Thin-Film Composite Pressure Retarded Osmosis Membranes for Sustainable Power Generation from Salinity Gradients

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Supporting Information

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NGAI YIN YIP, ALBERTO TIRAFERRI, WILLIAM A. PHILLIP, JESSICA D. SCHIFFMAN, LAURA A. HOOVER, YU CHANG KIM AND MENACHEM ELIMELECH*

Department of Chemical and Environmental Engineering
Yale University
New Haven, CT 06520-8286
(*E-mail: menachem.elimelech@yale.edu)

Materials and Methods

SEM Imaging of Fabricated Membrane. All micrographs were acquired using a Hitachi Ultra-High-Resolution Analytical Field Emission Scanning Electron Microscope (FE-SEM) SU-70. To obtain cross-sections, wet membrane samples were flash-frozen in liquid nitrogen and cracked by bending. Both membrane surface and cross-section samples were air-dried overnight prior to sample mounting. Surface samples were coated for 30 s and cross-section samples for 45 s with gold-platinum using an Emitech SC7620 sputtering machine.

Determination of Membrane Water Permeability. Intrinsic water permeability of the TFC-PRO membranes was evaluated in a laboratory-scale crossflow RO test unit (Ang et al., 2007). The effective membrane area was 20.02 cm^2, the crossflow velocity was fixed at 21.4 cm/s, and the temperature was maintained constant at 25 ± 0.5 °C. The loaded membrane was first compacted with DI at an applied pressure, ΔP, of 20.7 bar (300 psi) until the permeate flux reached a steady state (at least 15 h). The pressure was then lowered to 17.2 bar (250 psi) and pure water flux, J_w, was calculated by dividing the volumetric permeate rate by the membrane area. Intrinsic water permeability, A, was determined by dividing the water flux by the applied pressure, $A = J_w/\Delta P$.

Determination of Membrane Channel Mass Transfer Coefficient. The mass transfer coefficient, k, for NaCl in the spacer-filled channel was determined from PRO experiments with membranes LP#1, MP#1, and HP#1 using a 0.5 M NaCl draw solution and a DI feed solution. All other experimental parameters and procedures were kept identical to the PRO performance tests. The mass transfer coefficient was determined by fitting the water flux to eq 9. The average value of k from the 3 membranes tested was used in the prediction of PRO performance with seawater draw.

Water Flux Measurements in PRO System Under Applied Hydraulic Pressure. A commercial asymmetric cellulose triacetate (CTA) FO membrane (Hydration Technology Inc., Albany, OR) was tested in a laboratory-scale crossflow PRO test unit. A schematic of the PRO system is shown in Figure S1. The custom built cell has an effective membrane area of 20.02 cm^2 on both sides of the membrane. The unit was operated with co-current crossflow with mesh spacers in both feed and draw channels. A variable speed gear pump (Cole-Parmer, Vernon Hills, IL) was used to circulate the feed solutions in a closed loop at a flowrate of 1.0 L/min. A high pressure pump (Hydra-cell pump, Wanner Engineering, Minneapolis, MN), a back pressure regulator, and a bypass valve (both Swagelok, Solon, OH) were employed to circulate the draw solutions in a closed loop at a flowrate of 1.0 L/min and control the applied hydraulic pressure. A water bath (Neslab, Newington, NH) kept the temperature of both feed and draw solutions constant at 25 ± 0.5 °C.

The PRO experiment was conducted using a 4.0 L synthetic seawater draw solution and a 2.0 L synthetic river water feed solution (Table S1), with the CTA membrane oriented in PRO configuration (i.e. with the active layer facing the draw solution). After the temperature of the system has equilibrated, the solutions were circulated to the membrane cell and the applied hydraulic pressure difference, ΔP, increased to 10.34 bar (150 psi). The weight of the feed solution is recorded every 3 min in a data-logging program, and the average water flux is calculated over 5 data points after it had stabilized (i.e. 15 min interval). The applied hydraulic pressure difference is reduced in 2.07 bar (30 psi) steps to 0 bar and the corresponding water flux recorded; that is, six water flux data points were logged at ΔP = 0, 2.07, 4.14, 6.21, 8.27, and 10.34 bar (0, 30, 60, 90, 120, and 150 psi).

Results and Discussion

Validation of the PRO Water Flux Model. To validate the derived water flux model, a commercial CTA membrane was tested in a PRO system under a range of applied hydraulic pressures. Characteristic parameters A (0.355 L m^{-2}h^{-1}bar^{-1}), B (0.32 L m^{-2}h^{-1}bar^{-1}), and S (595 μm), of the CTA membrane based on our recent study (Yip et al., 2010) were used in conjunction with the derived water flux equation (eq 9 of manuscript) and the power density equation (eq 14 of manuscript) to predict the water flux, J_w, and power density ,W, as a function of applied hydraulic pressure, ΔP. The model predictions for J_w and W along with the measured J_w at ΔP between 0 and 10.34 bar are presented in Figure S3. The good agreement between actual and predicted water flux values substantiates the validity of the derived model. Therefore, eqs 9 and 14 can be utilized to adequately project the peak power densities achievable by our fabricated TFC-PRO membranes by extrapolating the experimental PRO water flux at no applied hydraulic pressure.

