Supporting Information

Performance Limiting Effects in Power Generation from Salinity Gradients by Pressure Retarded Osmosis

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RESULTS AND DISCUSSION

Influence of ECP, ICP and Reverse Salt Flux on Membrane Salt Concentration Profile. A schematic of the salt concentration profile across a thin-film composite membrane operating in PRO mode (i.e., active layer facing the draw solution) is shown in Figure S2. The solid black lines show the actual salt concentration profile and the actual concentration difference across the membrane active layer is denoted by ΔC_{actual}. The effective osmotic pressure across the membrane is lower than the osmotic pressure difference between the bulk draw and feed solutions (i.e., $\Delta\pi_m < \pi_{D,b} - \pi_{F,b}$) due to the detrimental effects of external concentration polarization (ECP) in the draw solution, internal concentration polarization (ICP) within the porous support, and reverse salt flux, J_s^R, across the membrane. Here, we discuss the influence of ECP, ICP, and reverse salt flux on the salt concentration profile across the membrane in PRO.

(a) External Concentration Polarization. The salt concentration at the active layer is lower than the bulk draw solution concentration (i.e., $C_{D,m} < C_{D,b}$) due to the dilutive effect of ECP (Figure S2). As water permeates across the membrane, it dilutes the draw solution and lowers the salt concentration at the active layer interface, $C_{D,m}$, resulting in a reduction in effect concentration difference, ΔC_m, across the membrane. This phenomenon at the draw solution side is called external concentration polarization.

(b) Internal Concentration Polarization. At the feed side, ICP causes the salt concentration at the active-support layer interface, $C_{F,m}$, to be higher than the bulk feed solution concentration (Figure S2). As water permeates across the membrane, the feed solutes are selectively retained by the semi-permeable active layer. The accumulation of solutes within the porous support increases $C_{F,m}$, and diffusion works to restore this local concentration to the bulk feed solution concentration, $C_{F,b}$. However, the membrane porous support acts as an unstirred boundary layer and hinders the diffusion of feed solutes out of the support layer. This effect, termed internal concentration polarization, elevates the salt concentration within the membrane support layer and reduces the effective concentration across the membrane, ΔC_m.

(c) Reverse Salt Flux. The semi-permeable membrane employed in PRO is not perfectly rejecting and therefore reverse flux of draw solute, J_s^R, occurs across the membrane (Figure S2). The permeation of solute from the more concentrated draw solution into the feed solution side results in a decrease in $C_{D,m}$ and an increase in $C_{F,m}$. The reverse draw solute flux is exacerbated ICP, where the leaked solute accumulates in the porous support and further increases the interfacial salt concentration. On the draw side, the interfacial salt concentration, $C_{D,m}$, decreases as the draw solute permeates across the membrane. Both these effects produce a reduction of the effective membrane concentration, ΔC_m.

The salt concentration profiles when one of the phenomena (i.e., ECP, ICP, or reverse draw salt flux) is absent are indicated in Figure S2 (dashed blue line, dotted red line, and dot-dashed green line, respectively). Compared with ΔC_{actual}, the effective concentration difference for these three hypothetical cases (denoted in subscript as “no ECP”, “no ICP”, and “no J_s^R”) is higher — underlining that these phenomena reduce ΔC and hence, lower the osmotic driving force across the membrane.

