

Supporting Information

for

Mono-/Bi-valent Anion Resource Recovery via Electrodialysis Fabricated with Dual-Side-Chain Functionalized Poly(aryl ether sulfone) Anion Exchange Membranes

Junbin Liao ^{a,*}, Qishun Zhang ^a, Yu Xu ^a, Shiyu Zhou ^a, Yifan Xu ^a, Wenlong Ding ^a,
Zhiqiang Wu ^a, Haoyu Liu ^a, Yanqing Xu ^a, Huimin Ruan ^a, Jiangnan Shen ^{a,*}

^a College of Chemical Engineering, Zhejiang University of Technology, Hangzhou
310014, China.

* Corresponding Authors: Junbin Liao (E-mail: jbliao@zjut.edu.cn); Jiangnan Shen (E-mail: shenjn@zjut.edu.cn).

1. Materials and Chemicals

A commercial CEM Type-II was received from FUJI film Corp. (Japan). (Surface area resistance: $3.55 \Omega \cdot \text{cm}^2$; IEC: $2.03 \text{ mmol} \cdot \text{g}^{-1}$, tested in 0.5 M NaCl (aq.); and thickness ca. $165 \mu\text{m}$). Commercial anion selective Neosepta AMX (Surface area resistance: $2.85 \Omega \cdot \text{cm}^2$; IEC: $1.62 \text{ mmol} \cdot \text{g}^{-1}$, tested in 0.5 M NaCl (aq.); and thickness ca. $170 \mu\text{m}$) was obtained from Tokuyama Co-ASTOM Japan.

2. Thermogravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) experiments were performed using a SDT Q600 V8.2 Build100 thermogravimetric analyzer under a flow of N_2 .

3. Surface Area Resistance

Prior to testing, the AEM samples were immersed in 0.5 M NaCl (aqueous) solution for 12 h. The samples were then placed between two custom-made compartments filled with

0.5 M NaCl (aqueous) solution. These compartments were connected to a conductivity meter to measure and record the conductivity value. The surface area resistance was calculated using Equation (1):

$$R = \frac{1000}{\lambda_0} - \frac{1000}{\lambda_1} \quad (1)$$

where R ($\Omega \cdot \text{cm}^2$) is the surface area resistance, the λ_0 (mS/cm) is the ion conductivity across the membrane on both sides, and λ_1 (mS/cm) is the blanking ion conductivity.

4. Ion Exchange Capacity and Limiting Current Density

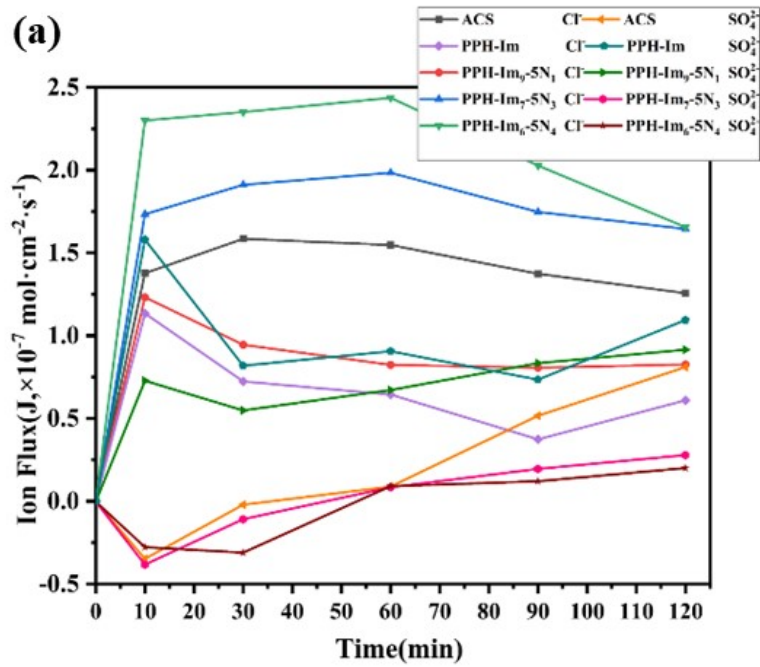
Ion exchange capacity (IEC) serves as a crucial parameter for quantifying the density of ion exchange groups within the IEM. In the case of AEM in Cl^- form, the IEC was determined through titration. The AEM was immersed in 0.5 M NaCl aqueous solution to ensure complete replacement of Br^- ions with Cl^- ions. After 24 h, the IEM was extracted and any residual NaCl solution on the surface was thoroughly rinsed off with deionized (DI) water. Subsequently, it was exposed to 60 mL of 0.5 M Na_2SO_4 solution for another 24 h. This process led to complete release of Cl^- from the AEM into the solution. The concentration of Cl^- was determined *via* titration using 0.05 M AgNO_3 solution with K_2CrO_4 as the indicator. Finally, the IECs of the AEMs were calculated using the provided Equations (3).

