Supplementary Information

Polyelectrolyte Nanofiltration Membranes for Base Separation and Recovery

Joshua L. Livingston[1], Abigail Cafferty[2], Riley Miller[1], Allison V. Cordova-Huaman[1], Jin Zhang[2], G. Kane Jennings[1], and Shihong Lin[1,2 *]

[1]Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee, 37205
[2]Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, Tennessee, 37205

*Corresponding Author: Shihong Lin, shihong.lin@Vanderbilt.edu

S1 Preparation of Carboxylic Acid Terminated Substrates

S1.1 Gold Substrates for PM-IRRAS

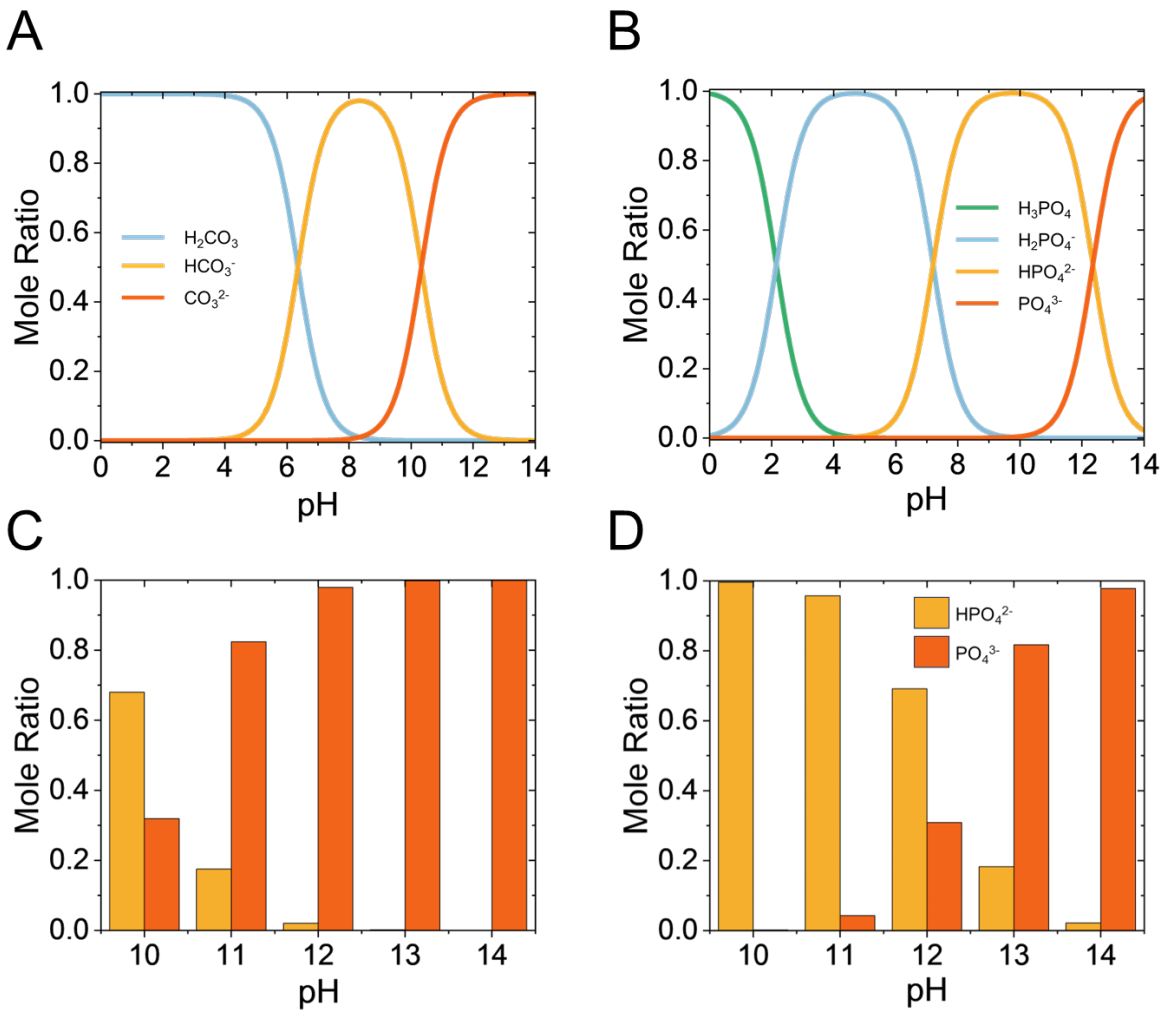
Single-sided polished boron-doped silicon wafers were rinsed with water and ethanol and then dried in a stream of N_2. Gold substrates were prepared by sequentially evaporating chromium (100 Å) and gold (1250 Å) onto the silicon wafers. Chromium and gold were deposited at a rate ≤ 2 Å/s in a diffusion-pumped chamber with a base pressure of 4 × 10-6 Torr. Before use, gold substrates were thoroughly rinsed with ethanol and dried under a stream of N_2. The gold-coated wafers were placed in a 1 mM ethanolic solution of 11-mercaptoundecanoic acid (MUA) overnight to yield a carboxylic acid-terminated self-assembled monolayer (SAM). After this, the films were subsequently rinsed with ethanol, water, and ethanol, and then dried in a stream of N_2. Dried films were exposed to PDADMAC and PSS solutions until the desired number of bilayers was deposited on the surface. Then, PM-IRRAS using a Bruker Tensor 27 was performed on the samples.

