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Application of Multistage Concentration (MSC) Electrodialysis to Concentrate Lithium from Lithium-Containing Waste Solution

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Abstract: In order to manufacture lithium carbonate to be used as a raw material for a secondary lithium battery, lithium sulfate solution is used as a precursor, and the concentration of lithium is required to be 10 g/L or more. Electrodialysis (ED) was used as a method of concentrating lithium in a low-concentration lithium sulfate solution, and multistage concentration (MSC) electrodialysis was used to increase the concentration ratio (%). When MSC was performed using a raw material solution containing a large amount of sodium sulfate, the process lead time was increased by 60 min. And the concentration ratio (%) of lithium decreased as the number of concentration stages increased. In order to remove sodium sulfate, methanol was added to the raw material solution to precipitate sodium sulfate, and when it was added in a volume ratio of 0.4, lithium was not lost. Using a solution in which sodium sulfate was partially removed, fourth-stage concentration ED was performed to obtain a lithium sulfate solution with a lithium concentration of 10 g/L.

Keywords: electrodialysis (ED); lithium; lithium-ion battery; lithium sulfate; multistage concentration (MSC)

1. Introduction

1.1. General Introduction

Metal resources currently in use can be divided into mine resources and renewable resources. Urban mining means that metal resources, which are industrial raw materials, are widely distributed in the form of products or waste, which means that they exist quantitatively on a mine scale. These are renewable resources. The amounts of waste catalyst, waste lithium batteries, and electronic waste are steadily increasing, and among them, the amount of waste lithium batteries is greatly increased. As the demand for lithium, a raw material that is a key component of electric vehicle batteries, is increasing, technology for recovering it from waste resources is required [1,2]. The market demand for electrolytes that make up lithium-ion batteries is expected to have an annual average growth rate of 42% from 2019 to 2025 [3]. Lithium is the main material of the fourth industrial revolution. Lithium-based batteries are rechargeable chemical batteries with excellent technical performance and high working voltage and energy density [4]. In addition, the charging and discharging life cycle is long, and they can be implemented with light weights, so the demand in the electric vehicle market has greatly increased [5]. In the Republic of Korea, because the amount of lithium is very small, the country is dependent on imports, so if the supply is insufficient compared to global demand, the domestic industry will be affected. So there is a need for a method to maintain an internally stable lithium supply and demand.

The amount of lithium in saltwater is about twice as large as that in ore, and many studies have been conducted on recovering lithium from brine [6–10]. In order to recover lithium from brine, a purification process is required due to the large amount of impurities. The concentration of lithium is also low, so the energy consumption required is high and the process takes a long time [6–12]. Lithium carbonate is mainly used in industry, and in order to prepare lithium carbonate from a lithium sulfate solution, the concentration of lithium ions in the lithium sulfate solution must be at least 10 g/L [13]. In general, the recovery of lithium from brine can be done by commercialized processes with natural evaporation and evaporative concentration, but this has the disadvantage of low energy efficiency and recovery. Lithium recovery by solvent extraction is effective at a lithium concentration of 1.0 g/L or more, and there are increased process cost and environmental pollution due to the use of organic extractant [11,14,15]. Electrodialysis (ED) is a process used to concentrate the desired component or separate it from impurities by selectively passing ions through an ion exchange membrane in an electric field. It is environmentally friendly because almost no byproducts are generated during the process and no additional chemical treatment is required to reuse the reagents afterward. Research using ED to recover lithium has been reported, and ion exchange membranes used for ED have been developed. Most of the previous studies use seawater or brine as a raw material and contain about 200 ppb lithium and impurities (potassium, magnesium, and sodium) [6–9].

Therefore, in this study, seawater or brine was not used as a raw material, but electrodialysis was used to concentrate lithium in the raffinate after the hydrometallurgy of cobalt and nickel. A basic study was conducted to concentrate high concentration lithium from the waste solution containing about 3000 ppm lithium.

