공학석사 학위논문

염수에서의 리튬 회수를 위한 배터리 공정 시스템

Battery system for recovering lithium from salt water

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서울대학교 대학원

화학생물공학부

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지도교수 윤 제 용

이 논문을 공학석사 학위논문으로 제출함

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화학생물공학부 에너지환경화학융합기술 전공

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Abstract

Lithium is an important resource in many fields of technology, and the demand for lithium is highly increased as the development of rechargeable batteries. In general, lithium can be found from several sources such a hard mineral, brine lakes, and seawater. Nowadays, the main lithium resource is salt lake, especially located in South America, and it contains various cations such as sodium, potassium, magnesium and calcium. The conventional lithium recovery process is the "lime soda evaporation process"; however, this method is time consuming, inefficient and environmentally harmful. Therefore, new technology for highly selective and environmentally friendly lithium recovery from brine water is urgently required. This research investigates the battery system to extract lithium from salt water, which is containing various cations, using $Li_{1-x}Mn_2O_4$ positive electrode and Ag/AgCl negative electrode. The performance of the battery system showed highly selective and efficient for lithium recovering from salt water which has same concentration of lithium, sodium, potassium, magnesium, and calcium ions (30 mM). And we demonstrated this battery system for recovering lithium from artificial brine water that the compound of chemical is similar with Salar de Atacama (mole ratio: Na/Li ≈ 15.7, K/Li ≈ 2.2, Mg/Li ≈ 1.9) which is brine lake located in Chile. By repeating the battery

system, we can condense high purity of LiCl solution from the brine water as consuming 1.0 Wh per 1 mole of lithium recovery.

Keyword: lithium recovery, battery system, $LiMn_2O_4$, lithium ion selectivity
Student Number: 2011-22928

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Chapter 1. Introduction

As the industrial development of the world, lots of countries are pouring their efforts into the competition for scarce resources such as petroleum and this competition is spreading to rare earth resources and rare metals. Especially, lithium is one of the energy resources and it is receive a lot of attention as the alternative resource to substitute petroleum in the near future. The demand for lithium significantly increased since the development of handheld devices and large-capacity rechargeable batteries for an electronic vehicle are expected to be in increasing demand in the near future (Ebensperger *et al*., 2005; Mohr *et al*., 2012).

  In general, lithium can be found from several sources such a hard mineral, brine lakes, and seawater. However, the efforts for recovering from hard mineral or seawater suffer from the technical complexities of the extraction process which requires acid treatment with the high temperature up to 1000℃ or the inefficiency for extracting low concentration of lithium in seawater (0.17 mg/L) (Averill and Olson, 1978; Bukowsky *et al*., 1991; Bardi, 2010). For this reason, currently the main lithium source relies upon brine lakes which are located especially on South America and more than 80% of lithium carbonate is

produced from brine lakes. Since brine water from these lakes typically contain a mixture of salts such as sodium, potassium, calcium, magnesium, boron, chloride and sulphate beside lithium, the highly selective lithium recovery becomes more important (Hamzaoui *et al*., 2003).

The existing process of recovery lithium from brine lakes is known as the "lime soda evaporation process" which includes one year long time consuming solar evaporation process in pond and produces lithium carbonate by adding excess lime and pH adjustment. This process greatly suffers from low recovery efficiency of lithium especially influenced by the coexisting minerals such as magnesium, needless to say long time requirement and the tremendous burden to environment resulting from industrial waste production in large quantities as well as lavish water consumption, urgently requiring new technology for highly selective and environmentally friendly lithium recovery from brine water (Tahil, 2007).

In Chile, there is conflict and friction between the local residents and mining companies over water rights. Fresh water is an important to inhabitant and fauna in the local area such as flamingoes; however, mining industry already consumes 65% of the water in the Salar de Atacama region. To prevent indiscriminate development ignored environmental and ecosystem, Chile government passed an environmental protection law, which requires all future

mining projects in Chile to be subjected to an environmental impact assessment in advance. So ecological and environmental should be considered when we are considering development of mineral resources (Tahil, 2007).

In this study, we develop the battery system for recovering lithium which has high selectivity of lithium from various cations, especially magnesium ion. For this selectivity of lithium ion, spinel $LiMn_2O_4$ electrode is used for positive electrode since the λ-MnO_2 adsorbent developed from spinel $LiMn_2O_4$ has been reported to use ion exchange for extracting lithium from seawater (Kanamura *et al.*, 1996; Yoshizuka *et al.*, 2002; Yoshizuka *et al.*, 2006; Nishihama *et al.*, 2011). Spinel $LiMn_2O_4$ is also well known as one of the positive electrode materials for lithium batteries, and it is available materials with low cost, environmentally harmless and high charge capacity. Wu Li et al. has proposed the rechargeable lithium batteries with aqueous electrolyte, using $LiMn_2O_4$ for positive electrode (Li *et al.*, 1994). Kanoh, et al. reported the electrochemical method to recover lithium from aqueous solution, and they used λ-MnO_2 for lithium selective material with Pt-wire for counter electrode. Note that this method was not based on a battery system (Kanoh *et al.*, 1993).

In this work, we investigated the highly selective and energy efficient lithium recovery system from the intervention of various cations, especially magnesium ion, using the battery system. In addition, the efficacy of this battery system

was examined with representative simulated brine water, which chemical composition is similar with "Salar de Atacama" brine lake in Chile, the world's largest active source of lithium.

Chapter 2. Literature Review

2.1. Existing methods for lithium recovery

2.1.1. Evaporation process

Figure 1 shows the existing process of recovery lithium from brine lakes, and it is known as the "lime soda evaporation process" which is commercialized to product lithium carbonate from brine water. In this process, the salt water in brine lakes pumped into solar evaporation ponds and left more than 1 year to concentrate the brine until the lithium chloride concentration rises up to $6000 - 60000$ mg/L. As the salt water becomes more concentrated, different salts crystallize. Afterwards, the solution is treated by lime ($Ca(OH)_2$) to extract magnesium from brine. In sequence, sodium carbonate (Na_2CO_3) is added to precipitate out insoluble lithium carbonate.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 (\downarrow) + CaCl_2$$