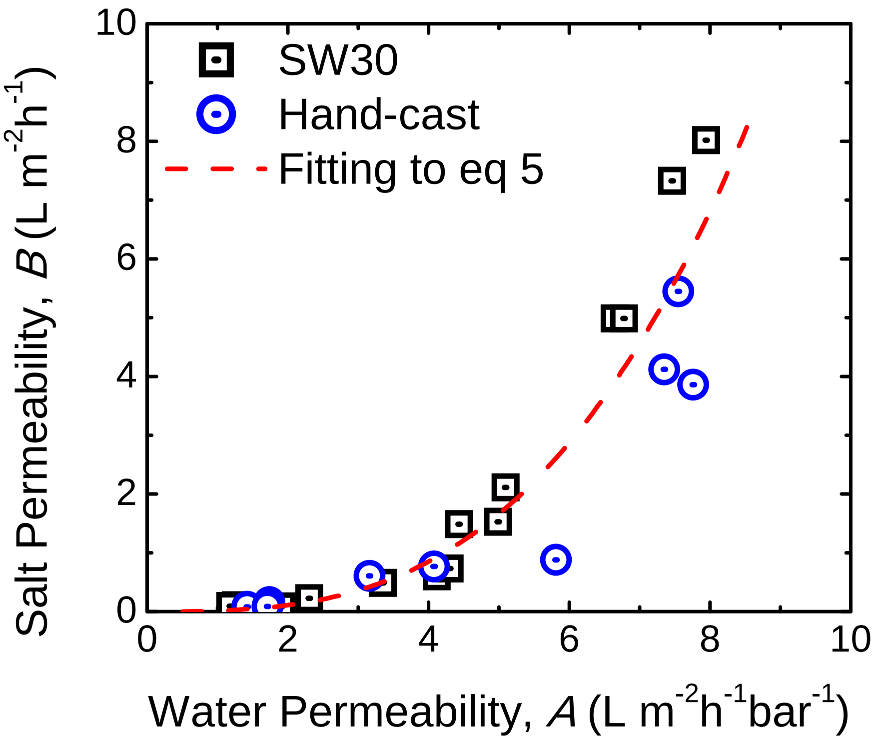

FIGURE S1. Water and salt permeabilities of TFC polyamide membranes subjected to chlorine-alkaline modification. Black square symbols indicate commercial SWRO membrane, SW30, modified in this study. Blue circle symbols indicate data for post-treated handcast PRO membranes reported in our recent publication (Yip et al. "Thin-Film Composite Pressure Retarded Osmosis Membranes for Sustainable Power Generation from Salinity Gradients", *Environ. Sci. Technol.* **2011,** *45* (10), 4360-4369). *A* and *B* data is fitted to eq 5 for T = 298 K and M_w = 18 g/mol. Fitting parameter L^2/λ is determined to be 6.11 × 10^{-3} s^2/cm^2.