1.2. Theoretical Background of Electrodialysis

In electrodialysis, when an electric field is applied, cations move to the cathode and anions move to the anode by an electric potential gradient, and ions are selectively passed through an ion exchange membrane that has a charge, thereby selectively concentrating a target component or separating impurities. At this time, the cation and the anion exchange membranes form a pair, and they can be effectively concentrated by being installed in several pairs. Figure 1 shows the ion exchange principle and solution flow in a general electrodialysis apparatus. The raw material solution is introduced into the solution chamber, and ions move to be divided into a diluted or a concentrated solution. When a membrane and laminar flow boundary layer is formed, an increase in current density can rapidly decrease ions in the boundary layer, generating concentration polarization. When the concentration polarization increases, the electrical resistance increases and the required power increases rapidly, which can cause decomposition of water. The pH change of the solution generated by the electrolysis of water can damage the ion exchange membrane or cause scaling. In addition, a spacer, which is an insulating material, is placed between the membranes to prevent short circuit between them. This spacer can form turbulence that reduces polarization due to concentration gradient. As a main variable in research and at industrial sites, there is a water migration phenomenon from the dilution chamber to the concentration chamber. If the water transfer rate is high, the ion concentration ratio can be reduced, so the effect on water movement cannot be ignored. Although osmotic pressure due to a concentration difference is hardly generated while an electric field is applied to the ion exchange membrane, metal ions and hydrated water molecules can move together by electrolytic osmosis to increase the water transfer [16,17].

Generally, high volume ratio concentration (HVRC) and multistage concentration (MSC) are the methods of concentrating target components using ED. HVRC is a method of concentrating a target component by using the volume difference between a concentrate and a diluent. In this study, two or more stages of ED were performed through a continuous process, and the MSC method was used for the concentrated solution at high concentration. Usually, the optimal conditions in the first stage are confirmed by the HVRC method and concentrated to a high concentration by the MSC method [17]. In a previous study by the authors, the conditions for lithium concentration in waste liquid containing lithium were established by HVRC, and in this study, a high concentration of lithium was also achieved by MSC.

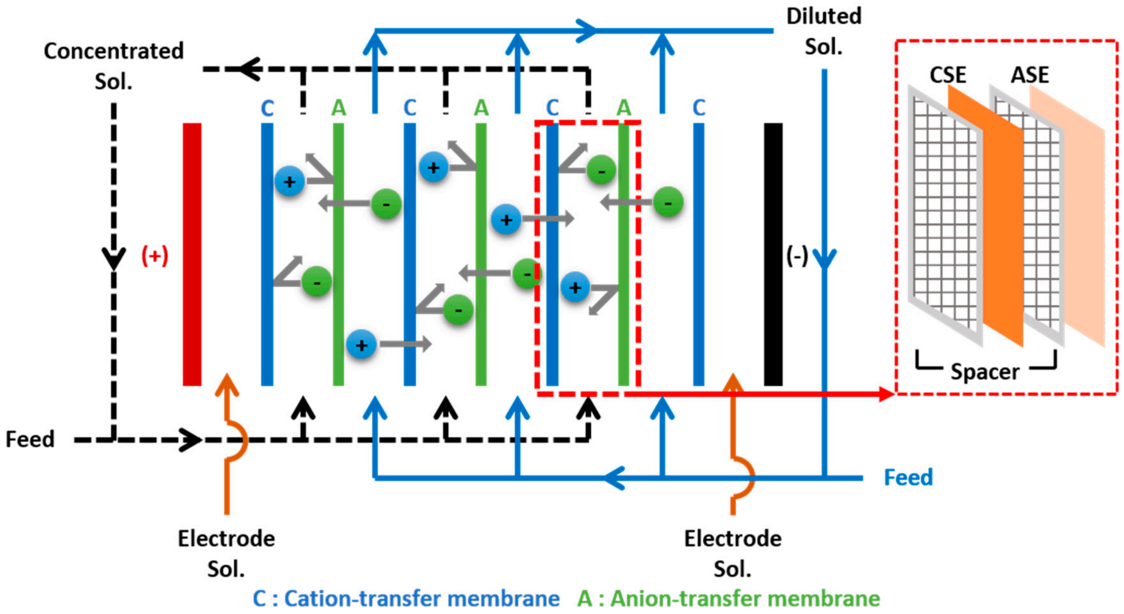

Figure 1. Schematic diagram of the electrodialysis process for the ion transfer.

2. Materials and Methods

2.1. Materials and Equipment

Similar to the composition of lithium-containing waste solution, a simulated solution was prepared using reagent-grade sulfate salt, and the composition is shown in Table 1. It contained 3.3 g/L lithium and a large amount of sodium as the remaining solution after cobalt and nickel were recovered from a waste secondary lithium battery. The simulated solutions were prepared using lithium sulfate ($Li_2SO_4 \cdot H_2O$, 99%, JUNSEI) and sodium sulfate (Na_2SO_4, 99%, DAEJUNG). The electrodialysis equipment used to concentrate lithium was a CJT-055 electrodialyzer (Chang Jo Tech. Co., Seoul, Korea). A photograph of the equipment and the main specifications of the equipment are shown in Figure 2 and Table 2, respectively. Each chamber can be injected with 2.0 L of solution, and the power supply can operate within the DC current range of 0–30 volts and 0–5 amperes. In order to study the ion exchange membrane and the equipment, the upper limit of the current was set to 3 ampere. Titanium electrodes coated with platinum were used for the anode and cathode. The cartridge consisted of 10 pairs of NEOSEPTA (Ion exchange membrane, ASTOM Co., Tokyo, Japan) cation-exchange (CEM) and anion-exchange (AEM) membranes and an additional CEM spaced between the ion exchange membranes. The effective area of the ion exchange membranes in the cartridge is 55 cm^2, and the main details of the membranes used in the study are shown in Table 3. Membrane stability is ensured below 40 °C, and the pH can be in a wide range from 0 to 14.

