



# Innovative lithium recovery technique from seawater by using world-first dialysis with a lithium ionic superconductor



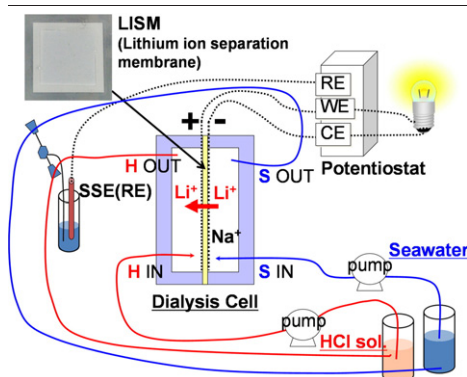
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## HIGHLIGHTS

- New method for Li recovery from seawater is proposed using the world-first dialysis.
- Li ionic superconductor as the Li separation membrane (LISM) was used.
- Only Li ions can permeate the LISM.
- The Li recovery ratios to approximately 7% after 72 h with no electrical supply.
- Li separation process generates electricity, requiring no external power source.

## GRAPHICAL ABSTRACT



World-first dialysis system for Li recovery from seawater with no electrical supply.

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## ABSTRACT

Lithium (Li) procurement is becoming a matter of importance worldwide. Herein, I propose a method for recovering Li from seawater by using world-first dialysis, wherein Li only permeates from the negative electrode side to the positive electrode side through a Li ionic superconductor functioning as a Li separation membrane (LISM). Measurements of the Li ion concentration at the positive electrode side as a function of dialysis duration showed that the Li recovery ratio increased to approximately 7% after 72 h with no applied electric voltage. Moreover, other ions in the seawater did not permeate the LISM. With both ends of the LISM bound with a negative and positive electrode, hydrated Li ion was transformed to Li ion only because Li ion can permeate through the LISM. This new recovery method shows good energy efficiency and is easily scalable and is thus suitable for the industrialised mass production of Li in South American countries, which have briny water containing Li.

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## 1. Introduction

Lithium (Li) – one of the 31 rare metal elements among the 112 known elements – is rapidly becoming a valuable commodity. In recent

years, the industrial importance of Li has increased due to its use in Li ion batteries and in the production of fuel for nuclear fusion reactors. For example, large-sized Li ion batteries are used as power supplies for electric vehicles and the storage of electricity in smart grids and smart houses. For such applications, a technique for the inexpensive manufacturing of large-sized Li ion batteries is required. In addition,

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tritium – a fuel used in nuclear fusion reactors – is produced using Li [1]; therefore, a large amount of Li is required.

In South America, Li is recovered from salt lakes and is currently being produced at the Atacama Salt Lake (SQM Co. Ltd. and Chemetall Co. Ltd.) in Chile and at the Hombre Muerto Salt Lake (FMC Co. Ltd.) in Argentina. The production of these two lakes accounts for approximately 70% of the world's Li production [2,3]. Moreover, there are more than 100 salt lakes in the Puna plateau, which is surrounded by the Andes, located at altitudes exceeding 3500 m. Areas such as the Uyuni Salt Lake, Rincon Salt Lake and Olaroz Salt Lake are expected to be developed for Li production in the near future. Li reserves in the South American countries of Chile, Bolivia and Argentina account for more than half of the world's Li reserves and have outstanding Li resources (brine water). Although Li extraction from chloride brine water is easy, the quantity of natural resources in these waters is limited. In contrast, the quantity of natural resources in sulphate brine water is large, but the processing technology is yet to be established.

Li is known to be present in seawater, and an enormous amount of total Li is contained in all of the seawater on earth. Therefore, the extraction of Li from seawater would allow a large amount of Li to be inexpensively acquired. Thus, the recovery of Li from seawater by using Li adsorbents has been extensively studied [4–11]. These techniques, however, require two steps: the adsorption and subsequent desorption of Li. Therefore, the Li recovery process from seawater is complicated. Furthermore, the selectivity of the Li adsorbents in the adsorption process used in these techniques is not high. Consequently, when these methods are applied to seawater, sodium (Na), for example, is adsorbed at the same time as Li because it is also an alkaline metal. An effective technique for the recovery of Li from seawater has not yet been established, and the research and development of innovative Li recovery technologies are therefore needed.

Hoshino developed a Li recovery technique from seawater, which uses organic membranes impregnated with an ionic liquid [12,13]. Although this technique can be used to recover Li from seawater, the poor durability of the ionic membrane is one of the main issues preventing the maintenance of good performance during stable long-term Li recovery. Building on this previous study, I report a world-first method for Li recovery from seawater by dialysis using a Li ionic superconductor as a Li separation membrane (LISM).

