Supporting Information

Zwitterionic Hydrogel-Impregnated Membranes with Polyamide Skin Achieving Superior Water/Salt Separation Properties

Thien Tran,[1] Shiwei Pan[1,2], Xiaoyi Chen[1], Xiao-Ci Lin[1], Adrienne K. Blevins[3], Yifu Ding[3], and Haiqing Lin[1,*]

[1] Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA.

[2] Wanhua Chemical Group Co., Ltd., Economic Development Zone, Yantai 264006, China.

[3] Materials Science and Engineering Program and Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309, USA.

[*] Corresponding author. Tel: +1-716-645-1856, Email: haiqingl@buffalo.edu (H. Lin)

Modification of IMs with MPD/TMC. The IMs were also modified with polyamides derived from TMC and *m*-phenylenediamine (MPD, Sigma-Aldrich) via the following GLIP procedure. First, an *s*IM sample was immersed in an aqueous solution containing 2 w/v% MPD (150 mL) and an equivalent amount of TEA (*i.e.*, 2 w/v% TEA) for 24 h. Second, the IMs were taken out of the solution, and the excess solution on the surface was removed by filter paper. Third, the sample was immersed into 100 mL hexane solution containing 0.1 w/v% TMC for 5 min. Finally, the sample was rinsed by hexane and dried in the air. The IMs modified with MPD-PA layers described here are denoted as *s*IM*x*-RO, as MPD and TMC are used to prepare RO membranes.

Water and salt transport properties. Figure S1 presents the A_W and Na_2SO_4 rejection of the *s*IM*x*-RO membranes. The average A_W of all *s*IM*x*-RO membranes is below 0.05 LMH/bar, and the Na_2SO_4 rejection increases from 42% ± 8% to 100% ± 4% as the PEGDA content increases from 20 wt.% to 40 wt.%. Unlike the *s*IMx-NF samples with the PA layers derived from PIP and TMC, the addition of MPD-derived PA layers significantly reduces the A_W. For example, *s*IM20 and *s*IM20-NF2 exhibit A_W of 0.5 ± 0.1 LMH/bar and 0.45 ± 0.02 LMH/bar, respectively, while *s*IM20-RO2 shows an A_W of only 0.02 LMH/bar. Therefore, only IMx-NF samples with PIP-derived PA layers were further characterized for FO applications.

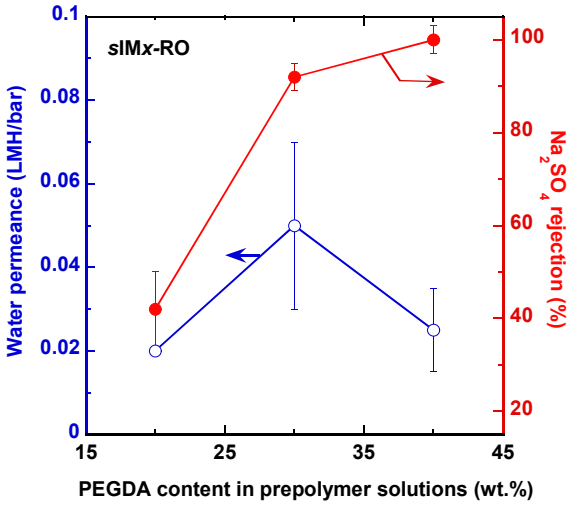

Figure S1. Effect of the PEGDA content in the prepolymer solutions on the pure-water permeance (A_W) and Na_2SO_4 rejection for the obtained *s*IM*x*-RO samples.

Table S1 provides the water permeance (*Aw*, LMH/bar), Na_2SO_4 permeance (*B*, LMH), and Na_2SO_4 and NaCl rejection of the *p*IMs and commercial membranes. Table S1 also shows the water contact angle of the membranes measured by a goniometer (model 190, Rame-Hart Instrument Co., Succasunna, NJ) via the sessile drop method (droplet size = 2 μL). The contact angle of both *p*IM330 and *p*IMZ20 increase after modification because of the PA layer. The contact angles of modified IMs are similar to those of NF90 and SW30-XLE.