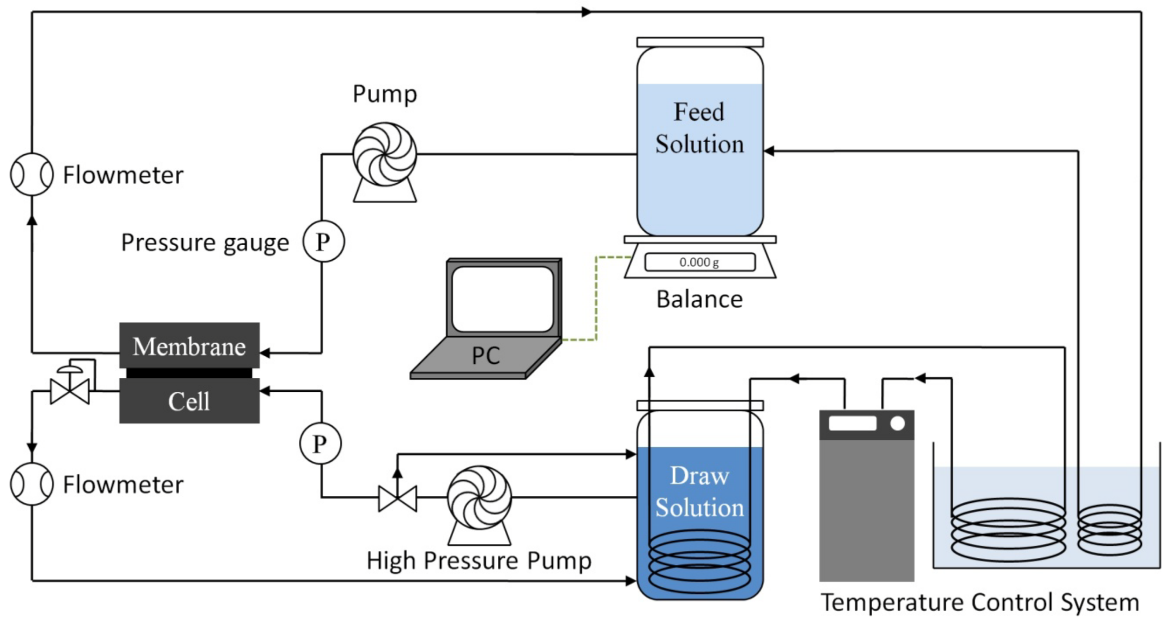

Figure S1. Schematic diagram of the laboratory-scale PRO system. Co-current crossflow of the draw and feed solutions is employed. A scale connected to a PC measures the mass of water permeating across the membrane from the feed solution, from which water flux is calculated.