$$MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 (\downarrow) + 2NaCl$$

$$2LiCl + Na_2CO_3 \rightarrow Li_2CO_3 (\downarrow) + 2NaCl$$
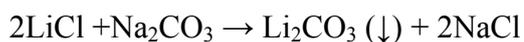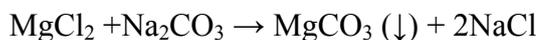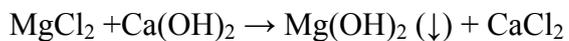
The lithium recovery from brine is difficult because its diluted concentration compared to other major elements in the solution (250-350 g/L). But the end of brine evaporation the brine water is highly concentrated in lithium and magnesium ions compared to other cations. The major problem of evaporation method is separating magnesium ion due to it is difficult to separate between lithium and magnesium ions. So, the ratio of magnesium to lithium is an important factor for lithium mining industry (Bukowsky *et al*., 1991; Hamzaoui *et al*., 2003).
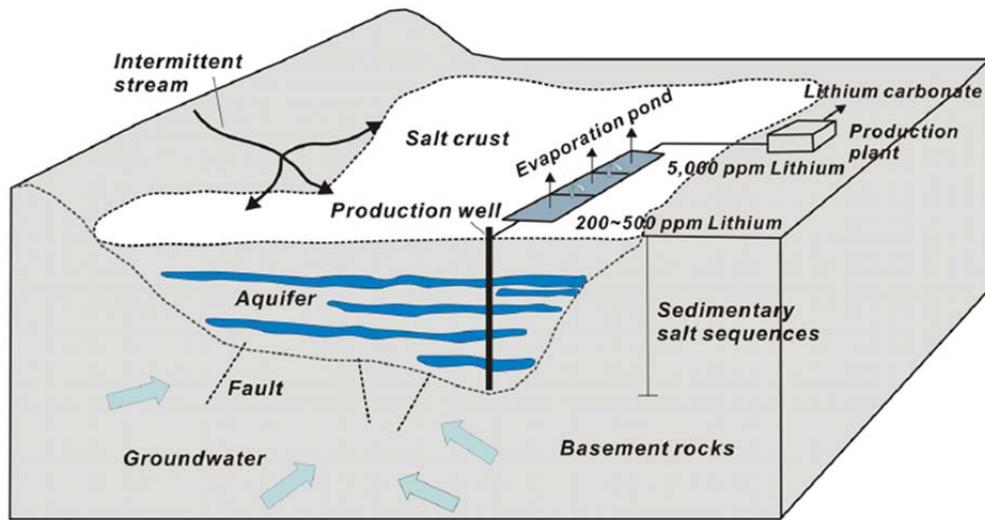
Figure 1. Conceptual model of brine lithium production for Marifill Mines, immediately adjacent to the Salar de Hombre Muerto (Ebisch *et al*., 2009).

2.1.2. Selective absorbent

The λ-MnO_2 adsorbent developed from spinel $LiMn_2O_4$ has been reported to use ion exchange for extracting lithium from seawater. It has high selectivity for lithium, especially compared with sodium. Nishihama et al. reported that the concentration efficiency of lithium from seawater by using the λ-MnO_2 adsorbent was about 11000 even though the concentration of lithium in seawater is quite diluted (0.17 mg/L) (Nishihama *et al*., 2011).

Figure 2 displays the schematic diagram of lithium recovery process from seawater. In this system, the absorption column contains λ-MnO_2 adsorbents and seawater is pumped in this column continuously. Lithium ions in seawater are selectively absorbed into λ-MnO_2. However, it is time consuming process and difficult to reuse since the manganese ions are extracted from the adsorbent after acid treatment.
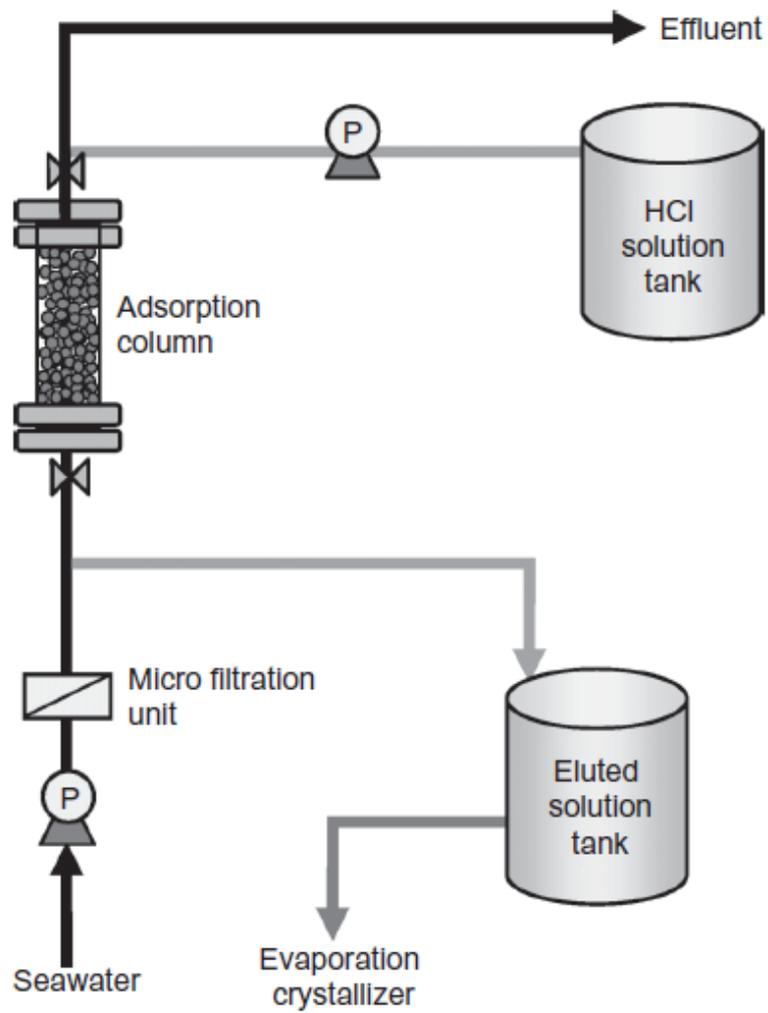
Figure 2. Schematic diagram of benchmark plan of lithium recovery from seawater (Nishihama *et al*., 2011).

2.1.3. Electrochemical method

Kanoh, et al. reported the electrochemical method to recover lithium from aqueous solution for the first time, and they used λ-MnO$_2$ for lithium selective material with Pt-wire for counter electrode. In this system, lithium ion selectively inserted and extracted into λ-MnO$_2$ with oxygen and hydrogen generation (Kanoh *et al.*, 1993). The system shows high selectivity of lithium ion, however, the system is energy consuming process and it needs to control pH conditions after extracting and releasing lithium ion.

2.2. The principle of lithium ion battery

A lithium-ion battery is one type of rechargeable battery composed of lithium which is the highest electrochemical potential and the lightest metal. In this battery system, lithium ions move between positive and negative electrode due to lithium metal is an unstable. During discharge, lithium ions move from the negative to the positive electrode, through the electrolyte and separator. During charging, a power source applies an over-voltage than that produced by the battery, then lithium ions migrate from the positive to the negative electrode.

Figure 3 displays the basic design of a lithium ion battery. The active materials of positive and negative electrodes are lithium compounds which have different electrochemical potentials. The typical cells use lithium metal oxides for positive electrode materials and carbon lithium intercalation compounds as negative electrode. The particle size, surface area, and traveling distance between the electrodes are related with the performance of the cells. The cell voltage is given by the Gibbs free energy between lithium ions in positive and negative electrodes. Most commercial cells have a voltage between 3 and 4 V.

