Supplementary Information (SI) for Industrial Chemistry & Materials.

Supporting Information of

MOF-based homogeneous ion exchange membrane for high-efficiency magnesium-lithium separation

Tong Mu[a,b,#], Geting Xu[a,b#], Zhihang Xia[a,b], Hao Qian[a,b],Yangbo Qiu[c], Wanji Zhou[d], Jiahao Yu[a,b], Junbin Liao[a,b,*], Jiangnan Shen[a ,b,*]

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

b State Key Laboratory of Advanced Separation Membrane Materials, National Key Laboratory of Green Chemical Synthesis and Transformation Technology, Zhejiang University of Technology, Hangzhou 310014, China.

c Department of Civil Engineering, The University of Hong Kong, Pokfulam, Hong Kong, SAR 999077, PR China.

d Salt Lake Chemical Engineering Research Complex, School of Chemical Engineering, Qinghai University, Xining 810016, Qinghai, China.

* Corresponding Authors:

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

Introduce

Table S1 Water and diameter of different metal ions in salt lake

Ion species	water and diameter（nm）	Water and layer thickness
Li^+	0.764	Large and stable (hydration layer 4)
Mg^{2+}	0.825	Large and stable (6 hydration layers)
Na^+	0.716	Large and stable (6 hydration layers)
K^+	0.662	Small and unstable (hydration layer 4)
Fe^{3+}	0.863	Maximum and stable (hydration layers 6-8)
Mn^{2+}	0.812	Large and stable (hydration layer 4)
Sr^{2+}	0.858	Small and unstable (hydration layer 3)

Characterization of materials

Characterization of surface morphology

The surface morphology of the prepared membrane materials was observed and characterized by cold field scanning electron microscope (SEM, Zeiss Gemini.500, Germany). The method specifically comprises the following steps of: drying a membrane to be observed at 80 DEG C to completely remove moisture, cutting the membrane into square sheets, and pasting the square sheets on an SEM circular observation table; and for characterization of the membrane section, cutting the membrane into strips and bending the strips, immersing the bent parts into a beaker filled with liquid nitrogen, quenching the membrane at low temperature of liquid nitrogen, and fixing the sections upward on the SEM cross section observation table for characterization shooting. In addition, in order to enhance the observation of the surface morphology of the original membrane and the modified membrane, the surface morphology of the modified membrane was observed by scanning the surface morphology of the modified membrane with a Dimension Icon microscope (Bruker Co.) Tapping mode acquisition was performed to obtain atomic force microscope (AFM) phase images of the prepared CEM samples.

Water Contact Angle, Water Uptake and Swelling Tests

To evaluate changes in hydrophilicity of the membrane surface, a static contact angle analyzer was used (OCA50AF, Germany) analysis, using the static water contact angle (WCA) of CEM surface, three points were taken on the surface of a certain size (3×3) membrane, i.e. three different areas were measured; to evaluate the properties of water uptake and swelling of the membrane, water uptake (WU) and swelling ratio (SR) were used. Initially, the membrane samples were immersed in DI water at room temperature for a duration of 24 h, after which any surface moisture was removed prior to measuring their mass and dimensions. Subsequently, the wet membranes underwent drying for 24 h, measuring once more. The calculations for WU and SR were tabulated in accordance with Equations (1) and (2), respectively[1,2].

$$\text{WU} = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100\% \quad (1)$$

$$\text{SR} = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \quad (2)$$

where M_{wet} (in g) and L_{wet} (in cm) are the weight and length of the wet membrane, M_{dry} (in g) and L_{dry} (in cm)are the weight and length of the dried membrane.

Surface Area Resistance Test

The surface area resistance was measured using a custom-made apparatus (MEIEMP-I, Hefei Chemjoy Polymer Materials Co., Ltd., China). Before the test, the required membrane was immersed in 0.5M NaCl solution for 24 hours to make ions completely filled in the membrane and ensure ion balance before the test. The test device was divided into two commercially available AEM and CEM to be tested. 0.5M NaCl solution was filled into two compartments to be tested respectively, and then 0.3M Na_2SO_4 solution was introduced into the electrode chambers on both sides as polar chamber circulating solution. The effective test area of the membrane was 7.065cm^2. The constant current of 0.5A was used during the test process. Use a multimeter to test the conductivity potential on both sides of the membrane, and make calculations as shown in Equation (3).

$$\text{R} = \frac{U - Uo}{I} \times S \quad (3)$$

where U(in V) represents the transmembrane voltage, U_0 (in V) represents the voltage of the blank group (without the membrane to be tested), I (in A) represents the constant current , and *S* (in cm^2) represents the effective test area.