S1.2 Silicon Substrates for Ellipsometry Measurements

Silicon wafers were rinsed with ethanol, water, and ethanol, dried with N_2, and then sonicated in ethanol for 30 min. The substrates were then rinsed with ethanol, dried with N_2, and immersed into piranha solution (H_2SO_4/H_2O_2, 7:3, v/v) for 30 min to hydroxylate the silicon oxide surface. The substrates were then immersed in water, rinsed with water and ethanol, and then dried with N_2. These piranha-treated substrates were placed into a 1 mM solution of 10-undecenyltrichlorosilane in anhydrous toluene for 3 h to yield a vinyl-terminated surface. The substrates were then rinsed in toluene, water, and ethanol, and dried in a N_2 stream. Carboxylic acid groups were obtained from these vinyl-terminated monolayers using a procedure described by Wasserman et. al. [1] In short, the vinyl-terminated films were exposed for 24 h to a permanganate-periodate oxidizing

47 solution ($KMnO_4$, 0.5 mM; $NaIO_4$, 19.5 mM; and K_2CO_3, 1.8 mM, pH 6.5). The samples were
48 then rinsed in $NaHSO_3$ (0.3 M), water, 0.1 N HCl, water, and ethanol and dried under a stream of
49 N_2. Dried samples were exposed to PDADMAC and PSS solutions. Spectroscopic ellipsometry
50 was employed to measure the thickness of PDADMAC/PSS membranes on the samples.

51 **S2. Speciation Behavior for Carbonate and Phosphate Systems**



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53 Figure S1: Speciation curves for (A) carbonate species (H_2CO_3, HCO_3^-, and CO_3^{2-}) and (B) phosphate species (H_3PO_4,
54 $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) describe the distribution of ions as the pH of the solution varies. Ion valence is
55 consequential in ion transport through the membrane active layer. As the pH increases, (C) HCO_3^- dissociates into
56 CO_3^{2-} and (D) HPO_4^{2-} dissociates into PO_4^{3-}.

57 $KHCO_3$ and K_2HPO_4 act as buffering agents in aqueous solutions, so each species accepts
58 or donates protons as the pH of the solution decreases or increases, respectively (Fig. S1A and

S1B). The pKa of an ionic species denotes the pH at which 50% of the species is deprotonated. Carbonate species have two pKa values, 6.35 and 10.33. When the pH is less than 6.35, H_2CO_3 is dominant, whereas HCO_3^- species are dominant between pH 6.35 and 10.33. As the pH of the solution increases, HCO_3^- species are increasingly deprotonated to form CO_3^{2-} (Fig. S1C). Phosphate species have three pKa values (2.12, 7.2, and 12.4) that must be considered. Below pH 2.12, H_3PO_4 is dominant. Between pH 2.12 and 7.2, $H_2PO_4^-$ is the dominant species. HPO_4^{2-} dominates between pH 7.2 and 12.4, while PO_4^{3-} dominates above pH 12.4 (Fig. S1D). Under alkaline conditions, the molar ratio of carbonate and phosphate species varies significantly and ultimately has an impact on ion partitioning into the membrane active layer.

