**High-performance crown ethers modified membranes for selective lithium recovery from high $Na^+$ and $Mg^{2+}$ brines using electrodialysis**

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**Captions:**

1. **Table S1.** Normalized Li recovery and conductivity reduction in $Na^+/Li^+$ brines
2. **Table S2.** Normalized Li recovery and conductivity reduction in $Mg^{2+}/Li^+$ brines
3. **Table S3.** The concentration of major ions in various Li-rich salt-lake brines
4. **Table S4.** Comparison of energy consumption and cost using different methods for $Li^+$ recovery
5. **Figure S1.** TGA of the spent membranes after use in the electrodialysis. (a) 12CE/CR671 in Mg/Li solution (2.2 mole/mole); (b)15CE/ CR671 in Mg/Li solution (2.2 mole/mole); (c) 18CE/ CR671 in Na/Li solution (3.6 mole/mole); (d) CR671.
6. **Figure S2.** Functions of voltage (V) and current (I) in electrodialysis with the membranes.

## 1. TGA of the membranes after the electrodialysis

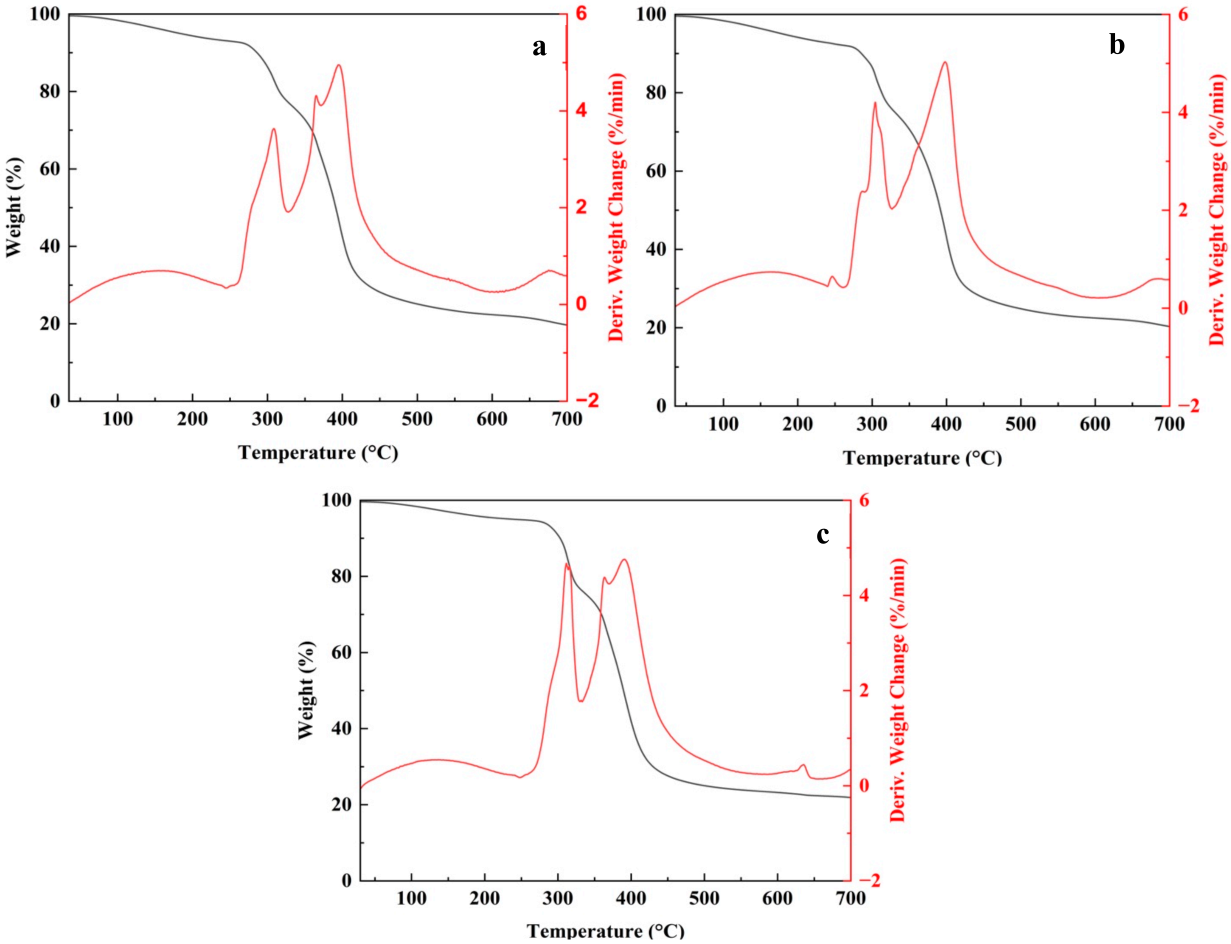


**Figure S1.** TGA of the spent membranes after use in the electrodialysis. (a) 12CE/CR671 in Mg/Li solution (2.2 mole/mole); (b)15CE/CR671 in Mg/Li solution (2.2 mole/mole); (c) 18CE/CR671 in Na/Li solution (3.6 mole/mole).