Table 1. Composition of Li-containing solution used in study.

Element	Li	Na	SO_4
Concentration (g/L)	3.3	60.0	148.0

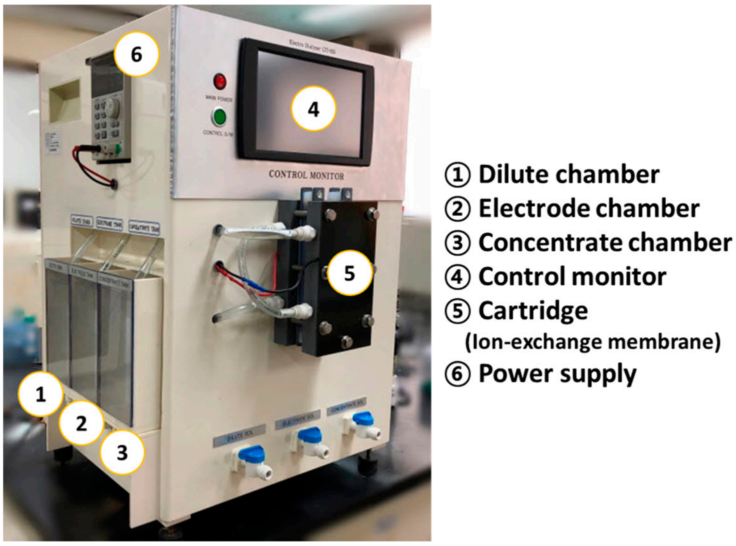

Figure 2. Photograph of the electrodialysis equipment.

Table 2. Specifications of Electro Dialyzer.

CJT-055		
Chamber	Dilute chamber	2.0 L (PVC)
	Electrode chamber	2.0 L (PVC)
	Concentrate chamber	2.0 L (PVC)
Effective membrane area		55 cm^2
Power supply (Rectifier)		DC, 30 V, 5 A
Primary power source		1 Ø, 220 V, 50 Hz/60 Hz
Cathode/Anode		Pt coated Ti (Pt/Ti)

Table 3. Characteristics of ion exchange membrane (NEOSEPTA).

NEOSEPTA	CEM (Cation Exchange Membrane)	AEM (Anion Exchange Membrane)
Type	Strong acid (Na type)	Strong base (Cl type)
Electric resistance *	1.8 ($\Omega \cdot cm^2$)	2.6 ($\Omega \cdot cm^2$)
Thickness	0.16 (mm)	0.15 (mm)
Characteristic	high mechanical strength	
Burst strength**	≥0.35 (MPa)	
Temperature	≤40 (°C)	
pH	0–14	

* Electric resistance: Measured on alternative current after equilibration with a 0.5 N NaCl solution at 25 °C; ** Burst Strength: Mullen Bursting strength.

2.2. Methods

The raw material solution was added to the dilution and concentration chambers at a constant volume ratio. Sodium sulfate (Na_2SO_4), used as the electrode solution, was prepared at a constant concentration, then 500 mL was added to the electrode chamber. The solution was sufficiently circulated for 5 min to remove residual air in the ion exchange cartridge and tube, then voltage was applied. It was applied as constant voltage of 10 volts, and the electrical conductivity of the solution in the dilution and concentration chambers over time was measured through the system's equipment. The experiment was terminated when the electrical conductivity of the solution in the dilution chamber became 1.00 mS/cm, where S (siemens) is the unit of conductivity and the reciprocal of the ohm (Ω) of electrical resistance, and 1 S = 1 A/V = 1 /Ω. At this time, there was a difference in the end time of the experiment depending on the volume ratio of the input solution and the initial concentration of ions. After the end of the experiment, samples were collected from the concentration and dilution chambers and analyzed by ICP-AES (Optima-4300 DV, Perkin Elmer Inc., Waltham, MA, US). The average energy consumption, average flux, concentration ratio, and water migration were respectively calculated by Equations (1)–(4), and the current was measured at intervals of 1 min through the device system to calculate the average current value, which was used in Equations (1) and (2).