Positive electrode: $Li_{1-x}MX_2 + xLi^+ + xe^- \leftrightarrow LiMX_2$

Negative electrode: $Li_xC_6 \leftrightarrow C_6 + xLi^+ + xe^-$

Cathode
(LiMX$_2$)

Anode
(Li$_x$C$_6$)

$$\text{LiMX}_2 + \text{C}_n \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} \text{Li}_{1-x}\text{MX}_2 + \text{Li}_x\text{C}_n$$
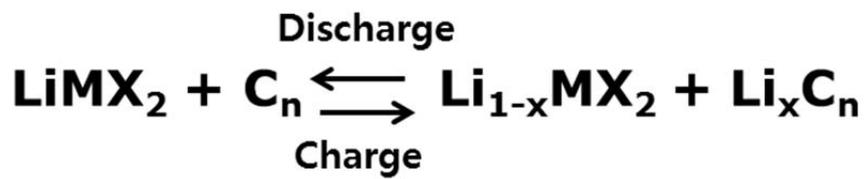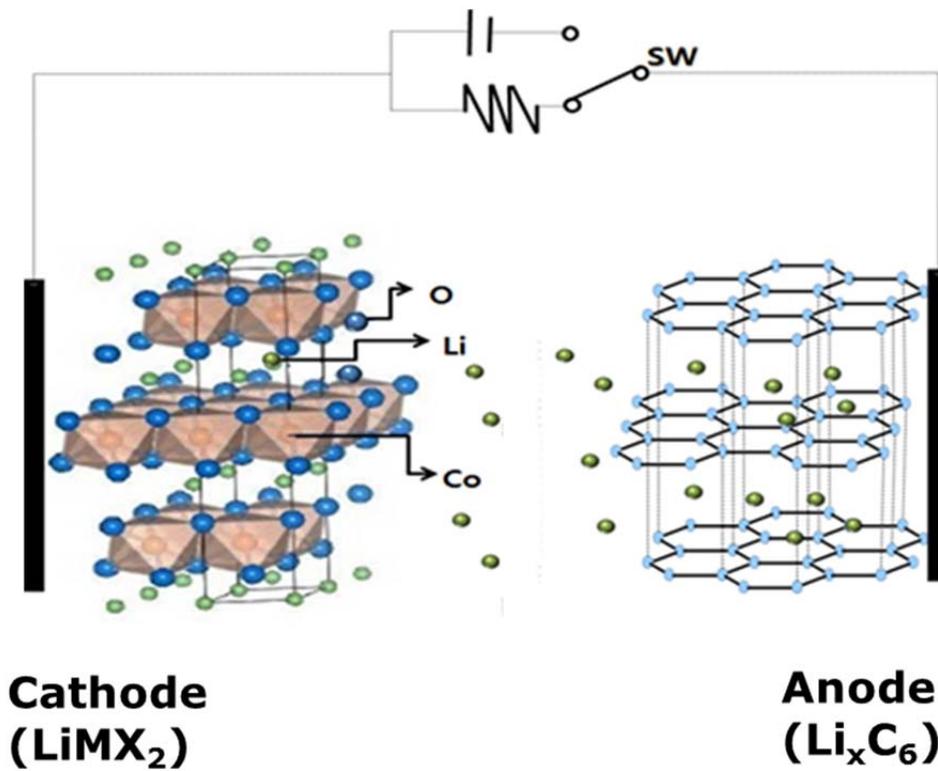
Figure 3. Schematic of a lithium ion battery cell. The cell consists of cathode, anode electrode, electrolyte, and separator (Chris K. Dyer, 2009).

The positive electrode materials consists of lithium cobalt oxide ($LiCoO_2$), lithium nickel oxide ($LiNiO_2$), spinel lithium manganese oxide ($LiMn_2O_4$), and lithium iron phosphate ($LiFePO_4$). The morphology, crystalline structure, chemical composition of the materials is important for the performance of positive electrode, and the properties of materials are shown in Table 1.

Table 1. Overview of rechargeable lithium ion battery positive electrode materials (Chris K. Dyer, 2009).

Materials	$LiCoO_2$	$LiNiO_2$	$LiMn_2O_4$	$LiFePO_4$
Capacity (mAh/g)	137	192	148	170
Potential (vs. Li/Li+)	3.0 – 4.4	3.6	3.0 – 4.5	3.5
Cycle life	>1000	Limited	Limited	>1000
Advantage	High rate capacity	High capacity	High potential Low cost	High rate capacity Good cycle ability
Disadvantage	Thermal instability High cost	Poor cycle ability Thermal instability	Low capacity Poor cycle ability	Poor conductivity

2.3. A battery system for desalting water

A concept of desalting water from a battery system has been reported in 2012, in this study, researchers desalted seawater by using a "desalination battery". The desalination battery is composed of a $Na_{2-x}Mn_5O_{10}$ nanorod positive electrode and Ag/AgCl negative electrode. This technology is similar to the four cycles of the capacitive energy extraction based on double-layer expansion (CDLE) (Brogioli, 2009; Brogioli *et al*., 2011), but the principle of desalting water is different. Instead of adsorbing ions in the electrical double layer, it is redox chemical reaction in metal oxide layer so it has higher capacity and lower self-discharging then CDLE (Pasta *et al*., 2012a).

 One noticeable study done by Pasta et al. was recently reported for recovering lithium from bine water which is based on the principle of rechargeable battery consisting of lithium iron phosphate (LFP) cathode and silver/silver chloride anode (Pasta *et al*., 2012b). Figure 4 shows the schematic representation of the working principle for recovery lithium from brine water. Briefly, The LFP and silver/silver chloride electrodes are submerged in brine water in their charged state. And then, by applying a negative current, lithium ions in brine water are captured in the electrodes. The next step, the brine is replaced with a recovery solution to release captured ions during discharging. In the last step, the

recovery solution is replaced with new brine water. .This study was quite successful for high selectivity of lithium ions free from the interference of coexisting ion of sodium as well as efficient energy consumption. However, this system greatly suffer from the interference of coexisting ion of magnesium which is essential elements in brine water (Hamzaoui *et al.*, 2003), resulting in the decrease of the efficient and selectivity of lithium recovery possibly through intercalation into LFP (Pasta *et al.*, 2012b).
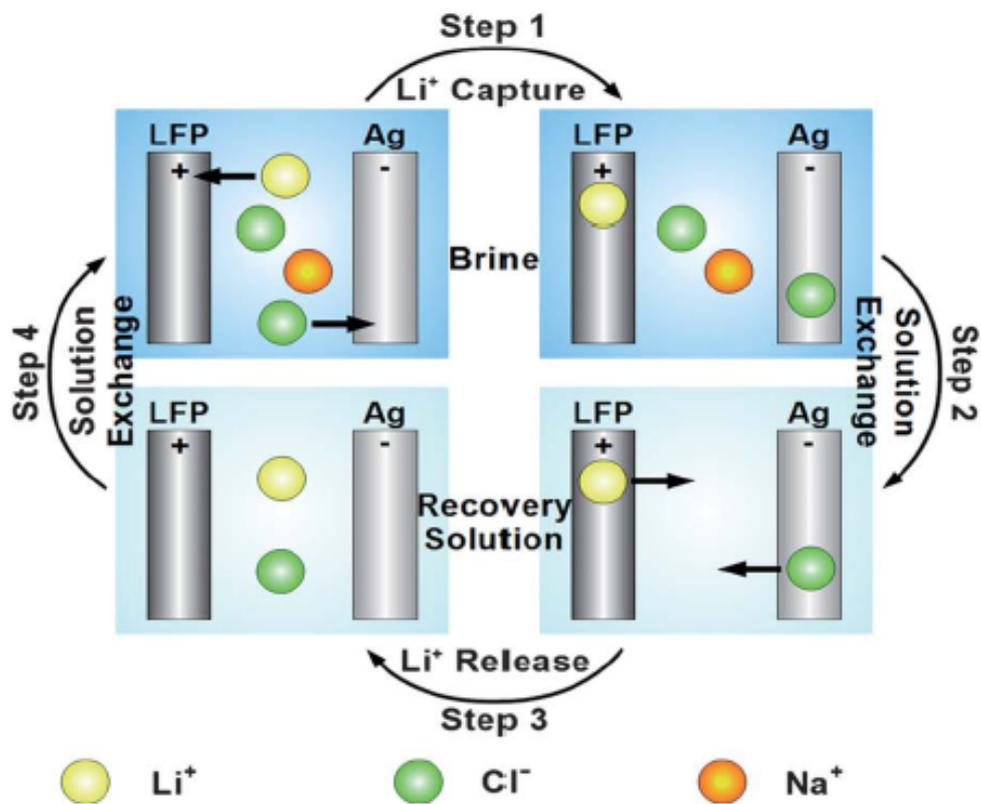
Figure 4. Schematic representation of the working principle behind a complete cycle of the lithium recovery: step 1, lithium capture in brine water; step 2, exchange with recovery solution; step 3, lithium release in recovery solution; step 4, exchange with brine water (Pasta *et al.*, 2012b).