Ion Exchange Capacity (IEC) Measurement

The ion exchange capacity (IEC) was determined using a standard ion-exchange process. The membrane sample was cut into small strips, dried in an oven, and weighed to obtain the dry mass (Mdry). The dried membrane was then immersed in a 0.1 M HCl solution for 24 hours to protonate the functional groups. Afterwards, the membrane was removed, rinsed thoroughly with deionized water to remove surface-acid residue, and subsequently immersed in a 0.1 M NaCl solution (volume = L_1) for 24 hours to exchange the H^+ ions for Na^+ ions. The released H^+ ions in a specific aliquot (volume = L_2) of the NaCl solution were then determined by titration with a 0.1 M NaOH solution, consuming a volume of L_3. The IEC value (mmol/g) was calculated using the following formula:

$$\mathrm{IEC}=\frac{0.1\times L3\times L1}{Mdry\times L2} \quad (4)$$

where L_1 denotes the total volume (in mL) of the NaCl solution used for immersion; L_2 represents the volume (in mL) of the aliquot taken from the NaCl solution for titration; L_3 is the volume (in mL) of the NaOH titrant consumed; and M_dry is the dry mass of the membrane sample (in g).

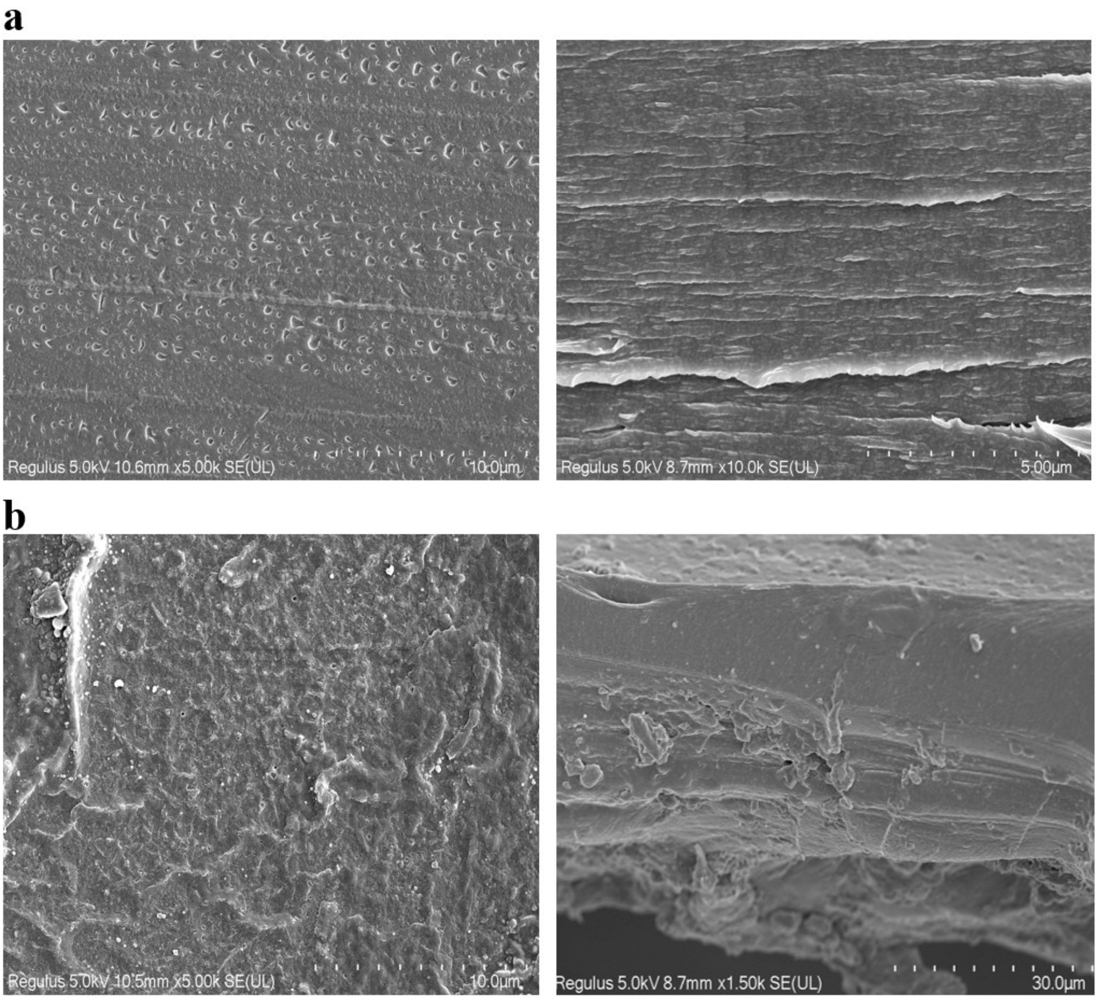
limiting current density

the limiting current density of the cation exchange membrane was determined by testing its current-voltage (I-V) curve. The test was conducted using a custom-built device. The membrane under test and two commercial AMX membranes were placed in the middle and on both sides of the device, respectively, dividing the entire device into four compartments. A 0.3 M Na_2SO_4 solution was added to the electrode compartments, while a 0.05 M NaCl solution was added to the compartments on both sides of the membrane under test. The initial current was set to 0.001 A, and then the current was gradually increased in increments of 0.0005 A. A multimeter was used to measure and record the voltage corresponding to the current at each moment.