The average energy consumption (E, kWh/m^3) can be obtained by Equation (1) [18], where U(V) is applied voltage, I(A) is applied current, and V(L) is the total volume of raw material solution (concentration chamber + dilution chamber input).

$$E = \int_0^t \frac{UI}{V} dt \tag{1}$$

The average flux (J, mol/m^2h) can be obtained by Equation (2), where m (g) is the mass of Li concentrated in the concentrated chamber, N is the number of pairs of alternating cation and anion exchange membranes, A (m^2) is the effective area of the exchange membrane, M is the molecular weight of lithium (g/mol), and t is the dialysis time (h).

$$J = \frac{m}{N \cdot A \cdot M \cdot t} \tag{2}$$

The concentration ratio (C_R, %) can be obtained by Equation (3), where C_f is the final concentration and C_i is the initial concentration of solution in the concentration chamber.

$$C_R\ (\%) = \frac{C_f}{C_i} \times 100 \tag{3}$$

The water migration (W_m,%) can be obtained by Equation (4), where V_D^f is the final volume of solution and V_D^i is the initial volume of solution in the dilution chamber.

$$W_m(\%) = \frac{V_D^i - V_D^f}{V_D^i} \times 100 \tag{4}$$

3. Results

3.1. Effects of Electrode Solution Concentration

As a result of electrodialysis by HVRC in the authors' previous study [19], the effects of the applied voltage and the volume ratio of raw material solution entering the initial concentration and dilution chamber were examined. Prior to MSC electrodialysis, the concentration of sodium sulfate to be used as the electrode solution was adjusted to 0.1–1.0 M to examine the effect of the solution concentration. Then 500 mL of raw material solution was added to the dilution and concentration chambers, and 500 mL of electrode solution was added to the electrode solution chamber. The experiment was conducted by applying a constant voltage of 10 V. Figure 3 shows the electrical conductivity of the diluent and concentrate solutions over time. As the concentration of the electrode solution increased, less time was required for the process to decrease the electrical conductivity of the diluent to 1.00 mS/cm. When 0.1 M Na_2SO_4 was used, it took 3 h 30 min, with 0.7 M Na_2SO_4 it was 2 h 5 min, and with 1.0 M Na_2SO_4 it was 1 h 55 min. With 0.7 M and 1.0 M Na_2SO_4 compared to 0.1 M Na_2SO_4, the process lead time was reduced by more than 1 h. Table 4 shows the ion concentration in the concentrate solution after the end of the experiment. The same experiment was conducted three times, and the average value of each ion concentration was calculated. As the concentration of the solution increased, the concentration of Li increased. With 0.7 M Na_2SO_4, lithium was concentrated to 4.53 g/L, and with 1.0 M Na_2SO_4, the concentration was slightly reduced to 4.19 g/L. Figure 4 shows energy consumption and average flux. As shown in Figure 4a, there was no significant difference in energy consumption from 41 to 43 kWh/m^2 depending on the concentration of electrode solution. As shown in Figure 4b, as the concentration of electrode solution increased, the average flux increased, and it can be seen that the ion migration rate per unit time is high. Therefore, it was effective to use a concentration of 0.7 M Na_2SO_4 or higher in the ED process.

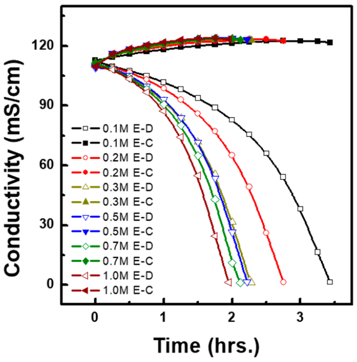

Figure 3. Effect of electrode solution concentration (M) on the electrical conductivity (D: Dilute solution, C: Concentrate solution, 10 V, D:C [1:1]).

Table 4. Analytical results of the concentrated solution after electrodialysis (ED) process (10V, D:C [1:1]).