Table S1. Water Permeance (A_W), Na_2SO_4 Permeance ($B_{Na_2SO_4}$), Na_2SO_4 Rejection ($R_{Na_2SO_4}$), NaCl Rejection (R_{NaCl}), and Water Contact Angle (θ)

Samples	A_w in RO[a] (LMH/bar)	$B_{Na_2SO_4}$ in RO[b] (LMH)	$R_{Na_2SO_4}$[c] (%)	R_{NaCl}[d] (%)	θ (°)
*p*IM30	0.18 ± 0.05	5 ± 1	35 ± 10	15 ± 3	40 ± 5
*p*IM30-NF1.5	0.14 ± 0.03	0.4 ± 0.1	82 ± 7	25 ± 7	58 ± 5
*p*IM30-NF2	0.15 ± 0.03	0.7 ± 0.1	75 ± 8	16 ± 5	63 ± 7
*p*IMZ20	0.22 ± 0.07	2.4 ± 0.6	57 ± 12	12 ± 5	36 ± 3
*p*IMZ20-NF1.5	0.20 ± 0.07	0.5 ± 0.1	85 ± 8	17 ± 4	61 ± 2
*p*IMZ20-NF2	0.18 ± 0.05	0.29 ± 0.02	90 ± 5	23 ± 8	70 ± 4
NF90*	13 ± 1	1.3 ± 0.1	98.9 ± 0.3	-	51 ± 7
SW30-XLE	0.8 ± 0.3	0.023 ± 0.02	99.5 ± 0.2	99.8 ± 0.2	54 ± 4
Aquaporin*	3.2 ± 0.8	1.9 ± 0.2	95 ± 1	94.5 ± 0.7	26 ± 5
HTI	0.53 ± 0.05	0.11 ± 0.04	98.5 ± 0.6	98.1 ± 0.2	63 ± 8

[a] Determined using dead-end permeation cells at 15 bar unless noted otherwise.
[b] Calculated using Equation 3 and Na_2SO_4 rejection.
[c] Feed is 2000 ppm Na_2SO_4 solution, P = 15 bar.
[d] Feed is 2000 ppm NaCl solution, P = 15 bar.
* The pressure during dead-end filtration was 10 bar.

Stability in acid and base solutions. A coupon of pIMZ20-NF1.5 membrane (diameter = 2 cm) was soaked in a 0.001 M HCl solution (pH = 3.0) or a 0.001 M NaOH solution (pH = 11.0) for 6 h to evaluate the membrane stability. Figure S2 presents the images of the membranes before and after being immersed in the acid/base solution. There are no physical changes in the sample, *i.e.*, no shrinkage or detachment of the PA skin layer, indicating the stability of the pIMZ20-NF1.5 membranes in these conditions.

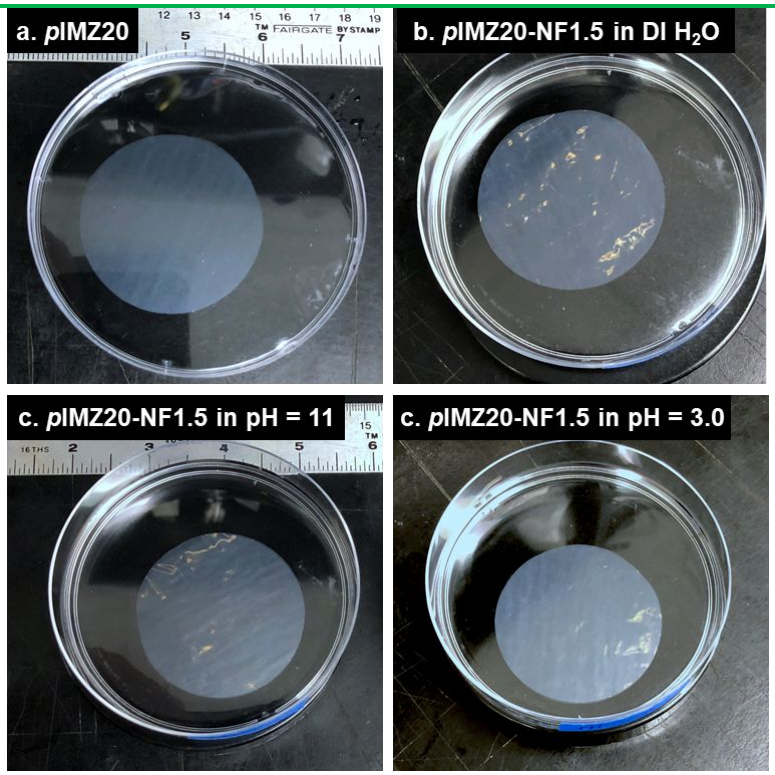

Figure S2. Images of (a) *p*IMZ20 and (b) *p*IMZ20-NF1.5 in DI water. Images of *p*IMZ20-NF1.5 after 6h in (c) pH = 11.0 solution and (d) pH = 3.0 solution.