Chapter 3. Methods

3.1. Fabrication of electrodes

3.1.1. LiMn$_2$O$_4$ electrode

The preparation procedure of LiMn$_2$O$_4$ positive electrode for lithium recovery system is described as follows. LiMn$_2$O$_4$ powder (Sigma Aldrich) (80% wt.), carbon black (Timcal) (10% wt.) and polyvinylidene fluoride (PVDF) (10% wt.) were mixed with N-methyl-2-pyrrolidone (NMP) to obtain slurry mixture. The resulting slurry was coated on the graphite sheet, then dried in vacuum oven at 60℃ for 12 hr to remove solvent. We extracted lithium from LiMn$_2$O$_4$ electrode by the electrochemical method before lithium recovery test to form the λ-MnO$_2$ electrode and enhance the selectivity of lithium ion. LiMn$_2$O$_4$ electrode was used as working electrode and platinum mesh was prepared for counter electrode. The reference electrode was an Ag/AgCl (KCl sat') electrode and a potential of 1.0 V (vs. Ag/AgCl) was applied to LiMn$_2$O$_4$/Pt cell in an aqueous solution containing 30 mM LiCl for 90 min.

The LiMn$_2$O$_4$ powder was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) measurements and X-ray

photoelectron spectroscopy (XPS). Powder XRD was performed using a Rigaku D/Max-3C diffractometer equipped with Cu Kα radiation source (λ= 0.15418 nm). XPS experiment was performed using Al Kα source at base pressures (<10-10 mbar.) (Sigma probe, ThermoFisher Scientific).
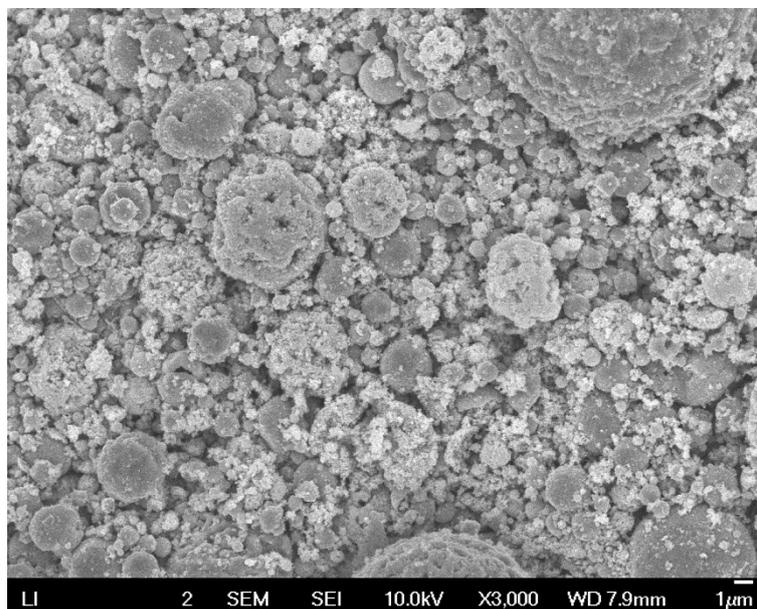
Figure 5. Scanning electron microscopy (SEM) image of spinel $LiMn_2O_4$.
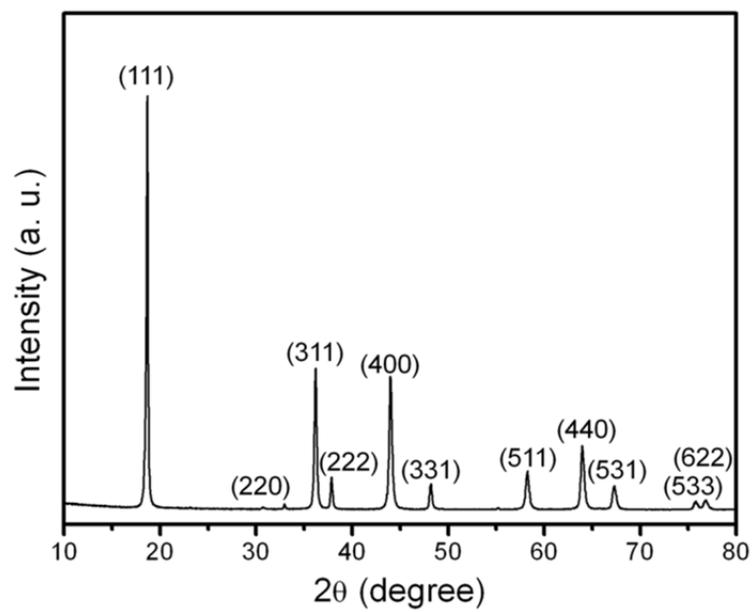
Figure 6. X-ray diffraction (XRD) pattern of spinel $LiMn_2O_4$.
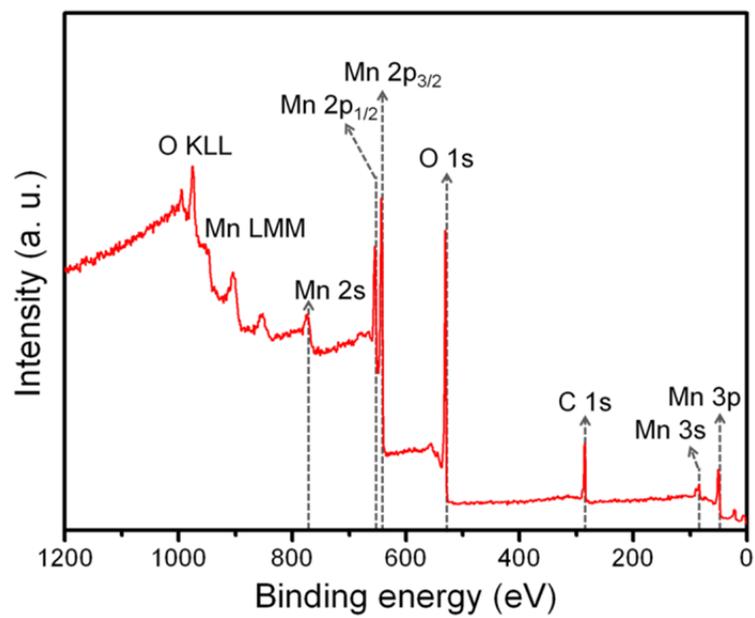
Figure 7. XPS survey spectrum of spinel LiMn$_2$O$_4$.

