

## Fundamental studies on application of supported liquid membranes for the recovery of lithium from seawater

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The separation and concentration of lithium using a supported liquid membrane is presented. The membrane consisted of a Teflon millipore membrane containing a kerosene solution of LIX54 and TOPO as a mobile carrier within the pores. Interposing the liquid membrane between two aqueous solutions with different pH values, lithium was transported against its concentration gradient and concentrated from the high pH solution to the low pH solution across the membrane. The selective separation of lithium from sodium was achieved by the supported liquid membrane technique.

### 1. INTRODUCTION

Lithium (Li) is used for primary and secondary batteries and catalysts, and in the near future its demand is expected to increase drastically. It is considered that the recovery only from mineral resources will lead to a lack of Li supply. Therefore, brines of seawater and geothermal water have been recently noticed as new resources.

Adsorption, solvent extraction, precipitation, etc. have been applied for the recovery and concentration of Li, while it is desired to develop more efficient and energy-saving methods. The goal of our study is the development of a recovery process by applying the liquid membrane separation method. The method is a highly selective and energy-saving separation technique in which the requisite amount of expensive extractants is only little compared to solvent extraction, and is regarded as a combined extraction/stripping process.

In this work, the separation and concentration of Li using supported liquid membranes (SLMs) impregnated with a mixture of LIX54 (the major component is  $\alpha$ -acetyl-m-dodecylacetophenone) and TOPO (tri-n-octylphosphine oxide) as a carrier has been

studied to examine a possibility of the recovery of Li from dilute aqueous solutions such as seawater. The effects of a number of operating conditions on the permeation rates of Li are presented. The observed results are also compared with a permeation model for concentrating Li across a liquid membrane.

### 2. PERMEATION MODEL

The schematic concentration profile for Li permeation through a SLM containing LIX54 (R) and TOPO (S) is shown in Figure 1. Li ion (L) in the feed phase permeates through the

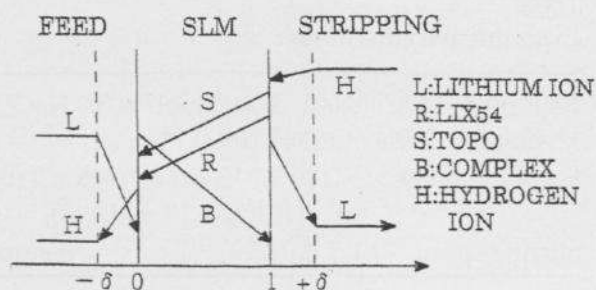


Figure 1. Permeation model.

following five steps into the stripping phase.

Step 1. Diffusion of L from the bulk of the feed solution to the feed-SLM interface through the boundary layer adjacent to the membrane.

Step 2. Extraction reaction (complex formation) between L, R and S at the feed-SLM interface to form the complex (B),  $\text{Li}(\text{LIX54})(\text{TOPO})_{1.2}$ .

Step 3. Diffusion of B from the feed to the stripping side of the SLM.

Step 4. Stripping of L at the stripping-SLM interface.

Step 5. Diffusion of L from the stripping-SLM interface to the bulk of the stripping solution through the boundary layer adjacent to the membrane.

When the permeation rate is controlled by the steps 1, 3 and 5, the time-dependent concentration of L in the feed phase is expressed by

$$L_F/L_F^0 = \exp \{-(A/V)K_{LO}m_0t\} \quad (1)$$

$$1/K_{LO} = (m_0/k_{LF}) + \{1/(D_B/\tau l)\} + (m_l/k_{LS}) \quad (2)$$

where  $m_0$  and  $m_l$  represent the distribution ratios and are obtained from extraction equilibrium experiments.

Furthermore, if the rate-controlling step is only the step 1, Eq.(1) reduces to

$$L_F/L_F^0 = \exp \{-(A/V)k_{LF}t\} \quad (3)$$

### 3. EXPERIMENTAL

The experimental apparatus for a SLM, which is shown in Figure 2, and the

experimental procedures were the same as described in previous papers [1,2]. The experimental conditions are shown in Table 1. A Teflon millipore membrane filter which has a thickness of  $125 \mu\text{m}$ , a pore size of  $10 \mu\text{m}$ , and a porosity of about 68% was used as the solid support membrane. The pores within the membrane were filled with LIX54/TOPO carrier by immersion in kerosene for about 2 hours and then in the membrane solution for about 15 hours. After the membrane was clamped between two glass half-cells, the feed and stripping solutions were carefully transferred into each cell. The stirrers were started as soon as each cell was filled with its respective aqueous solution. The Li concentrations in the feed and stripping phases were measured as a function of time.