Chemical Composition and Structure Characterization

The chemical composition of the prepared ion exchange membrane was characterized by ATR-FTIR using Fourier Transform Infrared Spectroscopy.(Nicolet 6700), scanning in the range of 500-4000cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer (Kratos Analytical, Shimadzu, Japan),scanning depth of 10 nm.

Result and discussion



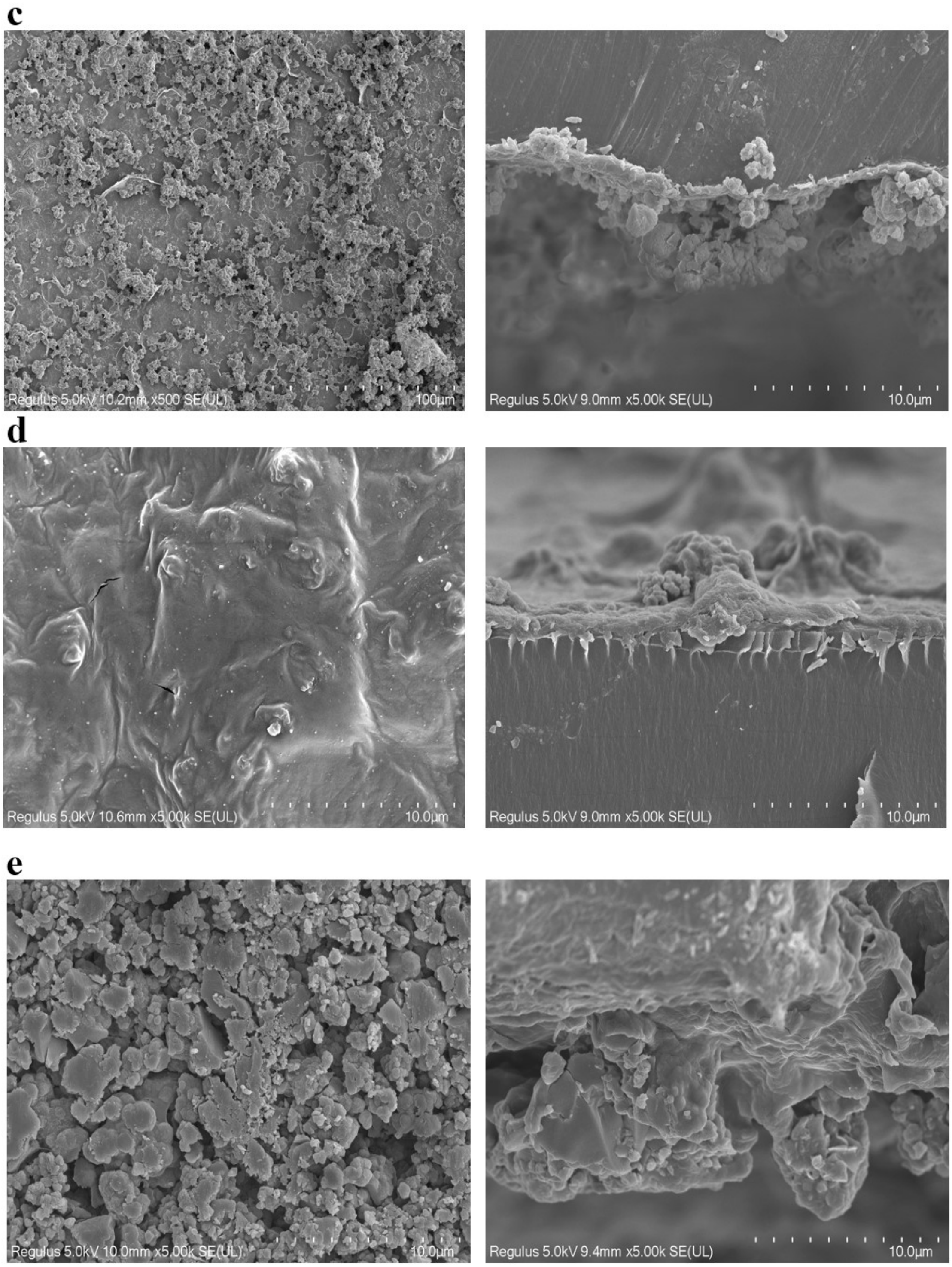
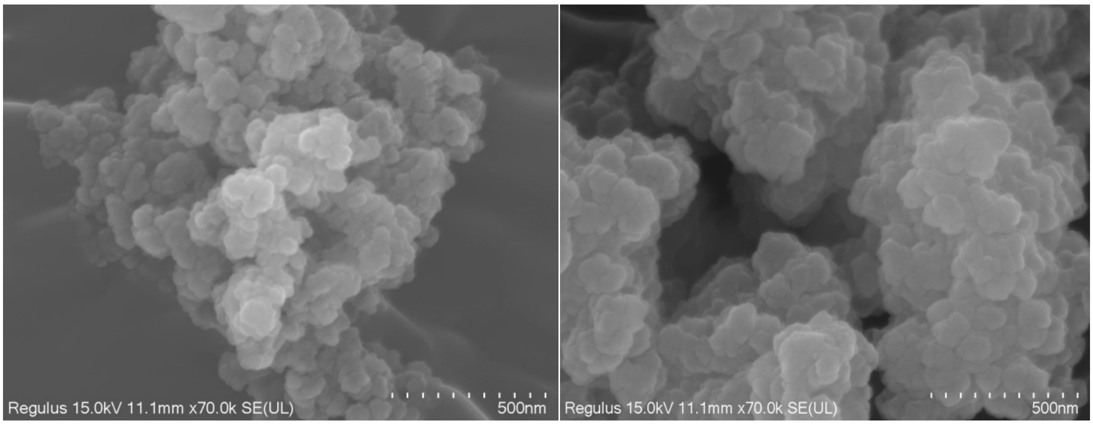