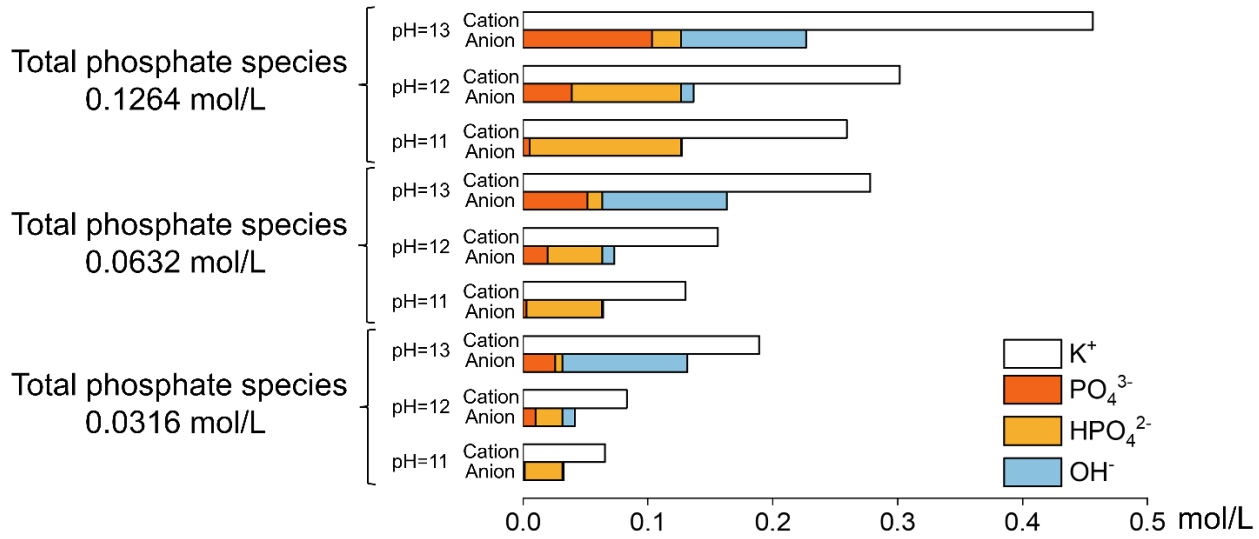


Figure S2: Nanofiltration feed solution compositions in molar equivalents of PO_4^{3-}, HPO_4^{2-}, and OH^- with varying pH (11, 12, and 13) and tot-C concentrations (0.0316, 0.632, and 0.1264 M). The bar chart demonstrates how the distribution of anions shift with the feed solution conditions, providing insight into mixed salt separation performance.

Phosphate species are in the divalent and trivalent anion form throughout the pH range of interest (Fig. S2). Such ions are excluded from our negatively PDADMAC/PSS membranes significantly more than OH^-. The trivalent anion is more prevalent as the pH of the feed solution increases, and accounts for ~80% of all phosphate species at pH 13 (Fig. S2).

S3. Carbonate and Phosphate Equilibrium Expressions

We quantified the carbonate and phosphate concentrations using mole balance, charge balance, and equilibrium expressions for each species. For example, speciation in the carbonate/hydroxide system is governed by the following equations:

$$H^+ + OH^- \rightleftharpoons H_2O \quad \text{(S1)} \qquad K_w = [H^+][OH^-] = 10^{-14} \quad \text{(S2)}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad \text{(S3)} \qquad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.35} \quad \text{(S4)}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad \text{(S5)} \qquad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.33} \quad \text{(S6)}$$

The concentration of each species is related to the total carbon concentration, $tot\text{-}C = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$, as follows:

$$\alpha_0 = \frac{[H_2CO_3]}{tot\text{-}C} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}} \quad \text{(S7)}$$

$$\alpha_1 = \frac{[HCO_3^-]}{tot\text{-}C} = \frac{[H^+]K_{a_1}}{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}} \quad \text{(S8)}$$

$$\alpha_2 = \frac{[CO_3^{2-}]}{tot\text{-}C} = \frac{K_{a_1}K_{a_2}}{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}} \quad \text{(S9)}$$

Using HCl as the titrant, each feed and permeate sample were titrated from initial pH to a set endpoint. The bulk concentration of CO_3^{2-} was quantified from the resulting titration curve utilizing the system charge balance. The initial charge balance in the system is defined as:

$$[H^+]_0 + [K^+]_0 = 2[CO_3^{2-}]_0 + [HCO_3^-]_0 + [OH^-]_0 \quad \text{(S10)}$$

