Supplementary Information

Continuous ion separation via electrokinetic-driven ion migration path differentiation: Practical application to lithium extraction from brines

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Method	Materials	Composition of brine (g L ⁻¹)	Mg ²⁺ /Li ⁺ ratio	Ion separation efficiency (%)	Lithium recovery rate (%)	Ref.
Force-based	AEM	$Li^+: 0.15 \\ Na^+: 3.4 \\ K^+: 0.78 \\ Mg^{2^+}: 3 \\ Ca^{2^+}: 0.04 \\$	20	44.2	27.7	Our work
Adsorption	H ₂ TiO ₃	Li ⁺ : 1.63 Na ⁺ : 59 K ⁺ : 18.7 Mg ²⁺ : 29 Ca ²⁺ : 0.23	17.8	> 99	$32.6 \text{ mg g}^{-1a)}$	1
	C@Li ₄ Ti ₅ O ₁₂	$\label{eq:linear} \begin{array}{l} Li^+: \ 0.011 \\ Na^+: \ 0.03 \\ K^+: \ 0.092 \\ Mg^{2+}: \ 0.044 \\ Ca^{2+}: \ 0.04 \end{array}$	4	> 99	28.46 mg g ^{-1a)}	2
	PVC-MnO ₂	Li ⁺ : 0.222 Na ⁺ : - K ⁺ : - Mg ²⁺ : 1.22 Ca ²⁺ : -	5.5	> 99	22.9 mg g ^{-1a)}	3
Solvent extraction	Trioctylamine	Li ⁺ : 5 Na ⁺ : - K ⁺ : 1 Mg ²⁺ : 96 Ca ²⁺ : -	20	67.9	98 (single stage)	4
	Tributyl phosphate and [Bmim] ₃ PW ₁₂ O ₄₀	Li ⁺ : 0.35 Na ⁺ : 1.84 K ⁺ : 0.62 Mg ²⁺ : 96 Ca ²⁺ : -	274	-	69.18 (single stage)	5
Nanofiltration	Polyamide thin-film composite	Li ⁺ : 0.141 Na ⁺ : 117 K ⁺ : 3.79 Mg ²⁺ : 5.64 Ca ²⁺ : 0.43	39	84.6	55	6

Table S1. Comparison of previously reported lithium extraction	n methods with our work.
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	Polyethyleneimine and trimesoyl chloride composite	Li ⁺ : 0.068 Na ⁺ : - K ⁺ : - Mg ²⁺ : 1.38 Ca ²⁺ : -	20	93.5	81	7
Selective- electrodialysis	IEM pairs (AEM & CEM)	Li ⁺ : 0.34 Na ⁺ : - K ⁺ : - Mg ²⁺ : 8.94 Ca ²⁺ : -	26.29	5 ^{b)}	60	8
	IEM pairs (AEM & CEM)	Li ⁺ : 0.34 Na ⁺ : 6.95 K ⁺ : - Mg ²⁺ : 6.95 Ca ²⁺ : -	20	1.7 ^{b)}	39.7	9

a) Li+ adsorption capacity (Q_e); b) Separation coefficient (F_{Mg⁻Li})



Fig. S1 A schematic illustrating ICP phenomena in the AEM-bridged typical microfluidic Hshaped electrokinetic system. When a DC electric field is applied across the microchannels, only anions pass through AEM due to anion perm-selectivity of the AEM, and simultaneously cations recede from the vicinity of cathodic side of the AEM to maintain system's electroneutrality. As a result, an ion depletion region where ions barely exist is induced in the top microchannel. Concurrently, cations in the bottom channel congregate to the vicinity of anodic side of the AEM also to maintain the system's electroneutrality, resulting in an ion enrichment region. This polarization of ion concentration is called ion concentration polarization.



Fig. S2 Schematics illustrating ion depletion region formation in (a) the AEM-bridged typical H-shaped electrokinetic system and (b) the system adopting the AEM with microholes.



Fig. S3 Schematics and fluorescence microscopic images of the ion depletion region formation in the case of the AEM (a) without and (b) with the microstructure (non-woven mat). Each scale bar in the images is 200 um. Without the microstructure, the hemispherical ion depletion region, induced by 3D helical vortices, is generated near the membrane. When the non-woven mat is located at the cathodic side of the AEM, the stabilized and flattened ion depletion region is formed as the electroconvection is confined to microporous structures of the non-woven mat, enabling effective manipulation of ion migrations.



Fig. S4 A schematic of the large-scale ion separation device. The device consists of three acrylic sub-frames that contains fluid channels, slots for membranes and electrodes, and holes for inlet/outlet tubing connectors. Between each sub-frame, an AEM and a multiscale-porous AEM layered with silicone gaskets are placed in their own slots, which can be readily detached from the device by disassembling the sub-frames. The main channel is 10 mm wide and 1 mm thick, splitting into the Mg²⁺ separation channel and Li⁺ extraction channel. A non-woven mat is positioned upon a microhole array of the multiscale-porous AEM to suppress the electroconvection and thus form a stable ion depletion region.



Fig. S5 A top view image of the large-scale device showing fluid flow and electricity application details.



Fig. S6 Influx rates of various cations at the (a) Mg²⁺ outlet and (b) Li⁺ outlet.

Large-scale device fabrication

Acrylic was selected as frame material due to its high transparancy allowing for observing fluid flow in the main channel as well as rigidity and insulation property. The sub-frames of the large-scale device were constructed by assembling smaller unit blocks to realize the main and buffer channel structure inside the frames. The unit blocks were cut using a vertical machining center (DNM II, Doosan Machine Tools, South Korea) and fluid channels, slots, and holes in the unit blocks were formed using a milling machine (KANDAN-2, Hwacheon, South Korea).

Each unit block was firmly bonded by applying chloroform (\geq 99.8%, Sigma Aldrich, USA) to contact surfaces. Two commercial AEMs (Fumasep, FTAM_E, Germany) were placed between the sub-frames in order to facilitate electric current while blocking fluid flow between the main and buffer channels. To allow fluid flow from the main channel to reach the Li⁺ outlet, a microhole array with 200 um-diameter holes and 100 um spacing between holes was formed in the anode-side AEM using a desktop engraving machine (DE-3 Desktop Engraver, Roland DG, Japan). A non-woven mat (Sontara LF50, DuPont, Australia) was stacked on the anode-side AEM to suppress electroconvetion near the membrane. The sub-frames equipped with the AEMs were assembled with screws and pneumatic tubing connectors were mounted on their own holes. Subsequently, carbon plate electrodes were inserted to the slots and electrode blocks including rubber O-ring, electrode block pressing plates were put on the blocks and tightened with screws. Lastly, silicone tubings (Cole-Parmer, USA) were connected to the tubing connectors. The experimental details and sample extraction method are the same with those of reference devices.

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