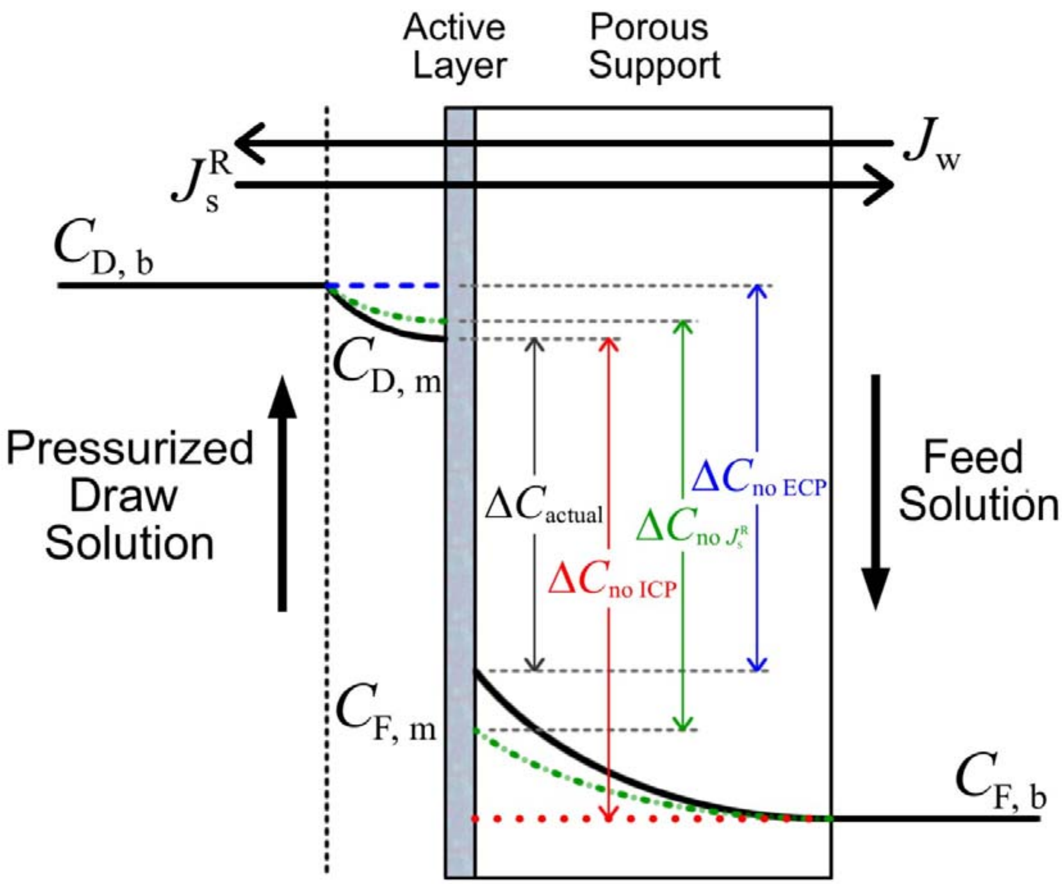

FIGURE S2. A schematic representation of the salt concentration profile across a thin-film composite membrane in PRO mode at steady state: i) under actual conditions (i.e., with all three detrimental effects present, indicated by the solid black lines), ii) with no dilutive external concentration polarization in the mass transfer boundary layer of the draw solution (dashed blue line), iii) with no concentrative internal concentration polarization within the porous support (dotted red line), and iv) with no reverse permeation of draw solute, J_s^R, into the feed side (dot-dashed green line).

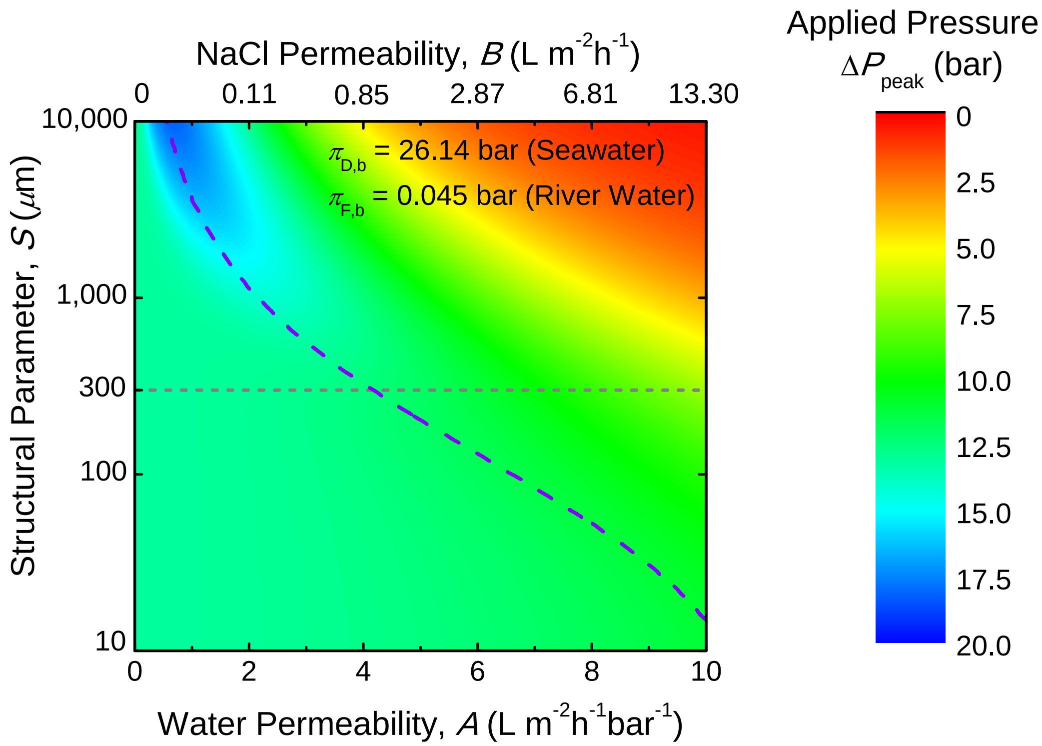

FIGURE S3. Applied hydraulic pressure required to achieve peak power density, ΔP_{peak}, as a function of active layer water and salt permeabilities (bottom and top horizontal axes, respectively) and support layer structural parameter, S (vertical axis). Dotted horizontal line represents a structural parameter of 300 μm, while dashed violet line indicates the active layer properties (values of A and B pair), where W_{peak} is maximized for a particular S. Osmotic pressures of the draw and feed solutions are 26.14 and 0.045 bar, respectively, simulating seawater and river water. The ECP mass transfer coefficient used in the calculations is k = 38.5 μm/s (138.6 L m^{-2}h^{-1}).