Since the concentration of K^+ in the system is unchanging, the charge balance at any point along the titration curve is represented by:

$$[H^+] + [K^+]_0 = 2[{CO_3}^{2-}] + [{HCO_3}^-] + [OH^-] + [Cl^-] \quad \text{(S11)}$$

88 The charge balance at any point along the titration curve can also be represented by:

$$[Cl^-] = ([H^+] - [H^+]_0) - 2\left([{CO_3}^{2-}] - [{CO_3}^{2-}]_0\right) - ([{HCO_3}^-] - [{HCO_3}^-]_0) - ([OH^-] - [OH^-]_0) \quad \text{(S12)}$$

89 The *tot-C* can be calculated given the pH and concentration of acid added at any point

90 along the titration curve and an initial pH_0.

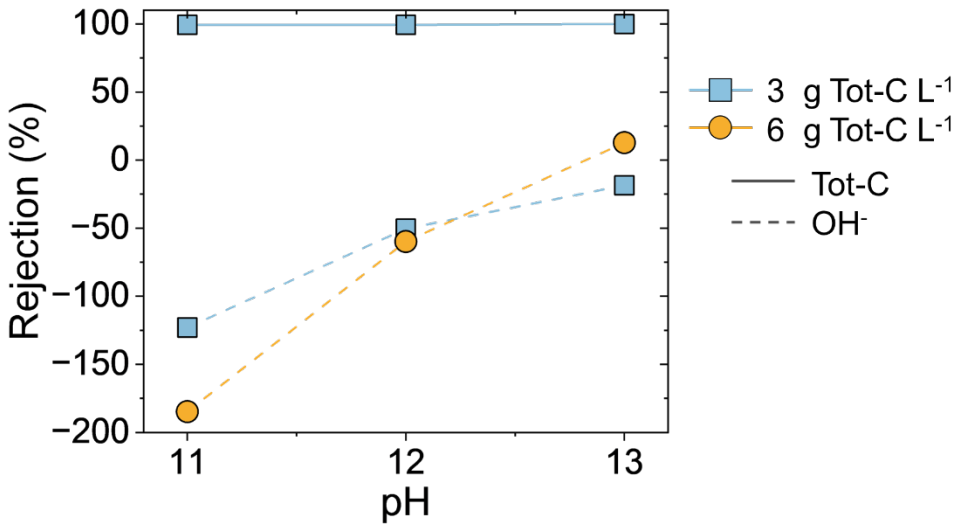
$$[Cl^-] = (10^{-pH} - 10^{-pH_0}) - 2(\alpha_2\ tot\text{-}C - \alpha_2\ tot\text{-}C) - (\alpha_1\ C_{Tot} - \alpha_1\ tot\text{-}C) - (10^{pH-14} - 10^{pH_0-14}) \quad \text{(S13)}$$

91 The concentration of CO_3^{2-} is calculated using $[{CO_3}^{2-}] = \alpha_2\ tot\text{-}C$ at every point along the

92 titration curve, corrected for change in sample volume, and averaged. Similar principles were

93 applied to quantify the concentration of phosphate.

94 **S4. NF90 Membrane OH^-/tot-C Separation Performance**



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96 Figure S3: The performance of the commercial NF90 membrane in OH^-/tot-C separations as the pH (11, 12, and 13)
97 and tot-C concentration (3 and 6 g tot-C L^{-1}) in the feed solution varies.

The NF90 membrane is incapable of discriminating between carbonate species. The commercial polyamide membrane removes >99% of all tot-C species, preventing HCO_3^- from partitioning into the membrane active layer. OH^- rejection is negative under all conditions investigated because it is the only monovalent anion capable of partitioning into the membrane with K^+ to maintain charge neutrality. Under such conditions, the OH^- rejection becomes less negative as the pH increases and grows more negative with increasing tot-C concentration in the feed solution (Fig. S3).

Supplementary References

1. S.R. Wasserman, Y.T. Tao, G.M. Whitesides, Structure and reactivity of alkylsiloxane monolayers formed by reaction of alkyltrichlorosilanes on silicon substrates, Langmuir 5 (1989) 1074–1087. https://doi.org/10.1021/la00088a035.