2. **Measurement of limiting current density (LCD)**

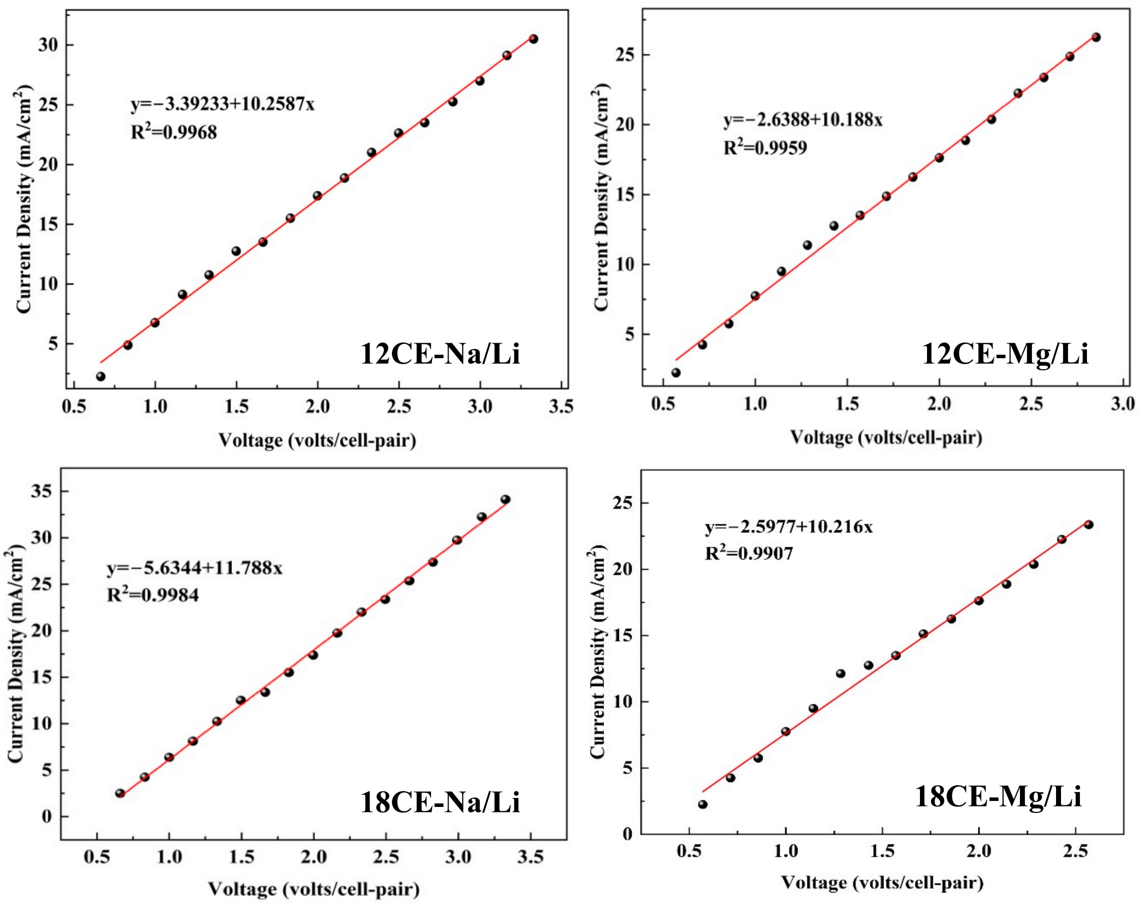


**Figure S2.** Functions of voltage (V) and current (I) in electrodialysis with the membranes.

3. **The performance of the membranes**

The efficiency of $Li^+$ recovery is influenced by current, voltage, and overall effective membrane area. The normalized $Li^+$ recovery is determined by assessing the mass of recovered lithium (in mg) per unit of electrical energy consumed per the total membrane area (in square centimeters, $cm^2$).

$$Normalized\ Li\ recovery = \frac{(C_{out} - C_{in}) \times V}{I \times Volt \times A} \quad (S1)$$

where, $C_{out}$ and $C_{in}$ are the lithium concentration of concentrate-out and concentrate-in (mg/L) of the electrodialysis system, V is the volume of the concentrate-feed tank (L), I and Volt are the current density (Amp) and voltage applied in the system (Volt), A is the total effective area of the 10 pairs membranes in the stack (80 $cm^2$).

The desalination efficiency of electrodialysis was calculated based on the conductivity reduction (Eq.S2):

$$\text{Conductivity reduction (\%)} = \left(1 - \frac{EC_d}{EC_f}\right) \times 100 \quad (S2)$$

where, $EC_d$ and $EC_f$ are the electrical conductivity of diluate-out and feed-in (in mS/cm), respectively, of the electrodialysis system.

During electrodialysis, the leakage rate of other cations, denoted as A (A=$Mg^{2+}$, $Na^+$), is calculated as:

$$A\ leaking\ rate\ (\%) = \frac{C_{out} - C_{in}}{C_{in}} \times 100 \quad (S3)$$

where, A=$Mg^{2+}$ and $Na^+$, $C_{out}$ and $C_{in}$ are the A concentration of concentrate-out and concentrate-in (mg/L), respectively, of the electrodialysis system.

As part of the investigation, the current efficiency is calculated as:

$$Current\ efficiency\ (\%) = \frac{\Sigma Fqz(C_{in} - C_{out})}{NI} \times 100 \quad (S4)$$

where, q designates the flow rate of concentrate-out (L/s), F represents the Faraday constant (96,485 C/mol), $C_{out}$ and $C_{in}$ denote the concentrations of concentrate-out and concentrate-in of the ions (mol/L), z denotes the charge of the ion, N represents the number of pairs of membrane cells, and I is the applied current (Amp).

The assessment of membrane permselectivity for cations in electrodialysis involved calculating relative transport numbers ($t_{A/Li}$). To determine these values, the amount of the certain cation A transported (e.g., A=$Na^+$ and $Mg^{2+}$, in meq) by the average concentration of equivalent cation A at both the initial (concentrate-in) and final (concentrate-out) stages. On the other hand, for $Li^+$, the calculation involved dividing the amount of $Li^+$ recovered (in meq) by the average concentration of equivalent $Li^+$ at the initial and final concentrations [1].

$$t_{A/Li} = \frac{Equivalent\ of\ A\ transported/average\ \ equivalent\ A\ concentration}{Equivalent\ of\ Li\ recovered/average\ \ equivalent\ Li\ concentration} \qquad (S5)$$

**Table S1.** Normalized Li recovery, conductivity reduction, and energy consumption in $Na^+/Li^+$ brines

| Membranes | Average current density (mA/cm²) | Normalized Li recovery (g/kWh-cm²) | Conductivity reduction (%) | pH of concentrate-out |
|---|---|---|---|---|
| 12CE/CR671 | 2.3 | 3.8 | 2.0 | 8.42 |
| | 9.4 | 2.9 | 5.6 | 8.27 |
| | 15.9 | 2.2 | 15.3 | 8.17 |
| 15CE/CR671 | 2.3 | 16.3 | 2.6 | 8.40 |
| | 9.4 | 3.1 | 12.4 | 8.25 |
| | 15.9 | 4.1 | 24.7 | 8.15 |
| 18CE/CR671 | 2.3 | 23.6 | 3.8 | 8.41 |
| | 9.4 | 3.8 | 5.0 | 8.26 |
| | 15.9 | 2.7 | 14.8 | 8.17 |