Concentration of Electrode Solution	Concentration (g/L)			Process Lead Time (min)
	Li	Na	SO_4	
Initial solution	3.30	60.00	148.20	-
0.1 M Na_2SO_4	3.38	57.86	167.65	205
0.2 M Na_2SO_4	3.38	53.66	158.89	165
0.3 M Na_2SO_4	3.69	59.32	174.99	135
0.5 M Na_2SO_4	3.68	56.99	169.99	135
0.7 M Na_2SO_4	4.53	66.45	201.52	130
1.0 M Na_2SO_4	4.19	64.95	193.67	120

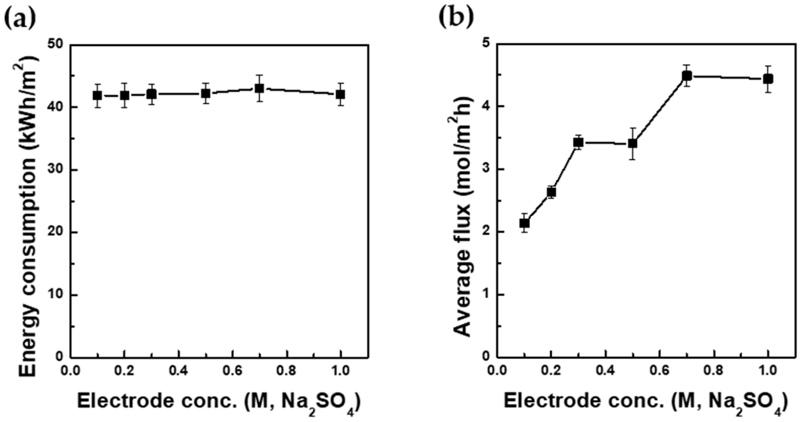

Figure 4. Effect of electrode solution concentration (M) by (**a**) energy consumption and (**b**) average flux (10 V, D:C [1:1]).

3.2. Concentration of Lithium by MSC Electrodialysis

As a result of electrodialysis by HVRC in the authors' previous study [19], the highest Li concentration was obtained with applied voltage 10 V, volume ratio (diluent:concentrate) = 3:1, and 0.7 M Na_2SO_4 electrode solution. This was selected as an optimal condition and applied to the MSC, and 900 mL was added to the dilution chamber and 300 mL to the concentration chamber to start the experiment. The ED process after the first stage was used as a feed solution in the second stage, and the third stage was supplied with feed solution in the same way. In order to confirm the continuous process, the raw material solution entering the second and third stages was not prepared and not used as simulation solution. The first stage was repeated 10 times, the second stage five times, and the third stage three times. The concentrate solution from each stage was collected in a bottle and used as a raw material solution in the next stage. The samples were taken from bottles to analyze the concentration of ions. The concentration of Li in each stage was compared, as shown in Figure 5. The concentration of lithium increased with the number of stages, and after the third stage, the lithium concentration was more than twice the initial concentration, at 6.95 g/L. Table 5 shows the results of ICP analysis for Li, Na, and SO_4 according to the stage, lithium concentration, and process lead time. Three components increased in concentration as the number of stages increased. In the case of lithium, the concentration increased from the initial concentration or from the previous stage, but the concentration ratio (%) tended to decrease compared to the previous stage. As the ions concentration in the raw material solution increases, the amount of water hydrated and moved during the ED process also increases. Therefore, as the number of stage increases, the volume of the concentrated solution increases after the process. As shown in Table 6, the volume changes according to the water migration acted to reduce the C_R (%) of lithium. The ion concentration in the raw material solution input at each stage increased, so the process lead time increased. The process lead time for ED in the first stage was 210 min, and in the third stage it increased significantly to 320 min.

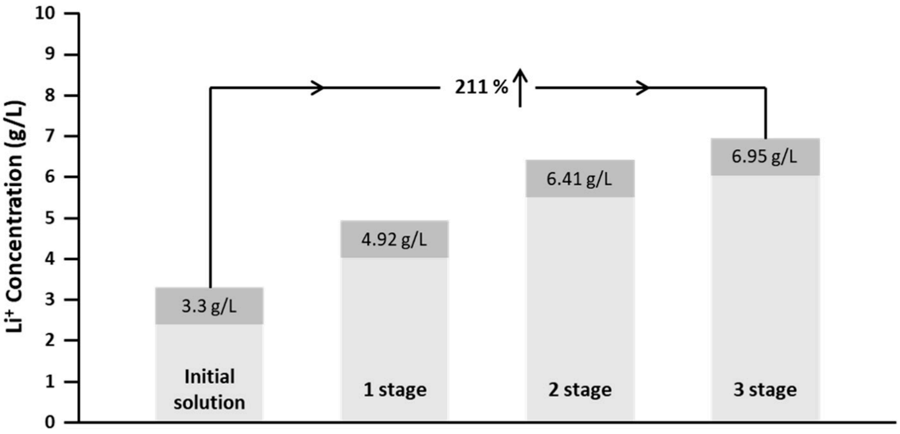

Figure 5. Effect of number of concentration stage on the Lithium concentration (10 V, 0.7 M Na_2SO_4, D:C [3:1]).

Table 5. Analytical results of the concentrated solution after multistage concentration (MSC) process (10 V, 0.7 M Na_2SO_4, D:C [3:1]).