3.1.2. Silver electrode

The negative electrode was prepared by pressing a mixture of Ag microparticles (5 - 8 μm, Sigma Aldrich) (80% wt.), super P (Timcal, 10% wt.) and polytetrafluoroethylene (PTFE) (10% wt.) and cut into rectangular shape. This Ag composite sheet was attached to the front of graphite sheet by using carbon paste (CANS).

3.2. Electrochemical system

In this study, the electrochemical reaction was carried out in batch type cell which contained 20 mL of electrolyte, as shown in Figure 8. The batch cell is rectangular parallelepiped shape. In the middle of the bottom, magnetic stirring bar was existed to increase the mass transfer between electrode surface and electrolyte.

The λ-MnO_2 electrode was used as positive electrode to capture the lithium ion from salt water, and the negative electrode was silver/silver chloride. The size of both electrodes were same (3.0 cm × 3.0 cm), and distance between two electrodes was approximately 1.0 cm.
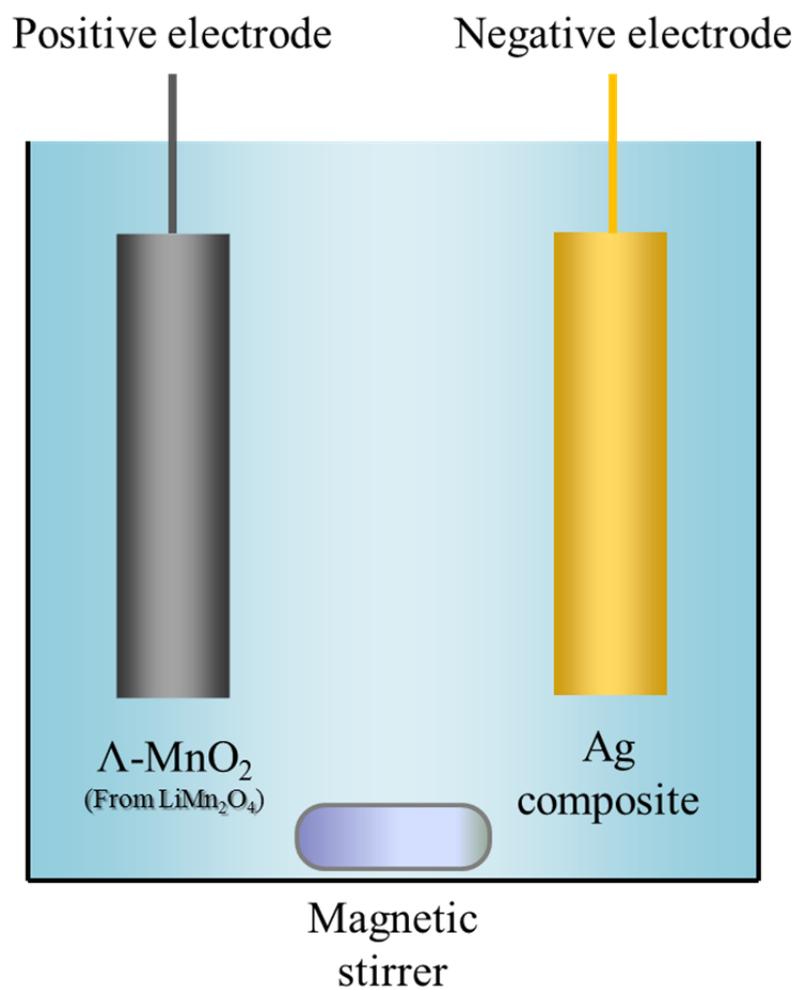
Figure 8. Schematic of the cell geometry, showing the λ-MnO$_2$ electrode and silver composite electrode.

3.3. Experimental methods

3.3.1. Ion selectivity test from various cations

Figure 9 shows the two step schematic process of lithium recovery from salt water (source water) in battery system. Salt water comprised of all the same concentration of NaCl, KCl, CaCl$_2$ and MgCl$_2$ other than LiCl (30 mM). The step 1 which describes the discharging process of the rechargeable battery generating energy intends to selectively insert lithium ion in salt water into the λ-MnO$_2$ positive electrode as chloride ion is captured by the negative electrode. The volume of source water was 20 mL.

The prepared cell was immersed in source water reservoir and discharged at a constant current of a ± 4.5 mA (0.5 mA/cm^2) current for 30 min under stirring condition. For electrochemical measurements, a battery cycler (WBCS3000, Wona tech) and a potentiostat/galvanostat (PARSTAT 2273, Princeton Applied Research) were used. The concentration of various cations was measured by ion chromatography (DX-120, DIONEX) with 0.5 mL sample solution after each step.

The energy consumption during the cycle is given by the circular integral of the cell voltage vs. charge plot (Figure 10) according to the follow equation (La Mantia *et al*., 2011; Pasta *et al*., 2012a; Pasta *et al*., 2012b,):