$$IEC = \frac{V \times c_{\text{Cl}^-}}{m} \quad (2)$$

where V (mL) is the volume of Na_2SO_4 (aq.) used to soak the sample, c_{Cl^-} (M) is the chloride ion concentration in the Na_2SO_4 (aq.) after soaking the sample, m (g) is the mass of sample.

The limiting current density was determined by analyzing the current-voltage curves of the prepared AEMs. The same equipment used for surface area resistance testing was employed for this purpose. During the test, the current range was set from 0 to 0.2 A with a current gradient of 0.01 A. Notably, the two central compartments were filled with 0.05 M NaCl solution, while the electrode chamber was filled with 0.3 M Na₂SO₄ solution.

5. Evaluation of Cl⁻/SO₄²⁻ Ion Separation



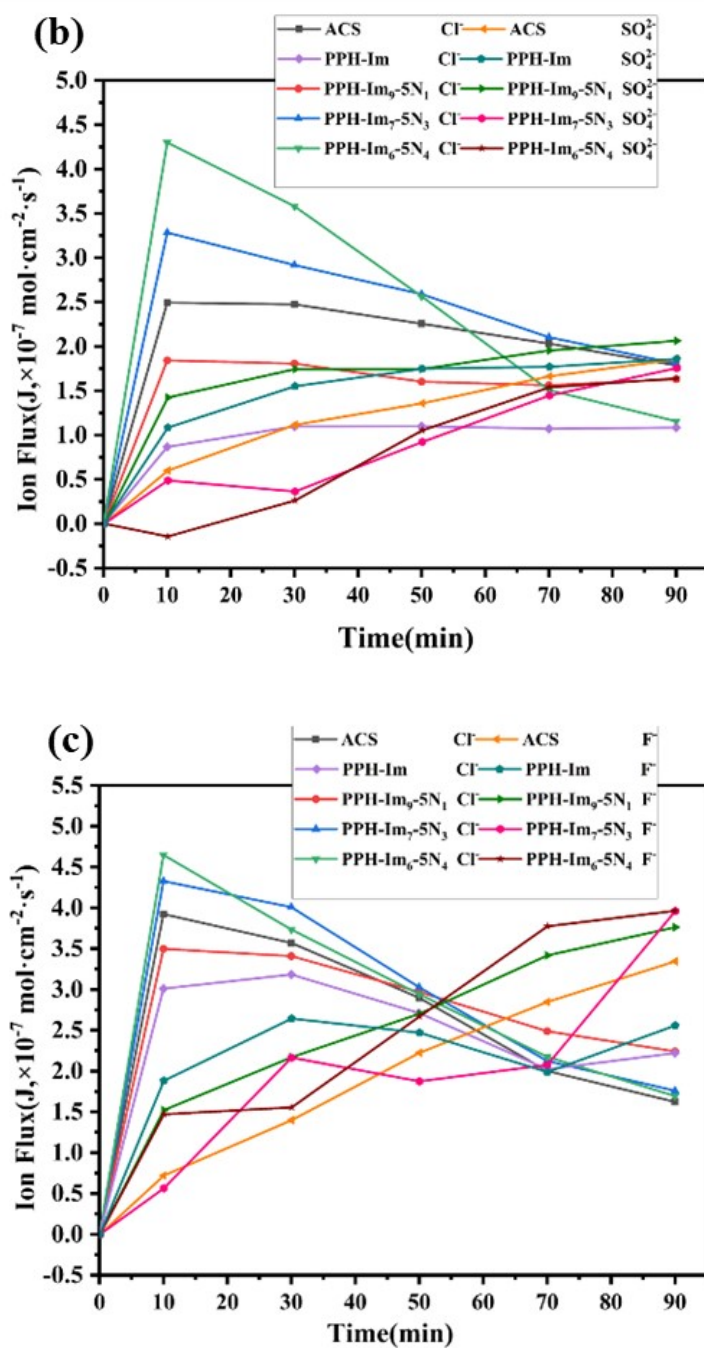


Figure S1. (a) Ion Flux of Cl⁻, SO₄²⁻ ions in DCs of EDs with PPH-sIm_{10-X}-5N_X (X = 0, 1, 3, 4) at 2.5 mA·cm⁻². (b) Ion Flux of Cl⁻, SO₄²⁻ in DCs of EDs with PPH-sIm_{10-X}-5N_X at 5.0 mA·cm⁻². (c) Ion Flux of Cl⁻ and F⁻ in DCs of EDs with PPH-sIm_{10-X}-5N_X at 5.0 mA·cm⁻².

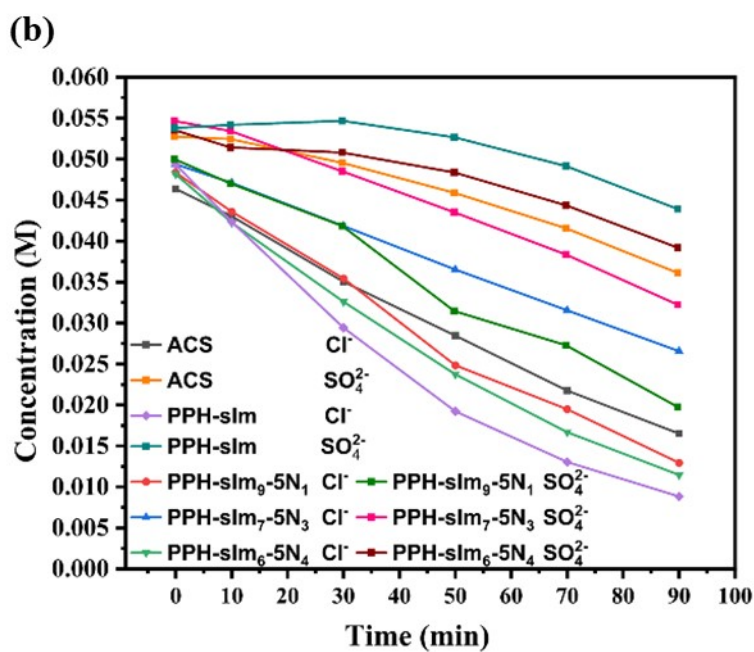
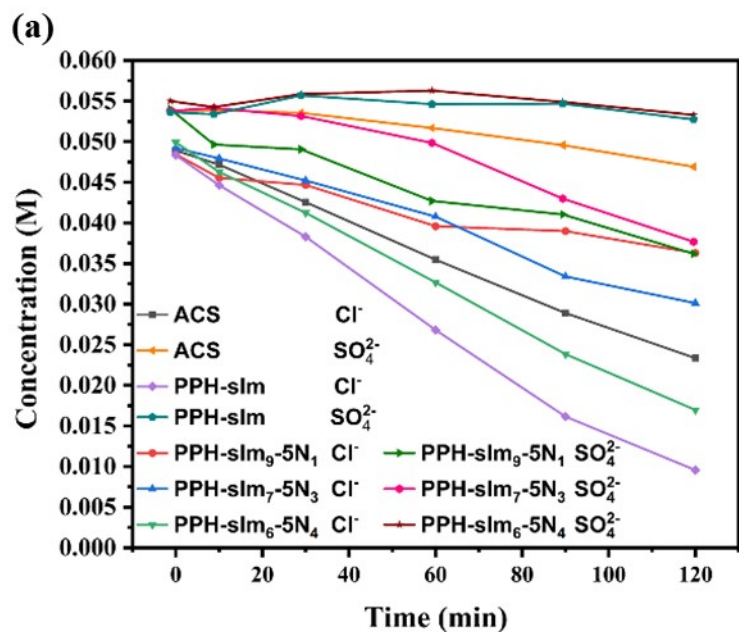