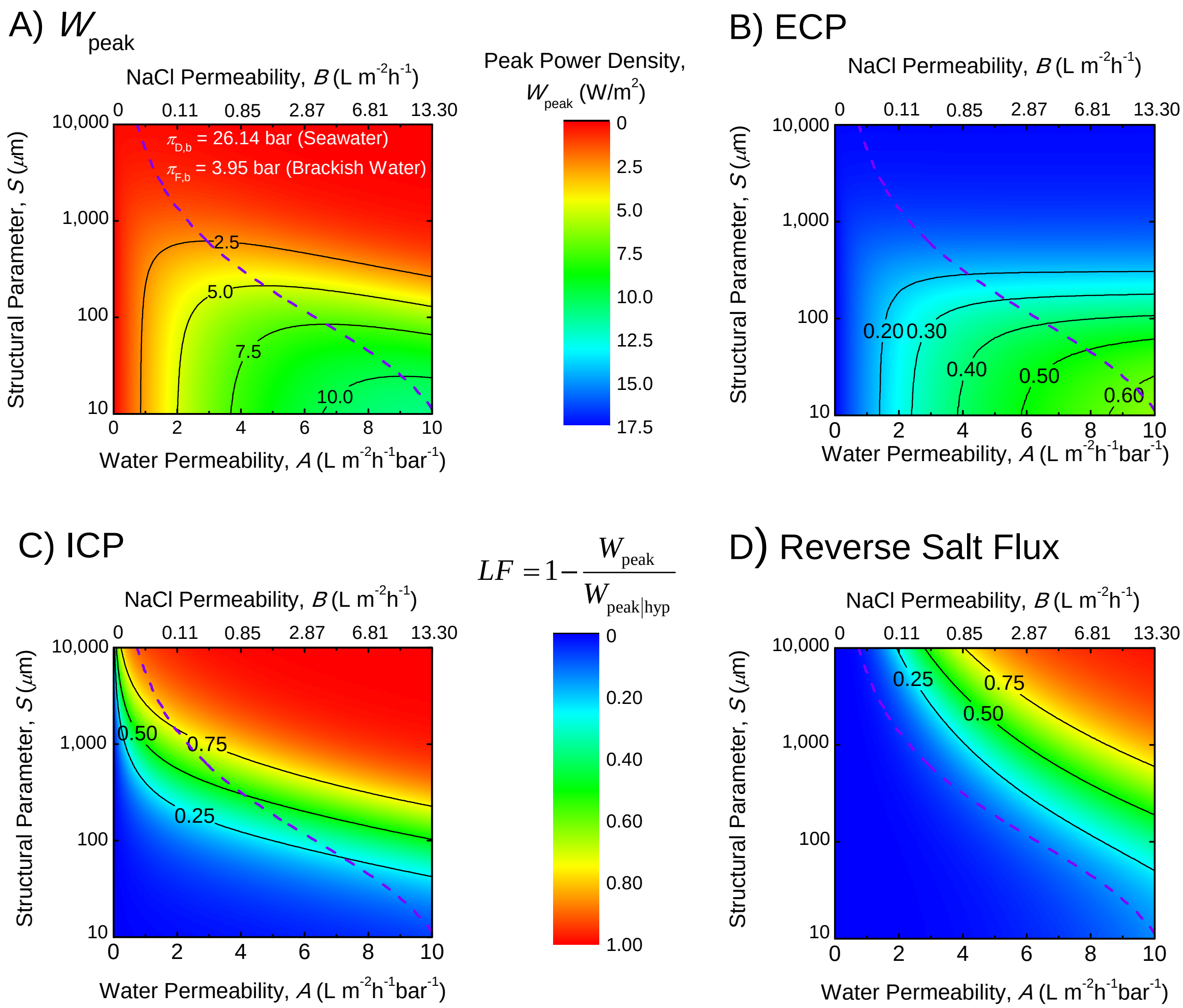

FIGURE S4. (A) Peak power density, W_{peak}, as a function of active layer water and salt permeabilities (bottom and top horizontal axes, respectively) and support layer structural parameter, S (vertical axis), and losses in W_{peak} due to the individual effect of the performance limiting phenomena: (B) ECP, (C) ICP, and (D) reverse draw salt flux. The scale bar for A) represents W_{peak}, while scale bars for B), C) and D) indicate the loss factor, $1–W_{peak}/W_{peak|hyp}$ (eq 8). Dashed violet line indicates $W_{peak,max}$. Osmotic pressure of the draw and feed solution is 26.14 bar and 3.95 bar, respectively, to simulate seawater and 5,000 ppm TDS brackish water. ECP mass transfer coefficient k = 38.5 μm/s (138.6 L $m^{-2}h^{-1}$).