Stage	Concentration (g/L)			Concentration (%) Compared to Previous Stage Sol.	Concentration (%) Compared to Initial Sol.	Process Lead Time (min)
	Li	Na	SO_4			
Initial sol.	3.30	60.00	148.20	-	-	-
1st	4.92	42.05	147.88	149.09%	149.09%	210
2nd	6.41	58.30	213.87	130.28%	194.24%	270
3rd	6.95	63.58	224.84	108.42%	210.61%	320

Table 6. Volume change of solution in chamber after MSC process (10 V, 0.7 M Na_2SO_4, D:C [3:1]).

Stage	Volume Change of		Water Migration (%)
	Concentrated Sol.	Diluted Sol.	
1st	300 mL → 670 mL	900 mL → 530 mL	41.11%
2nd	300 mL → 870 mL	900 mL → 330 mL	63.33%
3rd	300 mL → 1050 mL	900 mL → 150 mL	83.33%

However, as shown in Table 5, the concentrations of sodium and sulfate in the first stage of ED were lower than those of the initial raw material solution. Repeating the first stage and storing the concentrated solution, white columnar crystals occurred, as shown in Figure 6a. These crystals were dried and crushed and recovered as a powder, and then analyzed by XRD, and were found to be Na_2SO_4 (thenardite, syn) (Figure 6b). Seen in the form of crystals recovered before drying, it is considered to be $Na_2SO_4{\cdot}10H_2O$. After the first stage, the crystals were separated into a solid–liquid, and after separation, the solution was used in a second stage ED process. When the concentration of sodium sulfate in the initial raw material solution is high, crystals may be generated inside the ion exchange cartridge during ED. These crystals can cause problems such as damage to the ion exchange membrane and reduced current efficiency, so it is necessary to remove sodium sulfate from the raw material solution before the ED process.

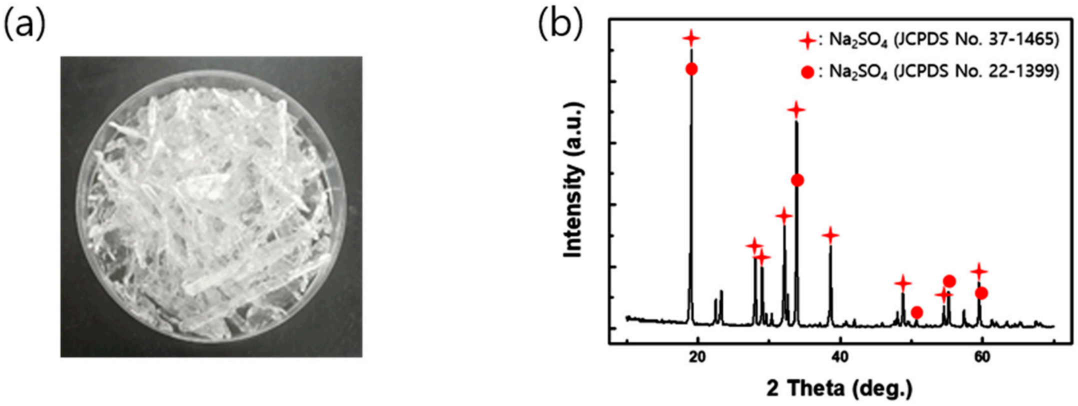

Figure 6. Photograph and result of XRD analysis of precipitate from 1st stage ED process by (**a**) precipitate and (**b**) XRD analysis of precipitate.

3.3. Sodium Sulfate Removal Process

In the previous experiment, when the concentration of Na and SO_4 in the raw material solution was high, a problem occurred: $Na_2SO_4{\cdot}10H_2O$ crystals were generated during ED. Methanol was used as a precipitant to remove sodium sulfate in solution. Since sodium sulfate has low solubility in methanol, sodium sulfate may be precipitated when methanol is added to the sodium sulfate solution [20,21]. Methanol was added to the solution based on the composition of Table 1 in a constant volume ratio, followed by stirring for 30 min to induce a reaction. After the end of the reaction, filtration was performed to separate solids. Methanol was added in a volume ratio of 0.1 to 1.0 relative to the volume of the raw material solution, and as the volume of added methanol increased, the removal rate (%) of Li, Na, and SO_4 increased, as shown in Figure 7. When the volume ratio of added methanol was 0.6 or more, the loss rate of lithium was 14% or more. It is preferable to proceed with the Na_2SO_4 removal process at a volume ratio of 0.4 or less of methanol with a lithium loss (%) of less than 0.3%. When the volume ratio of added methanol was 0.4, lithium loss was about 2%, Na removal was 65%, and SO_4 removal was 51%. Figure 8a shows the powder generated in the Na_2SO_4 removal process, and in Figure 8b the results of XRD analysis show that it was sodium sulfate. It is considered that the recovered powder can be used to prepare the electrode solution for ED process without purification.