Figure S2. (a) Concentration evolution of Cl⁻, SO₄²⁻ ions in DCs of EDs with PPH-sIm_{10-X}-5N_X at 2.5 mA·cm⁻². (b) Concentration evolution of Cl⁻, SO₄²⁻ ions in DCs of Eds with PPH-sIm_{10-X}-5N_X at 5 mA·cm⁻². multiple tests.

6. Dynamics simulation under electric field

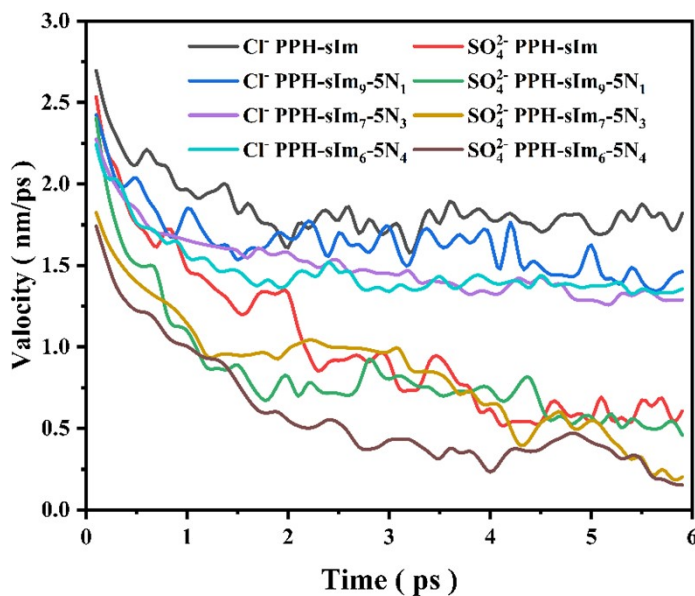


Figure S3 Velocity of Cl^- and SO_4^{2-} ions passing through PPH-sIm_{10-X}-5N_X (X = 0, 1, 3, and 4) under the driving force in electric field (unfit).

7. Comparison of Selectivity with Previously Reported Membranes

Table S1. Comparison of perm-selectivity ($P_{\text{SO}_4^{2-}}^{\text{Cl}^-}$) of PPH-sIm₆-5N₄ AEM with those from some typical reported mono-/bi-valent anion selective IEMs.

AEMs	Anion types	Current density	$P_{\text{SO}_4^{2-}}^{\text{Cl}^-}$	Ref
PDA/(Fe)PAA-M	0.1 M Na_2SO_4 and 0.1 M NaCl	5 $\text{mA}\cdot\text{cm}^{-2}$	5.6	1
sCOF/aAEM3	0.05 M Na_2SO_4 and 0.05 M NaCl	5 $\text{mA}\cdot\text{cm}^{-2}$	18.92	2
AIEM-12C	0.05 M Na_2SO_4 and 0.05 M NaCl	5 $\text{mA}\cdot\text{cm}^{-2}$	22.51	3
IM-PAES-sIM	0.05 M Na_2SO_4 and 0.05 M NaCl	5 $\text{mA}\cdot\text{cm}^{-2}$	9.52	4
PPH-sIm ₆ -5N ₄	0.05 M Na_2SO_4 and 0.05 M NaCl	5 $\text{mA}\cdot\text{cm}^{-2}$	26.27	This work

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