

# Crown ether functionalized polyimide membrane to construct supported ionic liquid membrane contactor for $Mg^{2+}/Li^{+}$ selective separation from aqueous solution

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## Abstract:

The stability of supported liquid membrane (SLM) is a key issue to be solved in its practical application such as high-efficient extraction of lithium ions from aqueous solution. Crown ethers containing polymer materials are considered as one of the most promising candidates for lithium selective recovery. Herein, a novel dibenzo-4-crown-4 ether-based polyimide (Poly(DAB14C4-6FDA) or 14C4@PI) with a molecular weight of 63 kDa and the crown ether content of  $1.36 \text{ mmol g}^{-1}$  was synthesized by condensation polymerization between di(aminobenz)-14-crown-4 (DAB14C4) and 4,4'-(hexafluoro-isopropylidene) diphthalic anhydride (6FDA). Meanwhile, the corresponding porous membrane (14C4@PI) fabricated by non-solvent induced phase separation was employed to construct SILM contactor using tributyl phosphate (TBP) and 1-butyl-3-methylimidazolium bis-trifluoromethylsulfonimide salt ([C<sub>4</sub>mim][NTf<sub>2</sub>]) mixed organic phase as liquid membrane phase and 0.5 mol/L HCl as extract phase for  $Mg^{2+}/Li^{+}$  selective separation. Results showed that the 14C4@PI membrane with the porosity of 80.5% displayed a high  $Li^{+}$  adsorption capacity (34.05 mg/g). When the  $Li^{+}$  concentration in the feed was 0.1 mol/L and Mg/Li mass ratio was 35.0, the  $Li^{+}$  initial flux of SILM contactor was  $0.128 \text{ mol/m}^2 \cdot \text{h}$ , and the separation factor of  $Li^{+}$  to  $Mg^{2+}$  ( $SF_{Li/Mg}$ ) was 19.1. Accordingly, the Mg/Li mass ratio was reduced to 2.4. The extraction rate of  $Li^{+}$  reached up to 42%, and the extraction rate of  $Mg^{2+}$  was less than 5%. The SILM contactor also exhibited a good stability owing to the strong electrostatic interaction between ILs and 14C4@PI membrane. Specially, the formation of TBP-Li-NTf<sub>2</sub> complex and a high binding energy between  $Li^{+}$  and crown ethers of 14C4@PI promoted the transport of  $Li^{+}$  from the feed to the extract phase. In summary, our current study provides an effective solution for lithium resources recovery in salt lake brines.

**Keywords:** Polyimide; Dibenzo-14-crown-4; Supported ionic liquid membrane; Mg/Li selective separation; Lithium adsorptive separation