electro convection (induced by electroosmotic instability)[8]. To overcome this inherent problem, we have invented this MP-IEM to suppress the electroconvection by confining ion-depleted region and it might be possible to adopt it to other IEM application like a ED.

S05. Comparison with the reverse osmosis

For few decades, reverse osmosis (RO) technology has been improved dramatically. It starts with 20 Wh/L for sea water desalination in 1970s. Owing to development of membrane technology, power consumption become less than 5 Wh/L recently[9]. Although, RO is currently the most energy efficient way for the sea water desalination, it requires significant investment in capital cost and tend to be less effective in processing high concentration feed (50-100kppm) such as waste water resulting from hydraulic fracturing[10]. These inherent two drawbacks of RO process explain why other desalination techniques still have merits; 1) Small scale desalination: In case of plant-scale where significant infrastructure investment is justifiable, RO is still considered as most economical process due to the economy of scale, and thus leading the market. However, for application such as small scale or household desalination, ED or other electrochemical techniques may be meritorious because electrochemical desalination process such as ED and ICP are tend to require much less capital cost and can be scalable. 2) Processing high concentration feed: In our previous paper, direct comparison with modern plant-scale desalination technique was conducted by overall cost analysis[6]. Generally speaking, ICP technique was shown to be applicable in processing high concentration brine, while RO should still be the method of choice for seawater desalination.

In this paper, we are focusing ourselves on improving electromembrane separation techniques used in ED/ICP/CDI, by addressing the key challenges of depletion zone formation. The idea presented in this work is clearly reducing the power consumption (as much as up to 75%, depending on exact configuration) compared to conventional electromembrane processes. While we are not improving things compared to the state-of-the-art RO process, our work is still meaningful since there are many situations where conventional RO cannot be a solution. Distributed, portable desalination for disaster relief is one example, and the problem of brine treatment is another such example[11].

S06. Cross-sectional image for MP-CEM

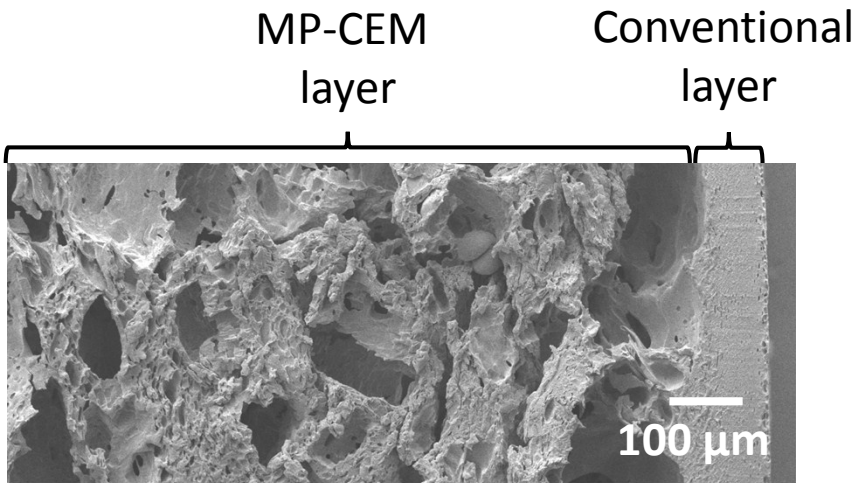

Figure S3. Cross-sectional scanning electron microscopy image of MP-CEM structure showing multiscale porous (MP)-CEM layer and conventional layer.

S07. Schematics of microchip platform

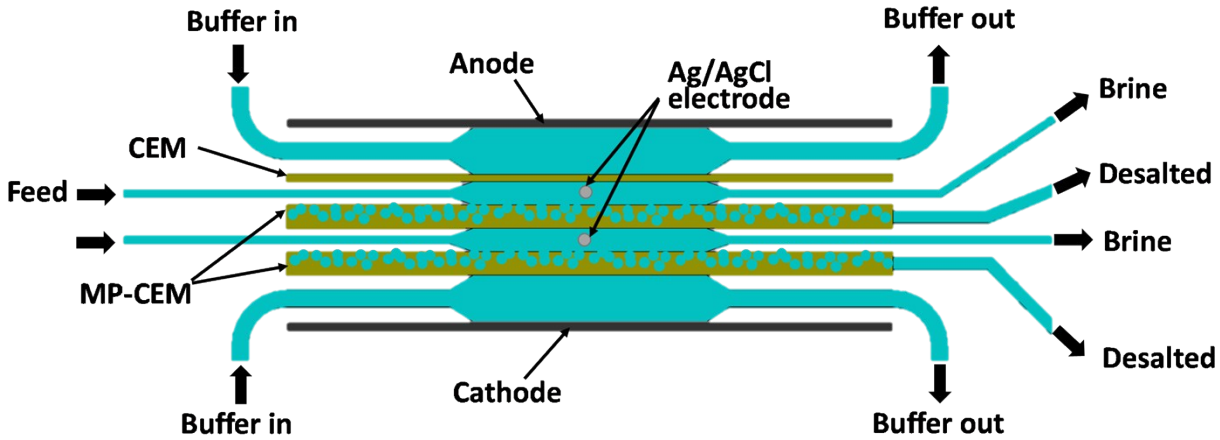

Figure S4. Schematics of microchip platform used for experiment shown in Figure 6. MP-CEM located in middle was measured for area resistance of CEM cell and desalination performance. Effective area of MP-CEM was 10 * 0.2 mm and gap between each MP-CEM was 1 mm. The flow rate of each desalted stream was 5 µL with recovery ratio in 0.5.

References

1 Y. Tanaka, in *Ion Exchange Membranes*, Elsevier, Amsterdam, 2nd edn., 2015, p. iii.

2 S. Koter, *Desalination*, 1994, **95**, 139–153.

3 M. Elimelech and W. a Phillip, *Science (80-.).*, 2011, **333**, 712–7.

4 N. Y. Yip and M. Elimelech, *Environ. Sci. Technol.*, 2012, **46**, 5230–5239.

5 S. J. Kim, S. H. Ko, K. H. Kang and J. Han, *Nat. Nanotechnol.*, 2010, **5**, 297–301.

6 B. Kim, R. Kwak, H. J. Kwon, V. S. Pham, M. Kim, B. Al-Anzi, G. Lim and J. Han, *Sci. Rep.*, 2016, **6**, 31850.

7 H. Daiguji, P. Yang and A. Majumdar, *Nano Lett.*, 2004, **4**, 137–142.

8 S. V. Pham, H. Kwon, B. Kim, J. K. White, G. Lim and J. Han, *Phys. Rev. E*, 2016, **93**, 33114.

9 R. F. Service, *Science (80-.).*, 2006, **313**, 1088–1090.

10 A. Fakhru'l-Razi, A. Pendashteh, L. C. Abdullah, D. R. A. Biak, S. S. Madaeni and Z. Z. Abidin, *J. Hazard. Mater.*, 2009, **170**, 530–551.

11 B. Kim, H. Kwon, S. H. Ko, G. Lim and J. Han, *Desalination*, 2017, **412**, 20–31.