Fig S1.SEM images of membrane (a)SPES-1; (b)SPES/PEI-2; (c)SPES/PEI/U/P-5; (d)SPES/PEI/U/P-15; (e)SPES/PEI/U/P-30

a



b

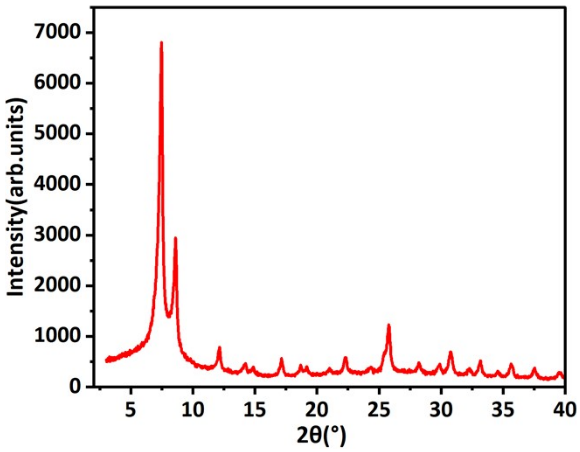


Fig S2. (a)SEM images of UiO-66-NH_2;(b) XRD patterns of UiO-66(Zr)–NH_2

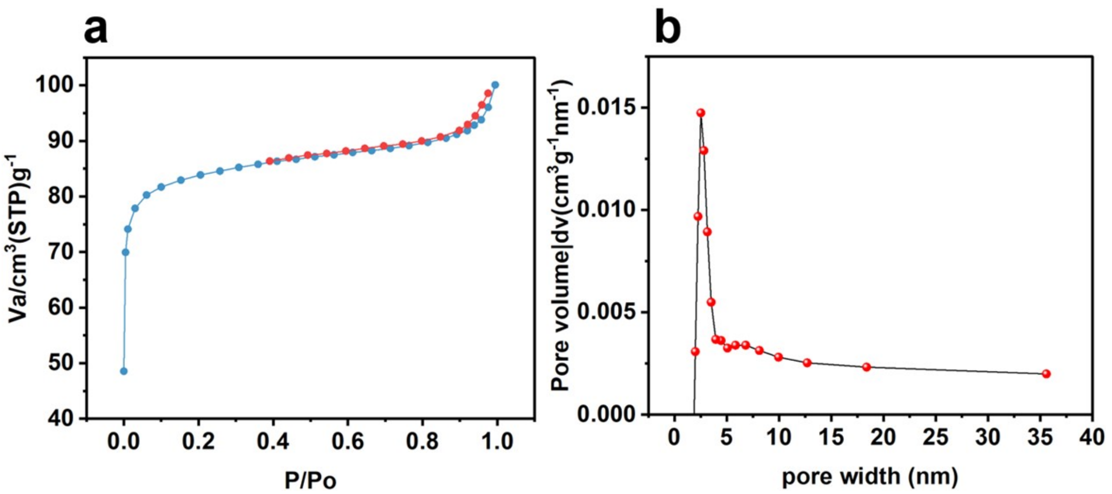


Fig S3. (a) N_2 adsorption–desorption isotherms of UiO-66-NH_2 and;(b) The pore size distribution of (a) UiO-66-NH_2