In addition, methanol is likely to be recovered through fractional distillation after sodium sulfate filtration. The recovered sodium sulfate and methanol can be reused to reduce the overall process cost.

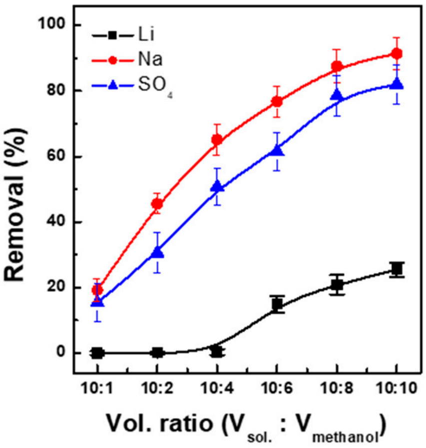

Figure 7. Effect of methanol addition on the sodium and sulfate removal (25 °C).

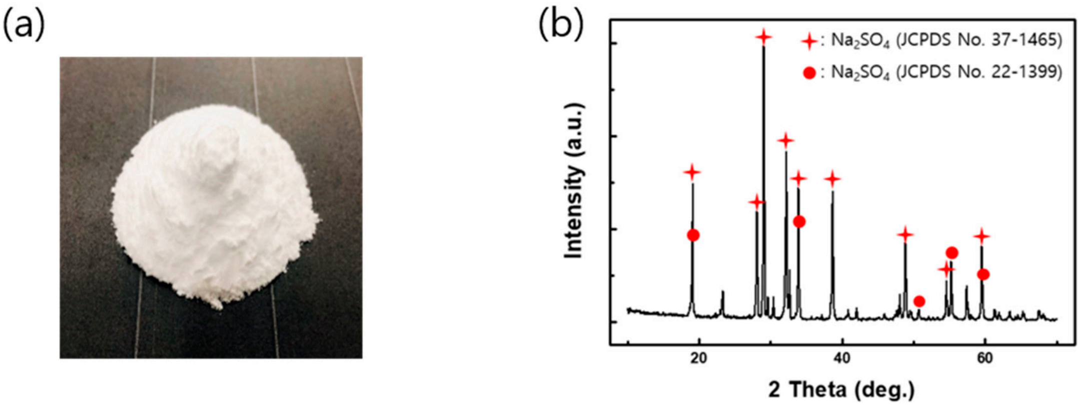

Figure 8. Photograph and result of XRD analysis of precipitate from Na_2SO_4 removal process by (**a**) precipitate and (**b**) XRD analysis of precipitate.

3.4. Concentration of Lithium by MSC Electrodialysis after Sodium Sulfate Removal Process

Sodium sulfate crystals were generated during concentration by ED using a raw material solution containing a large amount of sodium sulfate. Prior to the ED process, the MSC ED process was performed using a solution from which sodium sulfate was partially removed through a Na_2SO_4 removal process as a raw material. The first stage was repeated 20 times, the second stage eight times, the third stage five times, and the fourth stage three times. The concentrate solution from each stage was collected in a bottle and used as a feed solution in the next stage. Methanol was added to the raw material solution in Table 1 in a volume ratio of 0.4 to induce the reaction, and the solution from which sodium sulfate was removed was used as the raw material solution. Its composition is about 2.65 g/L Li, about 10 g/L Na, and about 71 g/L SO_4. In Figure 9, the concentration of lithium increased with the number of stages; it was concentrated to 10.02 g/L after four stages from an initial concentration of 2.65 g/L. Although the concentration of lithium was lower than that of the raw material solution, which had not undergone a Na_2SO_4 removal process, it showed a higher concentration even in the first stage, and the process time was shortened. Table 7 shows the concentration of lithium, sodium, and sulfate in each stage, the C_R (%) of lithium, and the process lead time. Compared to the initial concentration of lithium, the C_R (%) tended to increase, but compared to the previous stage, the rate tended to decrease gradually. This phenomenon occurred because water was migrated from the dilution chamber to the concentration chamber as shown in Table 8. In addition, it showed a tendency to increase the process lead time compared to the C_R (%) of lithium. However, compared to using a raw material solution that had not undergone a Na_2SO_4 removal process, a high C_R (%) is shown in a relatively short process lead time. If the concentration of components other than lithium is high in the raw material solution, it is considered efficient to perform ED after removal.