$$W = -\oint_C \Delta E \, dq$$

Where W is the energy (J), ΔE is the cell voltage (V), and q is the charge (C), respectively.
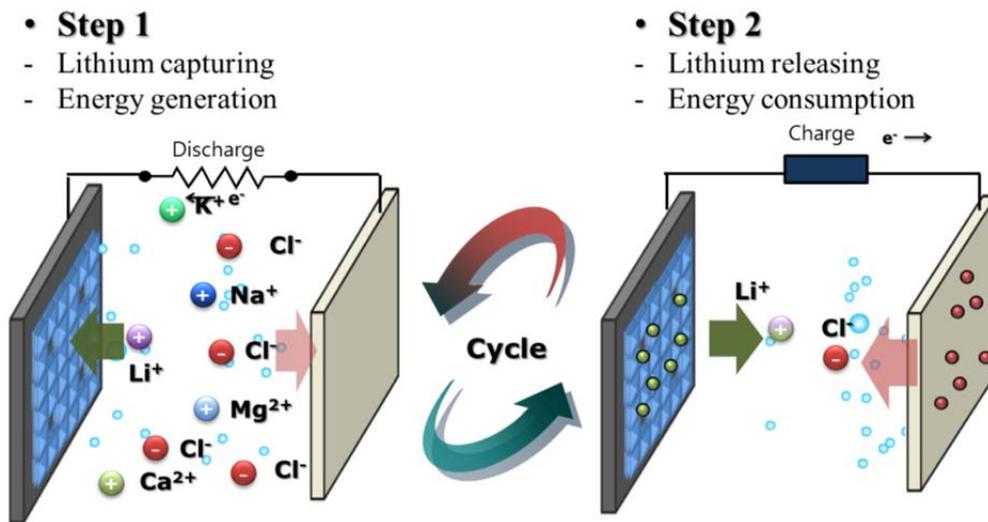
Figure 9. Schematic of the lithium ion capturing process in source water (1st step, discharging process) and lithium ion releasing process in reservoir solution (2nd step, charging process)
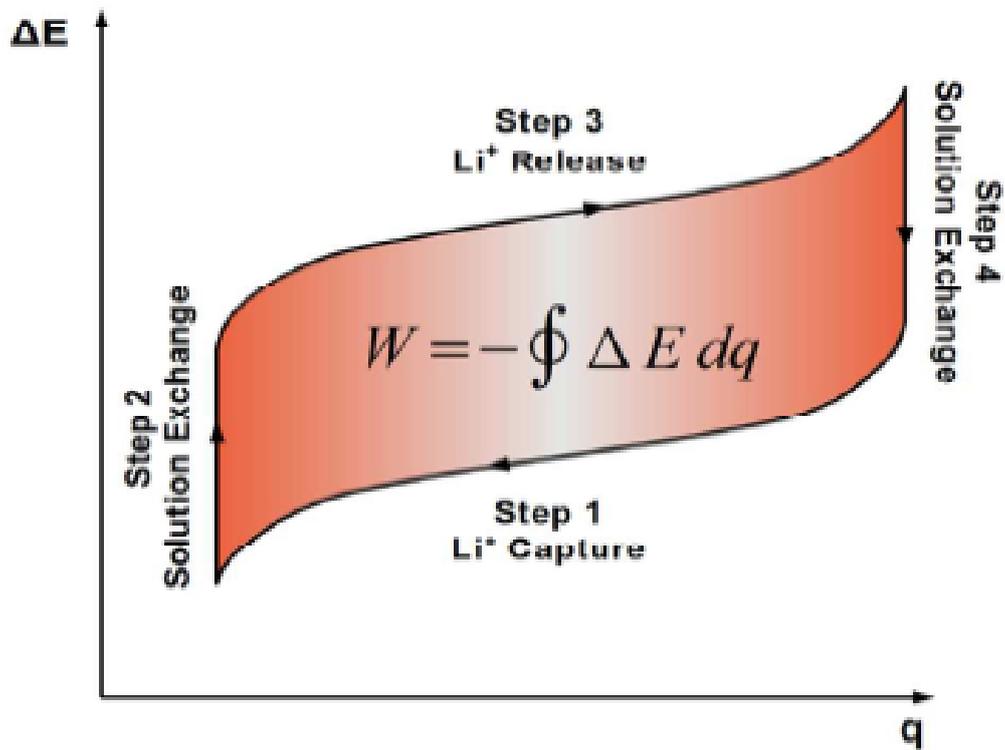
Figure 10. The energy consumption from a cycle of battery system cell potential (ΔE) vs. charge (q) (Pasta *et al.*, 2012).

3.3.2. Ion selectivity test from simulated brine water

To further demonstrate the efficacy of lithium recovery system, lithium recovery was examined with artificial salt brine which simulates brine water in lake, "Salar de Atacama" in Chile, the world's largest active source of lithium. The mineral composition of brine water is shown in Table 2, from this data, we prepared artificial salt brine. All the reagents were commercially available (Sigma Aldrich) and we mixed LiCl 0.21 M (8.9 g/L), NaCl 3.3 M (182.8 g/L), Na_2SO_4 0.172 M (24.3 g/L), KCl 0.46 M (3.43 g/L), $MgCl_2$ 0.4 M (3.81 g/L), $CaCl_2$ 0.0075 M (0.86 g/L) and H_3BO_3 0.06 M (0.371 g/L).

Figure 11 represents the lithium extraction process from the simulated brine water with 2 stage process. In the first stage, the prepared λ-MnO_2/Ag cell is immersed in the simulated brine and then discharged at a constant current to capture lithium ions. The next, the brine water is exchanged with the 1st reservoir solution (30 mM LiCl), and then the cell is charged to release ions, and this cycle is repeated four times. In the second stage, the λ-MnO_2/Ag cell is immersed in the 1st reservoir solution and carried out discharging step. Then, the 1st reservoir solution is replaced with the new recovery solution (2nd reservoir solution, 30 mM LiCl) and the cell is charged. The 2nd stage is also repeated four times.

A $\pm$ 4.5 mA (0.5 mA/cm^2) current was applied for 30 minutes under stirring

condition during discharging and charging step, and the concentration of various cations was measured by ion chromatography (DX-120, DIONEX) with 0.5 mL sample solution.

Table 2. The chemical composition of "Salar de Atacama" brine lake, Chile.

Ions	mg/L	Mole (mol/L)	Wt% [M]/[Li]	Mole ratio [M]/[Li]
Li^+	1,500	0.21	1	1
Na^+	76,000	3.3	50	15.7
K^+	18,500	0.46	12.3	2.2
Mg^{2+}	9,600	0.4	6.4	1.9
Ca^{2+}	310	0.00775	0.2	0.037
SO_4^{2-}	16,500	0.172	11	0.82
Cl^-	160,400	4.5	107	21.43
B^{3+}	640	0.0006	0.43	0.29
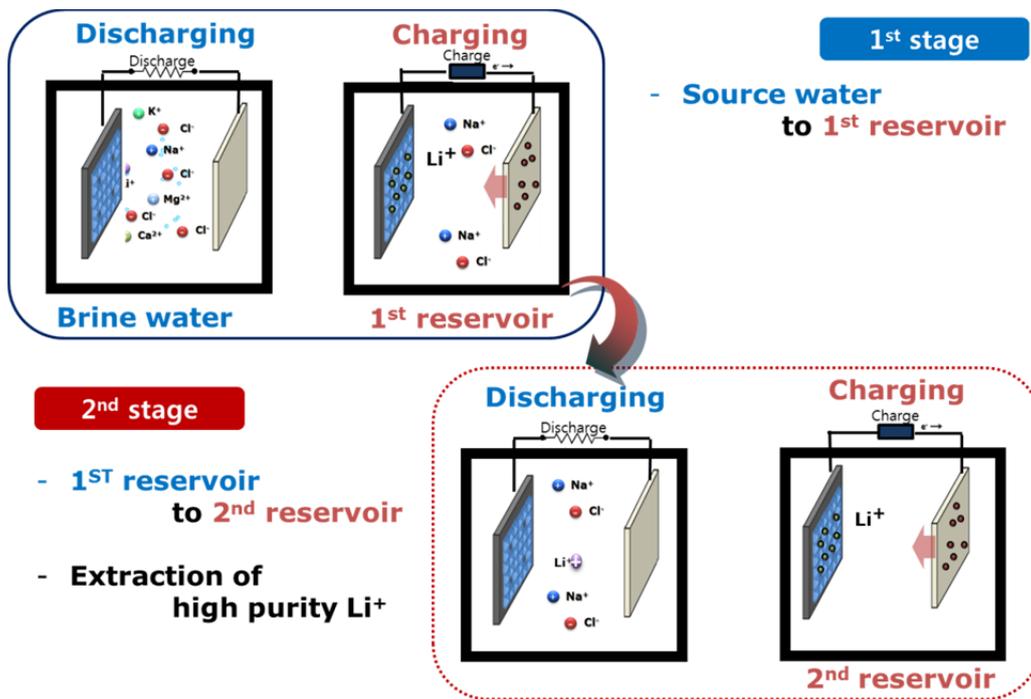
Figure 11. Schematic of lithium ion capturing process in simulated brine water.

3.3.3. Galvanostatic cycling test

For electrochemical measurements, a battery cycler (WBCS3000, Wona tech) and a potentiostat/galvanostat (PARSTAT 2273, AT Frontier) were used. Galvanostatic cycling test of λ-MnO$_2$/Ag cell was performed to examine sustainable cyclic ability of lithium recovery system at a current density of 1 mA/cm^2 over the voltage range 0 – 1.0 V in 1 M aqueous LiCl solution.

