



Process design for lithium recovery using bipolar membrane electro dialysis system



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ABSTRACT

This study aims to evaluate the effect of LMO (lithium manganese oxide) and enhanced BEDI (bipolar membrane electro-dialysis deionization) on the lithium ion desorption process for the recovery of lithium ions. The factors that influence lithium ion recovery are evaluated in reference to the pH, voltage, flow rates, and number of bipolar membrane sheets to present the optimal conditions. The research findings show that in the desorption of LMO lithium ions, the lower the pH, the higher the desorption rates. When the voltage was 6.5 V per sheet, the desorption rates were approximately 70%, and when flow rates were 0.44 mL/cm² min, the desorption was approximately 30 min faster than that at other flow rates. When the number of bipolar membrane sheets was 4, it was possible to control 4 the pH to under 4, a level at which lithium ions adsorbed onto LMO might affect the desorption phenomenon. For a combination of the conditions above, the desorption efficiency of lithium ions was approximately 70%, and the recovery time was reduced by approximately 180 min compared to when a chemical process was used for lithium ion desorption.

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1. Introduction

As interest in the environment has increased over the last two decades, restrictions on the thoughtless use of fossil fuels have been tightened accordingly, and the need to develop alternative technologies to replace the use of fossil fuels is being emphasized [1]. Among the various alternative technologies being developed, lithium batteries are drawing special attention as a clean energy resource that can replace fossil fuel. Lithium secondary batteries are used for various mobile devices, such as smart phones, digital cameras and laptop computers [2], and the recent advancement of lithium secondary battery technology enables the replacement of existing electric car batteries with lithium secondary batteries [3]. In addition, lithium micro-batteries are used for medical devices (cardiac pacemakers, hearing aids, and defibrillators) [4]. As lithium batteries are utilized in various industrial sectors, consistent efforts are focused on the further development of these batteries toward completely replacing the use of fossil fuels. As the lithium secondary battery industry is rapidly advancing, the demand for lithium metals is also increasing. The rapid increase of natural lithium production is outstripping the availability of

the estimated reserves. In particular, 90% of the lithium resource is concentrated in certain regions, such as China, Bolivia, Argentina, and Chile [5], and thus, some even worry that lithium resources might be politically abused.

As one of the solutions to the drain of the natural lithium ion reserves, the recovery technology of lithium metals from used lithium batteries or from solutions (such as sea water and waste water) that contain lithium metals rather than metallic reserves is attracting increasing attention [6]. The lithium recovery process is divided into the physical process and the chemical process. The physical process is to separate lithium metals from used lithium secondary batteries, and the chemical process is to recover lithium ions from sea water or other solutions. Because the physical process is designed to separate lithium ions only mechanically or physically from compounds of various metallic elements, other metallic ions may be recovered along with lithium ions. In contrast, the chemical process enables selective separation due to the special chemical processing, which is advantageous in recovering high-purity lithium ions [7].

One research study focused on the inorganic absorbents (LiNi_{0.5}Mn_{0.5}O₂, LiMn₂O₄, and Li_{1.33}Mn_{1.67}O₄), which detects lithium ions quite precisely in solutions [8]. For such inorganic absorbents, lithium manganese oxide with a spinel structure contains lithium ions as part of the structure, and thus, ions whose

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radius is greater than that of lithium ions cannot enter the structure. Hence, ions other than hydrogen ions, (whose radius is smaller than that of lithium ions), cannot enter the crystal of lithium manganese, thus leading to a high selective adsorption rate to lithium ions [9–11].

When inorganic adsorbents are used for lithium ion adsorption under conditions in which the density of lithium ions is low, the adsorption process may take days or even weeks. As a result, the recovery efficiency of lithium ions drastically decreases. This decreasing efficiency is a challenge to be overcome when lithium recovery technology is to be commercialized as inorganic adsorbents. The concept of lithium ion desorption stated above is to replace lithium ions in a manganese oxides with hydrogen ions, which causes lithium ions to leave the adsorbent. Because the density of hydrogen ions affects lithium ion desorption, chemicals such as hydrochloric acid are necessary in the process. In addition, an alkali solution is required to neutralize the hydrochloric acid, which raises the problems of recovery efficiency reduction and increased cost [12,13].

Hence, this study aims to design an eco-friendly electro-dialysis system that uses no hydrochloric acid as an improvement of the existing LMO adsorbent adsorption and desorption process and to apply the system to Neosepta bipolar membranes. In addition, the effect of the system on lithium ion recovery is also evaluated [14].