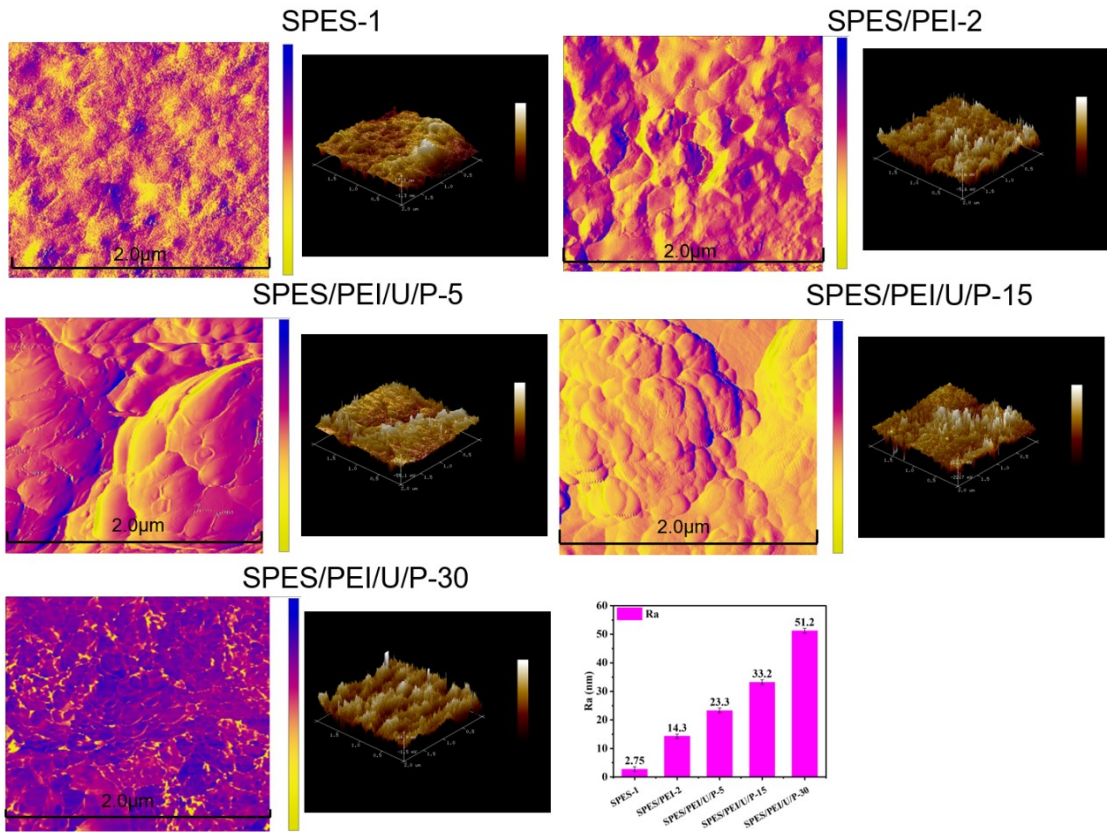


Fig S4. (a)AFM images of membranes

Concentration change curve during the selectivity test

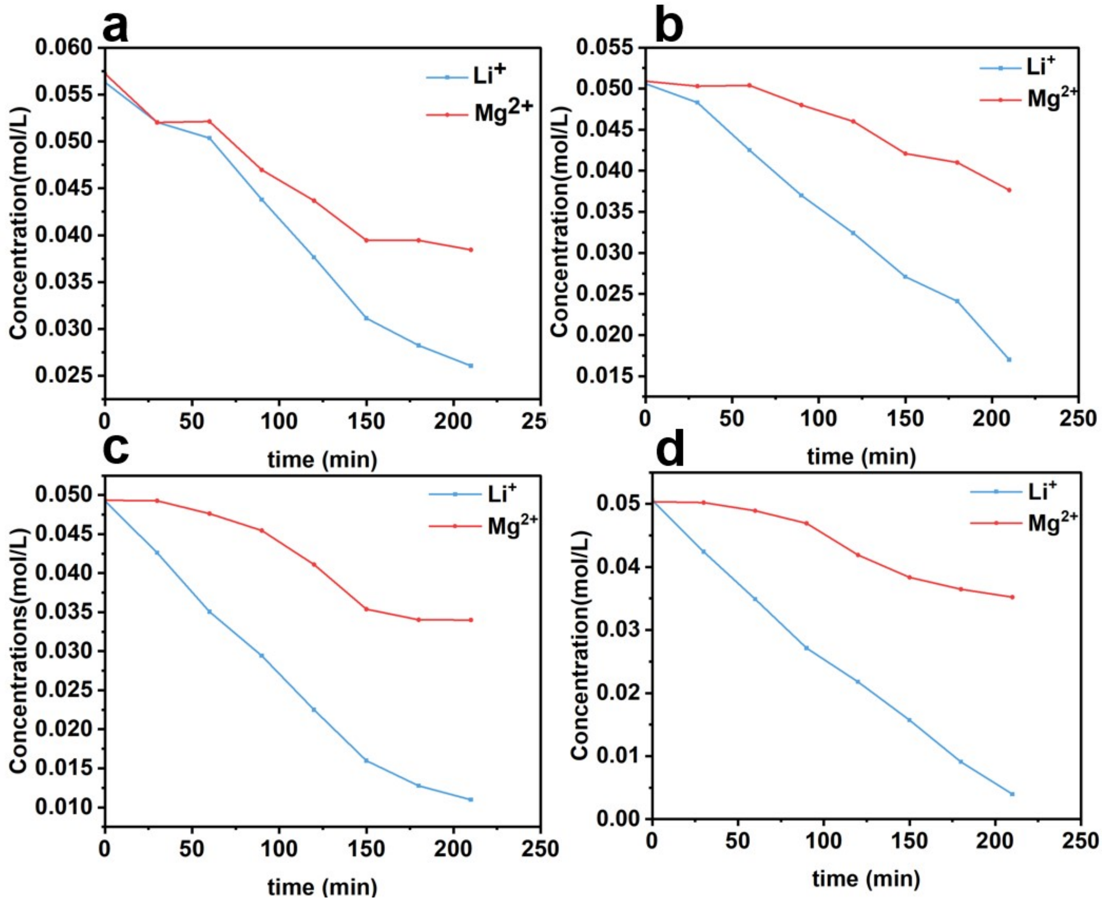


Fig S5.(a)Li^+/Mg^{2+} Ion Concentration Changes of SPES-1;(b) Li^+/Mg^{2+} Ion Concentration Changes of SPES/PEI-2;(c)Li^+/Mg^{2+} Ion Concentration Changes of SPES/PEI/U/P-5;(d)Li^+/Mg^{2+} Ion Concentration Changes of SPES/PEI/U/P-15;