Chapter 4. Results & Discussion

4.1. Ion selectivity properties from various cations

4.1.1. Concentration changes of source and recovery solution

Figure 12 (a) & (b) displays the concentration changes of lithium ion as well as other ions in salt water in source water container and recovery solution in reservoir container, respectively after each cycle comprising of discharging and charging process up to 4 cycles (Li$^+$: ●, Na$^+$: ■, K$^+$: ♦, Mg^{2+}: ▲, Ca^{2+}:▼), respectively. Note that this salt water contains equal concentration of various cations (30 mM) such as sodium, potassium, magnesium and calcium which ions were selected from the consideration that these cations popularly exist in natural salt brine.

As shown in Figure 12 (a), the concentration of lithium ions in salt water clearly was decreased in a gradual manner as a result of lithium ions intercalation into the λ-MnO$_2$ electrodes when the cell discharged. On the other hand, other ions such as sodium, potassium, and calcium were not decreased, showing clear indication of failure of intercalation into the λ-MnO$_2$ electrodes.

Figure 12 (b) shows that the concentration of lithium ions in reservoir solution was increased linearly as the cell containing lithium intercalated λ-MnO$_2$

electrodes was charged in reservoir solution. In addition, it is interesting to observe that partially magnesium intercalated λ-MnO$_2$ electrodes did not release magnesium at all, indicating quite successful lithium recovery system not suffering from the coexisting ion of magnesium. The excellent selectively for lithium ion can be explained by the crystal ionic radii of lithium ion which is perfectly fit to the tetrahedral sites of λ-MnO$_2$ spinel structure but is small for other metal ions (Kanoh *et al*., 1991).
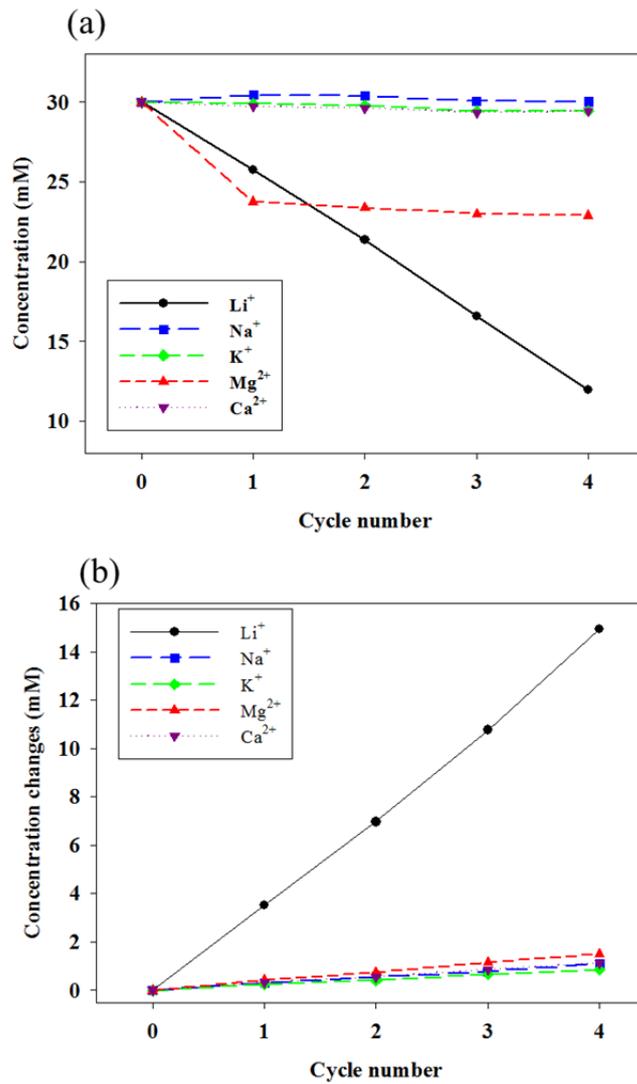
Figure 12. (a) Selective lithium ion capturing in source water (1st step, discharging process) and (b) selective lithium ion releasing in reservoir solution (2nd step, charging process) (Li$^+$: ●, Na$^+$: ■, K$^+$: ♦, Mg^{2+}: ▲, Ca^{2+}: ▼).

4.1.2. Charge/discharge potential profiles

Figure 13 (a) & (b) shows the charge/discharge potential profiles with time in λ-MnO_2/Ag cell at each cycle and their corresponding potential vs. charge plots, respectively. As the cycle is repeated, the discharging voltage is decreasing because the lithium ion concentration in salt water is diluted, according to the Nernst equation. From the potential vs. time plot in Figure 13(a), a potential profile in Figure 13 (b) can be obtained with the charge and cell potential plot, and the energy consumption can be calculated by equation (1). The energy required for one mole of lithium ion recovery from this salt water through charging/discharging cycle is 4.5 Wh, but this value can be further reduced by optimizing cell geometry using closer electrode distance.
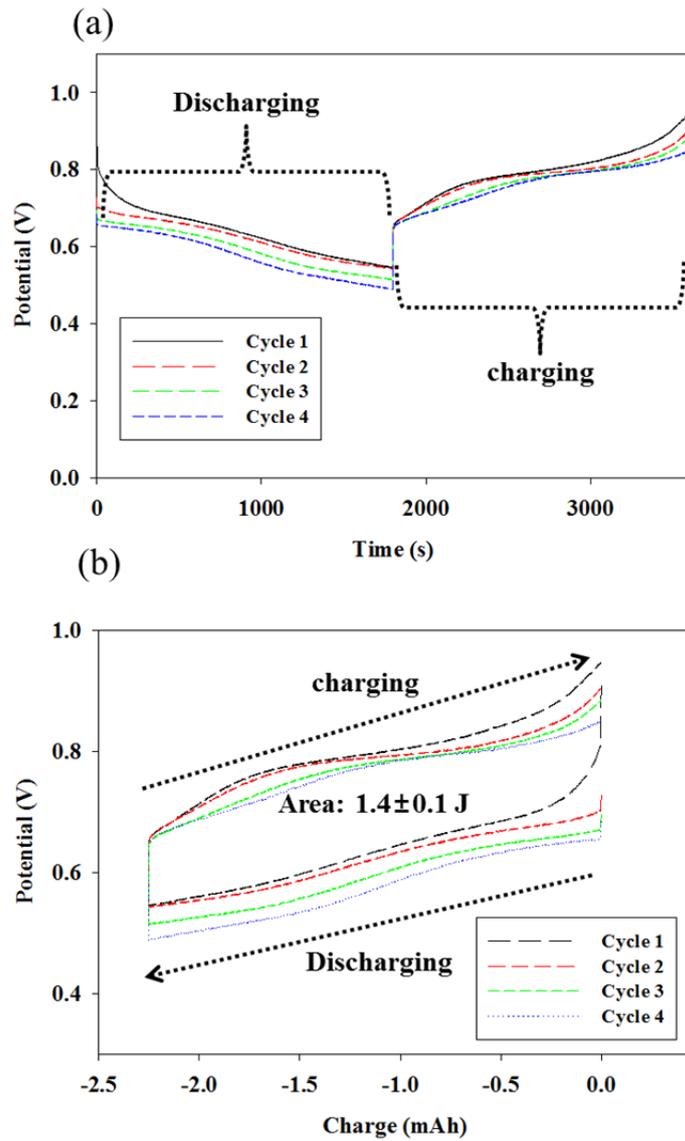
Figure 13. (a) The potential changes with time during discharging/charging process at each cycle in λ-MnO$_2$/Ag cell and (b) their corresponding total capacity with cycle number (the charge/discharge current density of 0.5 mA/cm^2).