Regarding electro-dialysis devices of bipolar membranes that produce hydrogen and hydroxyl ions by means of a water splitting reaction in the catalytic layer and in the application of voltage, the water splitting characteristic of bipolar membranes is utilized instead of directly using hydrochloric acid solution, as in the case of the existing electro-dialysis systems. Hydrogen ions are provided to extract lithium ions from LMO, and lithium ions are transferred to another section using positive ion exchange membranes. A lithium hydroxide results from the reaction to hydroxyl generated by water splitting.

The variables influencing BEDI (bipolar membrane electro-dialysis deionization) are referred to in the voltage setting; in the system designed for this study, the conditions and module size for lithium ion adsorption · desorption are also examined. In addition, the efficiency of lithium ion recovery is evaluated in comparison with the chemical desorption method with the same adsorbent used.

2. Experimental

2.1. Materials

This study involves development of the film used to form the module Neosepta CMX (positive ion exchange membrane, Astom Company, Japan) and Neosepta BP-1 (bipolar membrane, Astom Company, Japan). The properties of the film are presented in Table 1. To produce an electrolyte, Samchun's 98% pure potassium nitrate (KNO_3) was used, and to produce a lithium salts solution, Aldrich's 99% pure lithium chloride (LiCl) was used. Aldrich's 96% pure LiMn_2O_4 (lithium manganese oxide) was used as the inorganic adsorbent. None of the reagents used in the experiment underwent a separate refining process.

Table 1
Properties of the membranes applied to the BEDI module.

Membrane	Thickness (μm)	IEC (meq g^{-1})	Area resistance (Ωcm^2)	Voltage drop (V)
Neosepta-CMX ^a	220–260	1.5–1.8	2.0–3.5	–
Neosepta-BP-1 ^a	250–350	–	–	1.2–2.2

^a The data are gathered from the product provided by the Astom company.

2.2. Module design

As shown in Fig. 1(c), the BEDI module consisted of platinum-coated titanium electrodes, cation exchange membranes, and 3-mm-thick spacers made of PVC (polyvinyl chloride) for flow path setting. To protect the ion exchange membrane between films and between a film and a spacer, used was a 1-mm-thick separator made of PP (polypropylene) was used. With a bipolar membrane (BP) and a cation exchange membrane (C) alternating between the anode and cathode, a total of 8 compartment cells were formed. In addition, 2 electrolytic cells, 3 desorption parts, and 3 concentration parts were formed. The film was $12 \text{ cm} \times 13 \text{ cm}$ in size. The volumes of concentration part and desorption part are equally 500 mL.

At both electrodes, voltage was provided by means of a power supply, with a voltage range between 0 and 30 V. Each module was divided into sections by films, and the sections played three different roles: desorption, concentration, and electrolyte. On the plane where bipolar membrane hydrogen ions are discharged and in the area between the two ion exchange membranes, LMO was inserted and allowed to move randomly. During this period, LMO reacted with the hydrogen ions, which resulted in the desorption of lithium ions from the LMO and their transfer to the concentration part through the cation exchange membrane by the difference of electric potential. Potassium nitrate solution, which was used as an electrolyte, ran in front of the two pole plates. The sections were separated by bipolar membranes, so that the ions in the electrolyte could not flow into the desorption part or the concentration part. The electrolytic cell, the desorption part, and the concentration part were connected to a 1-L acryl water tank, and the solution from the module was recycled back to the acryl tank for continuous desorption in the circulation system.

A magnetic pump was used to prevent the LMO from lumping together and circulating in the system. The module was designed to increase the probability of reaction to hydrogen ions. The module's flow path was designed diagonally so that the detention time of solution in the module could increase [15,16].

2.3. Experiment of lithium ion chemical desorption

A chemical desorption experiment was conducted to compare the results with those of the BEDI module-based desorption experiment. To extract lithium ions using the LMO, which is an inorganic adsorbent for lithium adsorption, 23-h mixing was implemented in 500 mL of 1 M HCl solution. To separate the LMO from the HCl solution, filtering was followed by cleaning with distilled water and then with methanol. The product was dried at 80°C for 4 h in an oven.

To produce the lithium ion solution, 2.5 L of distilled water was used to dissolve 1.25 g of LiCl to produce LiCl solution. The LiCl solution was divided into 5 equal parts to make 5 samples, each of which had a different pH value ranging from 2 to 6, with a pH step of 1 by adding small amounts of 0.1 M HCl solution. Under the condition above, lithium ion desorption was implemented for 8 h, and sampling was conducted at intervals of 2 h. The lithium ion densities of collected samples were measured by ICP (inductively coupled plasma atomic emission spectrometer). The desorption rates of lithium ions were calculated using the following expression [17]:

$$\tau_{\text{desorption}} (\%) = \frac{C_f - C_i}{C_{\text{desorption}}} \times 100$$

where $C_{\text{desorption}}$ denotes the density of lithium ions adsorbed onto LMO that was gained from the LMO adsorption experiment. C_i

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