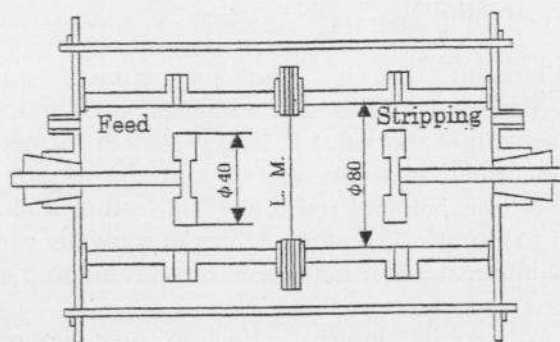


Figure 2. SLM apparatus.

Table 1  
Experimental conditions

Feed phase : $\text{LiCl}$ (0.001, 0.005 $\text{kmol/m}^3$ ) – $\text{NaOH}/\text{Na}_2\text{HPO}_4$ buffer	pH=12
Membrane phase : $\text{LIX54}$ (0.05, 0.15 $\text{kmol/m}^3$ ) – $\text{TOPO}$ (0.06, 0.18 $\text{kmol/m}^3$ ) - kerosene	
Stripping phase : $\text{LiCl}$ (0-1.0 $\text{kmol/m}^3$ ) – $\text{NaCl}$ (0, 0.1 $\text{kmol/m}^3$ ) – $\text{H}_2\text{SO}_4$ (0.01-1.0 $\text{kmol/m}^3$ ) or $\text{HClO}_4$ (0.1 $\text{kmol/m}^3$ )	
Stirring speed N : 1.5, 2.0 $\text{s}^{-1}$	Temperature : 298 K

## 4. RESULTS AND DISCUSSION

### 4.1. Effect of acid type and its concentration in the stripping phase

Figure 3 shows the Li concentrations of the feed ( $L_F$ ) and stripping phases ( $L_S$ ) as a function of time when sulfuric acid ( $\circ, \bullet$ ) and perchloric acid ( $\square, \blacksquare$ ) were respectively used as the acid in the stripping phase. The keys of  $\bullet$  and  $\blacksquare$  fall together. The permeation rates of Li are not affected by the acid type. The broken lines computed from Eq.(1) nearly agree with the observed values. The permeation rates were also independent of sulfuric acid concentrations above  $0.01 \text{ kmol/m}^3$ .

### 4.2. Effect of carrier concentration

The permeation rates of Li were measured by varying the carrier concentrations of LIX54 (R) and TOPO (S). The variations of Li concentration ( $L_F, L_S$ ) with time are shown in Figure 4. The permeation rate increases by increasing R and S concentrations from 0.05 and 0.06 to 0.15 and 0.18  $\text{kmol/m}^3$ . It is seen that after 4 hours  $L_S$  becomes higher than  $L_F$  and thus Li is pumped from the feed to the stripping phase. The broken and dotted lines in the figure represent the computed values from Eq.(1) for each carrier concentration, and the dotted-broken line is the calculated one by Eq.(3) for only the higher carrier concentration.

### 4.3. Effect of initial Li concentration in the stripping phase

Permeation experiments were carried out under conditions where the stripping phase initially contained Li 10 and 200 times the initial feed concentration of  $L_F^0 = 0.005 \text{ kmol/m}^3$ . Figure 5 shows the plots of  $L_F/L_F^0$  vs  $t$  and  $L_S/L_F$  vs  $t$ . It is seen that even under conditions in which Li exists in high concentration in the stripping phase, it permeates from the feed to the stripping phase at the almost same speed as in the case of  $L_S^0 = 0$ . For  $L_S^0$  of  $1.0 \text{ kmol/m}^3$ , the value of  $L_S/L_F$  starts from 200 and after 6 hours reaches about 400. Thus, Li can be successfully pumped from the lower to the higher concentration phase because its flow is coupled

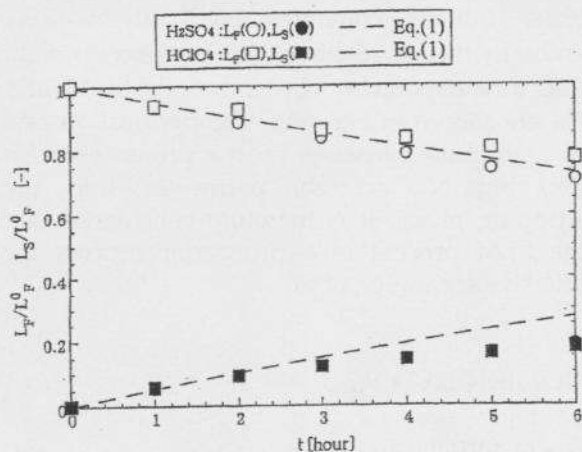


Figure 3. Effect of acid type in the stripping phase.