**Table S2.** Normalized Li recovery and conductivity reduction

| Membranes | Average current density (mA/cm²) | Normalized Li recovery (g/kWh-cm²) | Conductivity reduction (%) | pH of concentrate-out |
|---|---|---|---|---|
| 12CE-/CR671 | 2.3 | 15.2 | 0.2 | 8.53 |
| | 9.4 | 7.6 | 4.4 | 8.45 |
| | 15.9 | 5.6 | 13.4 | 8.41 |
| 15CE/CR671 | 2.3 | 24.7 | 0.5 | 8.56 |
| | 9.4 | 9.9 | 5.7 | 8.48 |
| | 15.9 | 12.1 | 16.5 | 8.39 |
| 18CECR671 | 2.3 | 19.5 | 0.2 | 8.53 |
| | 9.4 | 5.2 | 3.9 | 8.46 |
| | 15.9 | 4.4 | 13.1 | 8.41 |

**Table S3.** The concentration of major ions in various Li-rich salt-lake brines [2,3,4].

| Representative Lakes | Major ions concentrations (g/L) | | | | | |
|---|---|---|---|---|---|---|
| | $Li^+$ | $Mg^{2+}$ | $Na^+$ | $Ca^{2+}$ | $K^+$ | $SO_4^{2-}$ |
| Atacama Salar Brine, Chile | 3.02 | 17.60 | 61.90 | 0.41 | 28.20 | 37.90 |
| Uyuni Salar Brine, Bolivia | 0.84 | 16.70 | 105.40 | 3.33 | 15.70 | 21.30 |
| East Taijinar, China | 0.14 | 5.64 | 117.03 | 0.43 | 3.79 | - |
| West Taijinar, China | 0.26 | 15.36 | 102.40 | 0.19 | 8.44 | - |
| Yiliping, China | 0.32 | 23.20 | 80.10 | 0.15 | 11.89 | 15.27 |
| Chott Djerid, Tunisia | 0.06 | 3.40 | 80.00 | 1.60 | 5.60 | 6.70 |
| North Arm, USA | 0.04 | 9.38 | 100.80 | 0.35 | 5.50 | 19.70 |
| Wairakei geothermal brine, New Zealand | 0.01 | - | 0.11 | - | 0.16 | - |

**Table S4.** Comparison of energy consumption and cost using different methods for $Li^+$ recovery

| Methods | Concentrations in feed solution (mg/L) | | | Energy consumption (kWh/kg-Li) | Energy Cost (US$/kg-Li) | Li recovery efficiency (%) | Ref. |
|---|---|---|---|---|---|---|---|
| | $Li^+$ | $Na^+$ | $Mg^{2+}$ | | | | |
| Electrocoagulation | 1,000 | 7,871.3 | - | 64.0 | 3.84 | 95 | [5] |
| Hybrid capacitive deionization (H-CDI) | 1,457.4 | 7,590,000 | 9,600 | 23.3 | 1.4 | - | [6] |
| Membrane capacitive deionization (MCDI) | 24.9 | - | 86.4 | 0.3 | 0.018 | 38.4 | [7] |
| Electrodialysis (CIMS) | 24.9 | - | 86.4 | 0.33 | 0.0199 | - | [7] |
| Electrodialysis (monovalent exchange membranes) | 140.0 | 20,810 | 2,250 | 95.1 | 5.7 | 76.45 | [2] |
| Electrodialysis (15CE/CR671) | 818.5 | 9,839.2 | - | 4.26 | 0.26 | 90.5 | This study |
| Electrodialysis (15CE/CR671) | 818.5 | - | 6,301.8 | 4.02 | 0.24 | 80.5 | This study |

Note: energy cost was estimated at an electricity price of $0.06/kWh

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