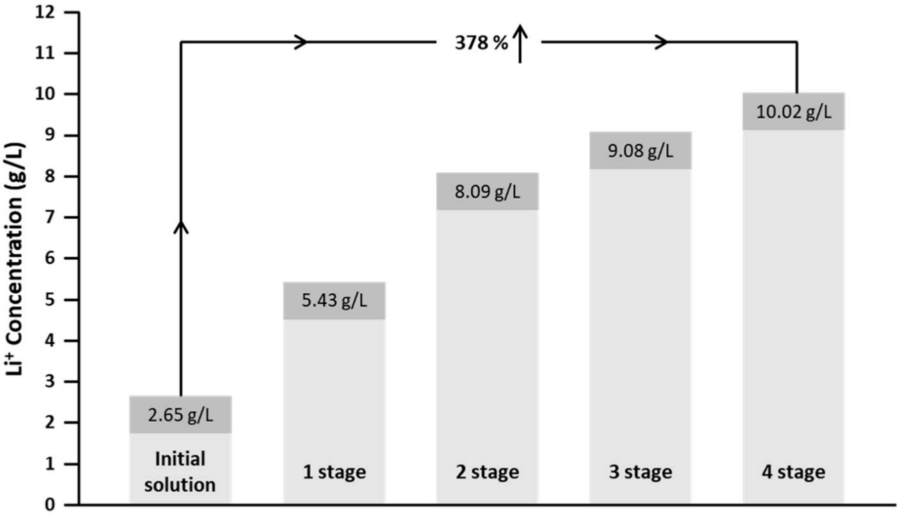

Figure 9. Effect of number of concentration stage on the lithium concentration after Na_2SO_4 removal process (10 V, 0.7 M Na_2SO_4, D:C [3:1]).

Table 7. Analytical results of the concentrated solution after Na_2SO_4 removal process and MSC process (10 V, 0.7 M Na_2SO_4, D:C [3:1]).

Stage	Concentration (g/L)			Concentration (%) Compared to Previous Stage Sol.	Concentration (%) Compared to Initial Sol.	Process Lead Time (min)
	Li	Na	SO_4			
Initial sol.	2.65	9.98	70.67	-	-	-
1st	5.43	20.67	142.54	204.91%	204.91%	150
2nd	8.09	30.09	208.21	148.99%	305.28%	210
3rd	9.08	36.92	260.78	112.24%	342.64%	260
4th	10.02	41.61	284.66	110.35%	378.11%	310

Table 8. Volume change of solution in chamber after Na_2SO_4 removal process and MSC process (10 V, 0.7 M Na_2SO_4, D:C [3:1]).

Stage	Volume Change of		Water Migration (%)
	Concentrated Sol.	Diluted Sol.	
1st	300 mL → 530 mL	900 mL → 670 mL	25.56%
2nd	300 mL → 810 mL	900 mL → 390 mL	56.67%
3rd	300 mL → 980 mL	900 mL → 220 mL	75.56%
4th	300 mL → 1020 mL	900 mL → 180 mL	80.00%

4. Conclusions

In this study, the valuable metals were recovered from the waste lithium secondary battery and a simulated solution was prepared with the same solution composition as the remaining filtrate. An experiment was performed to concentrate lithium from the simulated solution through a multi-stage concentration process using electrodialysis. The following conclusions were drawn:

(1) As the concentration of the electrode solution increased, the concentration ratio (%) of lithium increased and the process lead time decreased. When 0.7 M Na_2SO_4 was used as an electrode solution, the average flux during the process was high and the concentration ratio (%) of lithium increased, which was effective for concentration.

(2) In the case of multistage concentration electrodialysis using an initial raw material solution containing a large amount of sodium sulfate, sodium sulfate crystals were generated during the ED process. In addition, the concentration ratio (%) of lithium was low even after the third stage of ED, and a long process lead time was required.

(3) Sodium sulfate was precipitated by adding methanol to remove sodium from the raw material solution. As the volume of methanol increased, the sodium sulfate removal rate (%) increased, but the loss rate (%) of lithium also increased. When methanol as a raw material solution was added in a volume ratio of 0.4, sodium was removed by 65% and sulfate ion by 51%, and the loss rate of lithium was 0.3%.

(4) During multistage concentration (MSC) using electrodialysis with a solution from which sodium was partially removed as raw material, lithium was effectively concentrated to 10 g/L in the solution in four stages.

Author Contributions: Y.C., K.K., J.A., and J.L. carried out the experiments and analysis and interpretation of the data obtained. Y.C. and J.A. wrote and edited the paper. J.A. is the co-principal investigator of this work. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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