## 2. Experimental

### 2.1. LISM

Li ionic superconductor-type crystals such as  $\text{Li}_{1+x} \text{yAlx}(\text{Ti, Ge})_{2-x} \text{SiyP}_3 - \text{yO}_{12}$ ,  $(\text{Li}_x, \text{La}_y)\text{TiO}_z$  and  $(\text{Li}_x, \text{La}_y)\text{ZrO}_z$  can be used as LISMs. These materials can be obtained, for example, as plate-like sintered ceramics, and each material exhibits a Li ionic conductivity higher than  $10^{-4}$  to  $10^{-3} \text{ S cm}^{-1}$ . In this study, Li ion conductive glass-ceramics (Ohara Inc., Japan; LICGCTM) [14] was selected as the LISM because it exhibits a high Li conductivity of  $10^{-3} \text{ S cm}^{-1}$ . The area and thickness of the LISM-1 are  $20.3 \text{ cm}^2$  ( $\phi 5.08 \text{ cm}$ , circle) and  $0.25 \text{ mm}$ , respectively, and those of the LISM-2 are  $25 \text{ cm}^2$  ( $5.0 \text{ cm}$ , square) and  $0.18 \text{ mm}$ , respectively. The difference between LISM-1 and LISM-2 is the shape. This LISM is only permeable to Li ion in seawater, and other cations (Na, Mg, Ca and K) present in seawater are not permeated.

### 2.2. First Li recovery test (electrodialysis)

Fig. 1 shows the first proposed method for the recovery of Li from seawater by electro dialysis using the LISM-1. Seawater was flowed to the positive electrode side, and  $0.1 \text{ M HCl}$  as a Li recovery solution was flowed to the negative electrode side. An electrical potential was applied between the positive and negative electrodes by using a potentiostat. The positive and negative electrode materials were SUS306 and Ti–Ir alloy, respectively; their use prevents

electrochemical reactions from occurring in the seawater or recovery solution ( $0.1 \text{ M HCl}$ ).

The Li concentration of  $0.1 \text{ M HCl}$  was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima7000DV of PerkinElmer Co., Ltd.) and inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC-e of PerkinElmer Co., Ltd.), and the recovery ratio of Li was then investigated. The applied dialysis voltage was  $2 \text{ V}$ , and the duration of dialysis was  $24 \text{ h}$ .

### 2.3. Second Li recovery test (world-first dialysis)

Fig. 2 shows the second proposed method for Li recovery from seawater by using the world-first dialysis with LISM-2. In this method, the negative and positive electrodes are bonded to the right and left faces (the two main faces) of the LISM, respectively. In this configuration, the right and left faces of the LISM are held at constant negative and positive potentials, respectively. Thus, Li ions on the positive electrode side are recovered from seawater on the negative electrode side through the LISM.

Moreover, in the configuration shown in Fig. 2, a potential difference exists between the negative and positive electrodes, even when voltage is not applied. When a difference in Li concentration between the seawater and the Li recovery solution exists, Li ions flow through the LISM. In other words, Li ions can be recovered spontaneously from seawater without the application of outside voltage.

The principle of this world-first dialysis is similar to ion concentration cell. In case of ion concentration cell, ions move from high- to low-concentration solution through a salt bridge. In Fig. 2, since LISM acts as a salt bridge, Li ions can permeate from seawater to Li recovery solution through the LISM. In addition, although Li concentration in seawater is very low, only Li ions were successfully recovered from seawater.

## 3. Results and discussion

### 3.1. Li recovery by electro dialysis

The applied electro dialysis voltage was  $2 \text{ V}$ , and the duration of electro dialysis was  $24 \text{ h}$ . The current value is very low (i.e.  $2.69 \times 10^{-5} \text{ mA}$ ), and pH of seawater is neutrality (i.e. pH approximately 7), which is constant. After the Li recovery test by electro dialysis, the Li concentration in HCl was analysed by ICP-AES. However, the concentrations of Li and other ions were lower than the detection limit. Fig. 3 shows the principle of Li permeation through the LISM-1. Li ion is able to permeate through the LISM-1; however, Li and other ions in seawater exist as

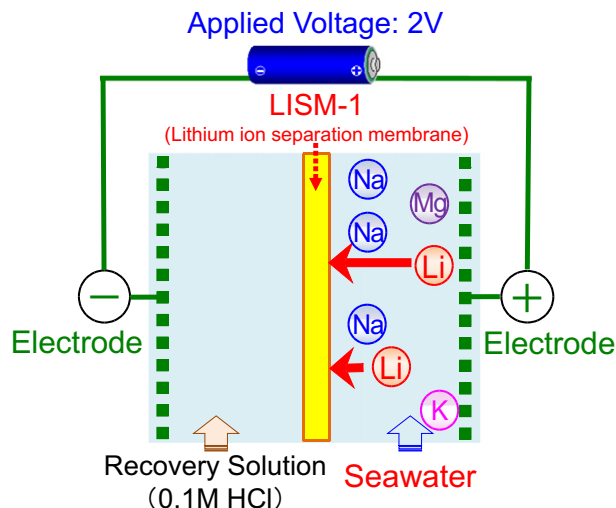


Fig. 1. Schematic of Li ion recovery from seawater by electro dialysis by using LISM.

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