$$L_F^0 = 0.005, R = 0.05, S = 0.06, (\text{pH})_S = 1, N = 1.5$$

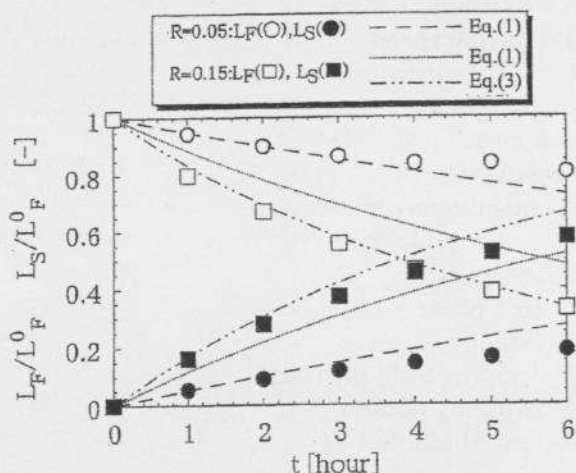


Figure 4. Effect of carrier concentration, R and S.

$$L_F^0 = 0.005, (\text{pH})_S = 1, N = 1.5$$

to a flow of hydrogen ions in the opposite direction.

### 4.4. Effect of initial Na concentration in the feed phase

The separation of Li ion from a coexisting cation and its effect on the permeation rate of Li



were tested in experiments in which the feed phase initially contained NaCl at  $\text{Na}_F^0=0.1$  kmol/m<sup>3</sup> being 20 times the Li concentration. The time-dependent concentrations of Li and Na are shown in Figure 6. The permeation rate of Li slightly decreases by the presence of Na ion, but Na scarcely permeates into the stripping phase. It is therefore considered that the SLM process is a promising process for selective separation of Li.

## NOMENCLATURE

A = membrane area  
 $D_B$  = diffusivity of complex  
 $K_O$  = overall mass transfer coefficient  
 $k$  = mass transfer coefficient in the boundary layer  
 $L$  = lithium concentration  
 $l$  = membrane thickness  
 $m$  = distribution ratio  
 $N$  = stirring speed  
 $R$  = LIX54 concentration  
 $S$  = TOPO concentration  
 $t$  = time  
 $V$  = volume  
 $\tau$  = membrane constant

### <Subscripts>

F = feed phase  
 $L$  = lithium  
 $l$  = stripping-SLM interface  
 $S$  = stripping phase  
 $0$  = feed-SLM interface

### <Superscript>

0 = initial

## REFERENCES

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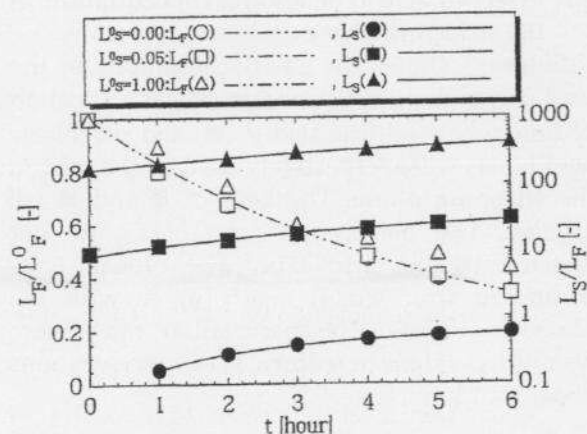


Figure 5. Effect of initial Li concentration in the stripping phase,  $L_S^0$ .

$L_F^0=0.005$ ,  $R=0.15$ ,  $S=0.18$ ,  $(\text{pH})_S=1$ ,  $N=1.5$

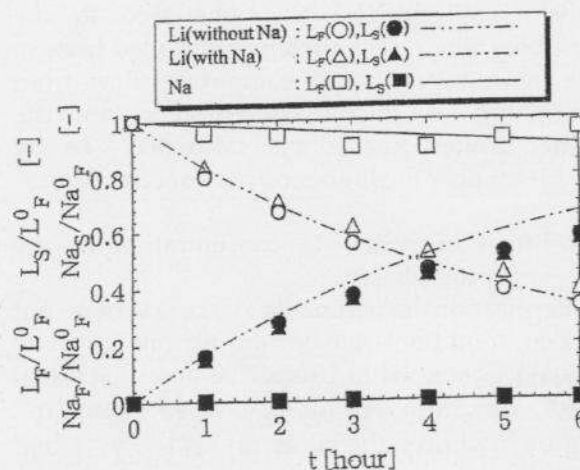


Figure 6. Effect of Na ion coexisting in the feed phase.

$L_F^0=0.005$ ,  $\text{Na}_F^0=0.1$ ,  $R=0.15$ ,  $S=0.18$ ,  $(\text{pH})_S=1$ ,  $N=1.5$