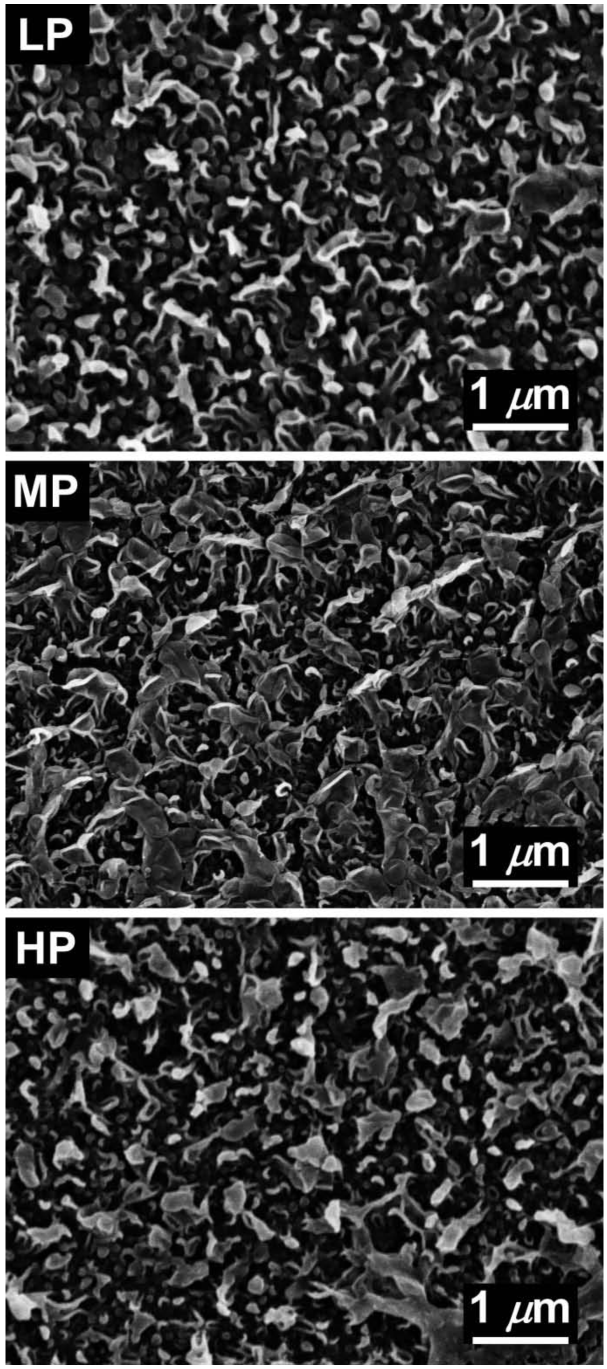

Figure S2. SEM micrographs of the polyamide active layer surface of the TFC-PRO membranes LP (top), MP (center), and HP (bottom).

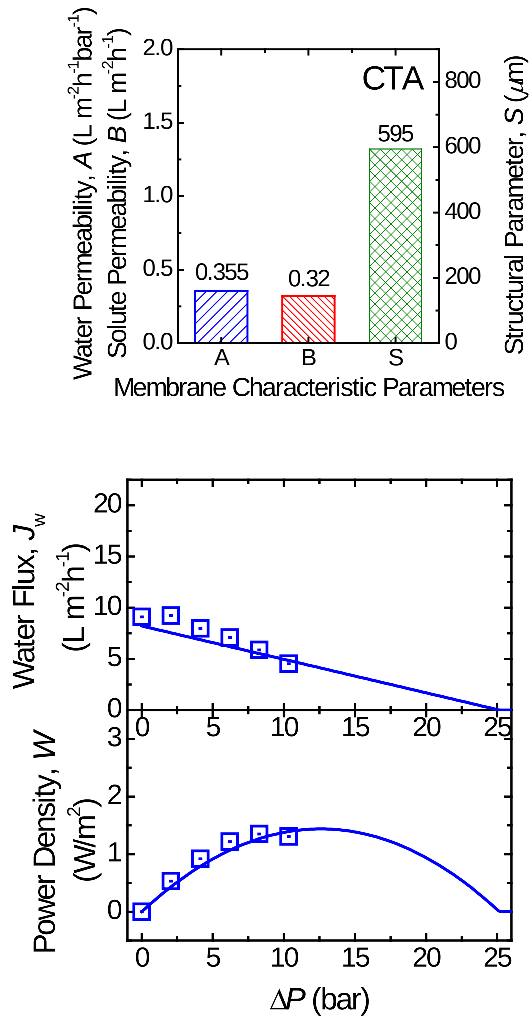

Figure S3. Plot of modeled water flux, J_w, and power density, W, as a function of applied hydraulic pressure, ΔP, for the commercial cellulose triacetate asymmetric FO membrane (CTA) using a synthetic seawater draw solution and a synthetic river water feed solution (solution compositions in Table S1). The characteristic parameters (top): intrinsic water permeability, A, solute permeability coefficient, B, and support layer structural parameter, S, are based on our earlier study (Yip et al., 2010). Symbols represent measured experimental water fluxes and power density of the membrane. Osmotic pressure of the synthetic seawater is 26.14 bar as determined by OLI Stream Analyzer software, and osmotic pressures of the synthetic river water is 0.045 bar, as calculated using the van't Hoff equation. All experiments and calculations are done for draw and feed solutions at 25° C.

Table S1. Ionic composition and osmotic pressure of synthetic seawater, brackish water, and river water solutions for PRO performance tests.

		[a]Seawater	[b]Brackish Water	[a]River Water
Ionic Concentration (mM)	HCO_3^-	2.38	0.068	0.86
	SO_4^{2-}	28.2	0.82	0.069
	Cl^-	545.0	15.5	0.16
	Ca^{2+}	10.2	0.29	0.33
	Mg^{2+}	53.2	1.52	0.15
	Na^+	468.0	13.3	0.23
	K^+	10.2	0.29	0.03
	Total Ionic Strength (mM)	696.0	19.9	1.74
	Osmotic Pressure, π (bar)	[c]26.14	[d]0.789	[d]0.045

[a] Major ion composition of average seawater and river water (Morel and Hering, 1993).

[b] Based on concentration of 1,000 ppm TDS with proportions of ions identical to seawater.

[c] Calculated from the corresponding solute concentrations using a software package from OLI Systems, Inc. (Morris Plains, NJ).

[d] Calculated using the van't Hoff equation.

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