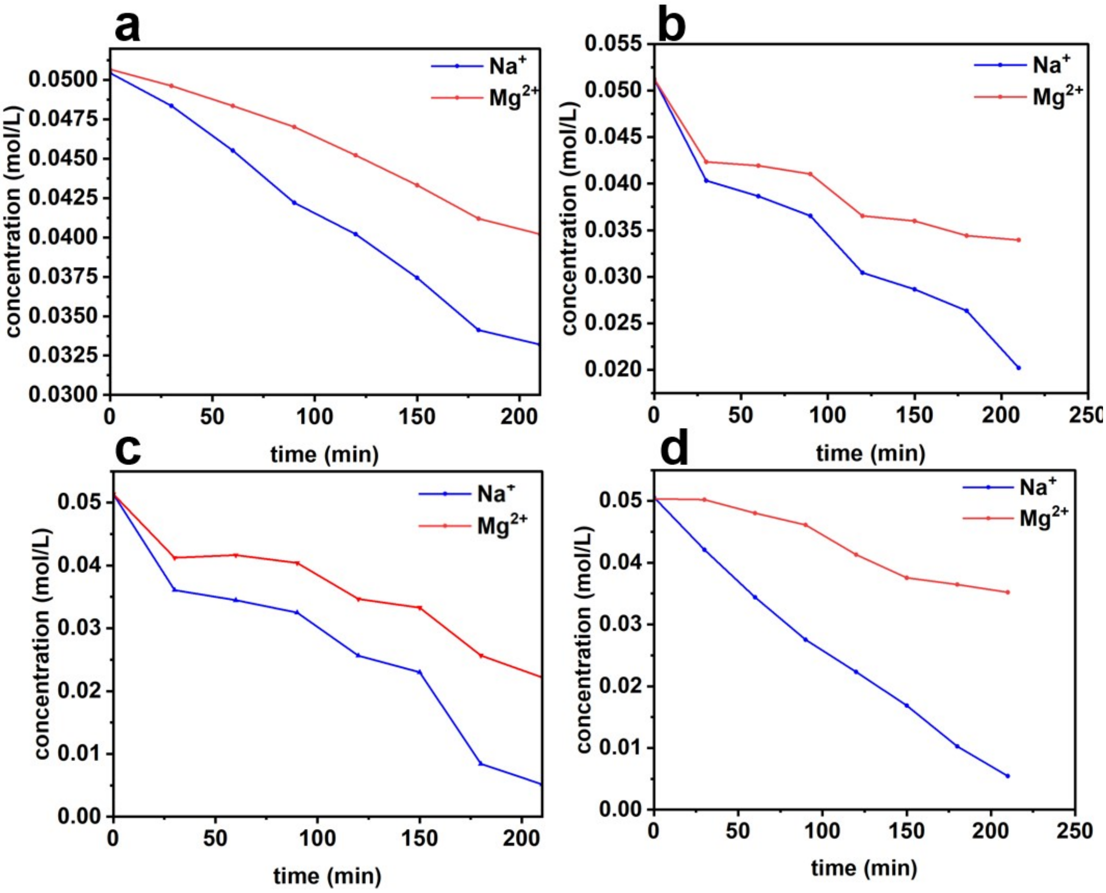


Fig S6.(a) Na^+/Mg^{2+} Ion Concentration Changes of SPES-1;(b) Na^+/Mg^{2+} Ion Concentration Changes of SPES/PEI-2;(c)Na^+/Mg^{2+} Ion Concentration Changes of SPES/PEI/U/P-5;(d) Na^+/Mg^{2+} Ion Concentration Changes of SPES/PEI/U/P-15;

Table S2 Perm-Selectivity test and flux of membrane materials(Li^+/Mg^{2+})

Current density（mA·cm^{-2}）	Name	J(Li^+) (mol·cm^{-2}·s^{-1})	J(Mg^{2+}) (mol·cm^{-2}·s^{-1})	Perm-Selectivity
2.5	SPES-1	1.06×10^{-8}	0.63×10^{-8}	1.8
	SPES/PEI-2	1.09×10^{-8}	0.44×10^{-8}	5.1
	U/P-5	1.29×10^{-8}	0.60×10^{-8}	6.6
	U/P-15	1.49×10^{-8}	0.56×10^{-8}	23.3
	U/P-30	1.59×10^{-8}	0.40×10^{-8}	32.2
5	U/P-30	1.63×10^{-8}	1.47×10^{-8}	13.8

Table S3 Perm-Selectivity test and flux of membrane materials(Na^+/Mg^{2+})

Current density（mA·cm^{-2}）	Name	$J(Na^+)$ (mol·cm^{-2}·s^{-1})	$J(Mg^{2+})$ (mol·cm^{-2}·s^{-1})	Perm-Selectivity
2.5	SPES-1	0.58×10^{-8}	0.35×10^{-8}	2.1
	SPES/PEI-2	0.86×10^{-8}	0.49×10^{-8}	3.1
	U/P-5	1.35×10^{-8}	0.84×10^{-8}	5.9
	U/P-15	1.43×10^{-8}	0.56×10^{-8}	16.2
	U/P-30	1.48×10^{-8}	0.50×10^{-8}	26.2

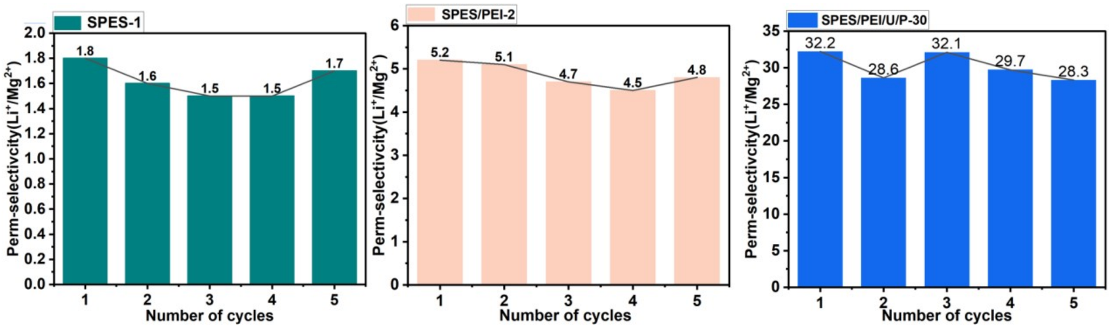


Fig S7 Selectivity changes after long-term cycling of different ion exchange membranes

Table S4 Examples of membrane material selectivity and Li^+ flux for published

studies

References	Membrane name	Initial Condition	P（Li^+/Mg^{2+}）Prem-selectivity	J（Li^+）
[3]	HSO_3-UiO-66@QPPO-20%	Diffusion dialysis	8.33	0.37mol·m^{-2}·h^{-1}
[4]	PEI@ZIF-8-NH_2+ TMC-1	Nanofiltration	7.86	0.687mol·m^{-2}·h^{-1}
[5]	TFN-(Zr/Ti)-2	ED	11.38	5.43 × 10^{-8} mol cm^{-2} s^{-1}
[6]	ZPEI-TMC/SPEEK	ED	12.43	9.87×10^{-9}mol·cm^{-2}·s^{-1}
	EB3-TFP2-QACOF/SPEEK	ED	25.2	1.25×10-8 mol cm^{-2} s^{-1}
[7]	PANI-Q24	ED	1.75	2.75×10^{-10}mol·m^{-2}·s^{-1}
[8]	M-12C4-0.50-PEI	ED	5.23	4.22×10^{-9} mol·m^{-2}·s^{-1}
[9]	PPY-I-10C	ED	1.71	2.64×10^{-10} mol cm^{-2} s^{-1}
[10]	monovalent-selective CEM	ED	6.8	
This work	**U/P-30**	**ED**	**32.2**	**1.63×10^{-8} mol cm^{-2} s^{-1}**

1 Q. Chen, Y.Y. Yao, J.B. Liao, J.H. Li, J.W. Xu, T.T. Wang, Y.Y. Tang, Y.Q. Xu, H. M.Ruan, J.N. Shen, Subnanometer Ion Channel Anion Exchange Membranes Having a Rigid Benzimidazole Structure for Selective Anion Separation, *ACS Nano* **16(3)** (2022) 4629-4641. 10.1021/acsnano.1c11264
2 M. Fujimura, T. Hashimoto, H. Kawai, Small-angle x-ray scattering study of perfluorinated ionomer membranes. 1. Origin of two scattering maxima, *Macromolecules* **14(5)** (1981) 1309-1315. 10.1021/ma00229a028
3 X.J.Zeng,L.Xu,T.Deng,Y.X.Wang,W.Xu,W.Zhang, Anionic MOFs Embedded in Anion-Exchange Membranes for the Separation of Lithium/Magnesium Cations,*ACS Sustainable Chem. Eng.* **Vol 11/Issue 35**(2023). 10.1021/acssuschemeng.3c00891
4 H.F.Jia , Y.C.Wang , L.Z.Yang , R.Fang, Development of an Environmentally Friendly nanofiltration membrane for efficient Lithium-Magnesium separation using ZIF-8-NH2 grafted polyamide, *Sep. Purif.Technol*,**Volume 362, Part 3, 30** July 2025, 131870. 10.1016/j.seppur.2025.131870
5 T.T.Xu, F.M.Sheng, B.Wu, M.A.Shehzad, A.Yasmina, X.X.Wang, Y.B.He, L. Ge, X.S.Zheng, T.W.Xu,Ti-exchanged UiO-66-NH2–containing polyamide membranes with remarkable cation permselectivity, *J. Membr. Sci,***Volume 615, 1** December 2020, 118608. 10.1016/j.memsci.2020.118608
6 H.Qian, G.T.Xu, S.S.Yang, E.H.Ang, Q.Chen, C.F.Lin, J.B. Liao, J.N. Shen, Advancing Lithium−Magnesium Separation: Pioneering Swelling-Embedded Cation Exchange Membranes Based on Sulfonated Poly(ether ether ketone), *ACS Appl. Mater. Interfaces* 2024, **16**, 18019−18029. 10.1021/acsami.4c00991
7 X.Pang, Y.Y.Tao, Y.Q.Xu, J.F.Pan, J.N.Shen, C.J.Gao, Enhanced monovalent selectivity of cation exchange membranes via adjustable charge density on functional layers, *J. Membr. Sci*, **595** (2020) 117544. 10.1016/j.memsci.2019.117544
8 S.S.Yang,S.J.Yu,L.Yu,Y.W. Liu,J.B.Liao,J.N.Shen, C.J. Gao, Cation Exchange Membranes Coated with Polyethyleneimine and Crown Ether to Improve Monovalent Cation Electrodialytic Selectivity, *Membranes* 2021, **11(5)**, 351; 10.3390/membranes11050351
9 X. Pang,X.H.Yu,Y.B.He,S.Dong,X.T.Zhao,J.F.Pan, R.N.Zhang, L.F.Liu,Preparation of monovalent cation perm-selective membranes by controlling surface hydration energy barrier, *Sep. Purif.Technol,***Volume 270**, (2021)118768. 10.1016/j.seppur.2021.118768
10 Amilton Barbosa Botelho Junior, Kristen Abels, Denise Crocce Romano Espinosa and William A. Tarpeh*,Lithium Extraction by Electrodialysis: Effect of Co-Occurring Ions for Application in Brine Processing,*J. Electrochem. Soc*. **172** 023501