4.2. Ion selectivity properties from brine salt

4.2.1. Concentration changes of first and second reservoirs

The lithium recovery process from brine water was examined with artificial salt brine which simulates actual brine water in lake, "Salar de Atacama" in Chile. The actual brine lake contains high concentration of various cations compared with lithium ions. For example, the molar ratio of Na^+, K^+, and Mg^{2+} over Li^+ are about 15.7, 2.2, and 1.9, respectively. To further concentrate lithium concentration, the lithium recovery procedure was done twice in a consecutive way.

In the 1st stage, the λ-MnO_2/Ag cell captured the lithium ions from source water (simulated brine water), and then the lithium ions were released to the 1st reservoir solution. The lithium ion concentration changes of 1st reservoir solution at 1st stage, as shown in Figure 14, was linearly increasing after each cycle, although the source water contained high concentration of sodium, potassium, and magnesium.

Figure 15 (a) & (b) displays the concentration changes of lithium ions and other cations of interest at 2nd stage of two consecutive charging/discharging processes. Figure 15 (a) represents the concentration changes of various cations in the 1st reservoir solution at 2nd stage (discharging step). The concentration of

lithium ions in salt water was gradually decreased as a result of lithium ions captured by the λ-MnO_2 electrodes. On the other hand, other cations were not decreased. As shown in Figure 15 (b), the concentration of lithium ion was excellently increased as a result of selective release from lithium inserted λ-MnO_2 in comparison with other coexisting cations. Especially, it is important to observe no significant release of magnesium from λ-MnO_2. This result shows that high purity of LiCl solution can be enriched by repeating the consecutive charging/discharging processes of this rechargeable battery system, even though the source solution contains a large amount of sodium, potassium, and magnesium ions.
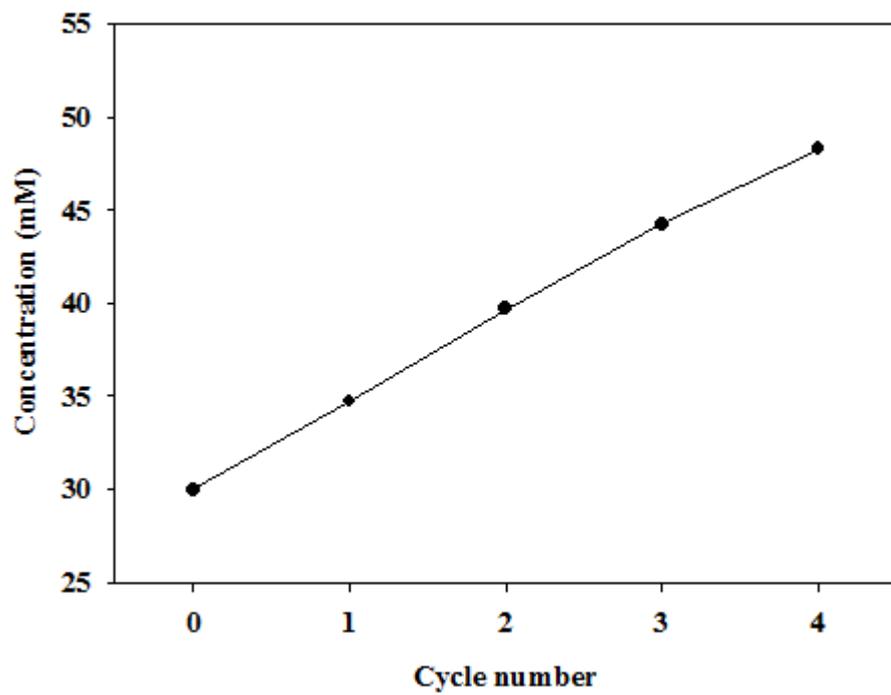
Figure 14. Lithium ion concentration changes in 1ˢᵗ reservoir solution at 1ˢᵗ stage (charging process).
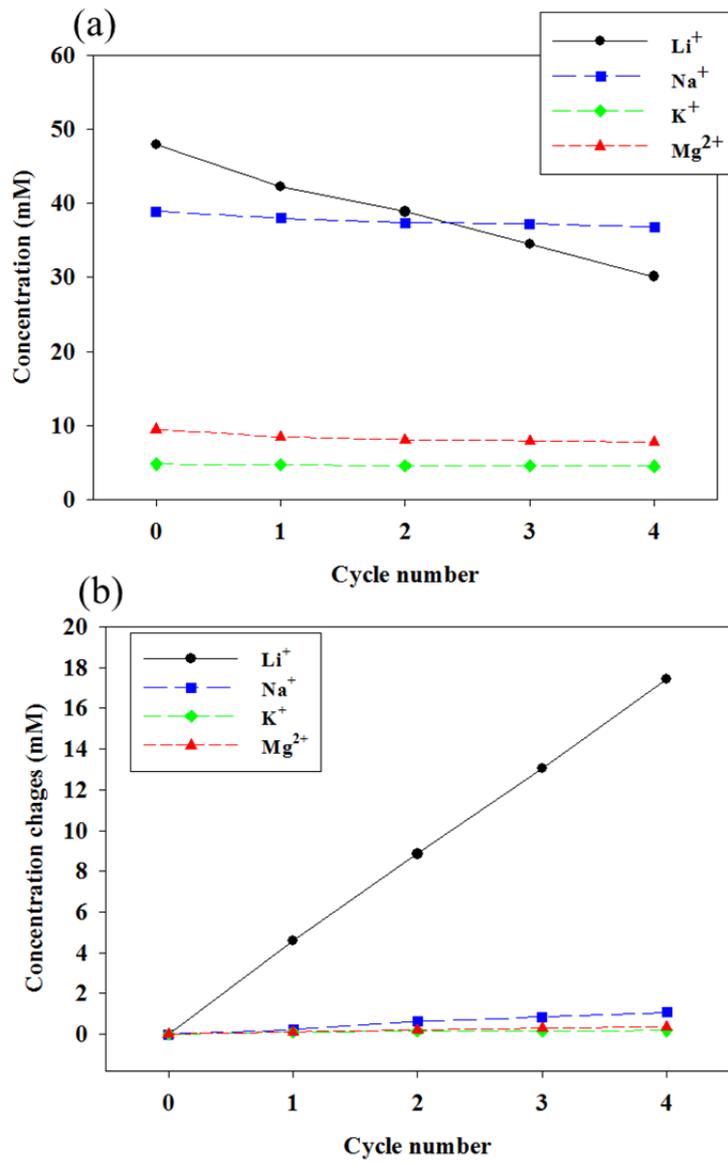
Figure 15. (a) Selective lithium ion capturing in 1st reservoir solution at 2nd stage (discharging process) and (b) The concentration changes of lithium and other cations in 2nd reservoir solution.

4.2.2. Charge/discharge potential profiles

Figure 16 (a) & (b) shows the potential vs. charge plot at each stage. In the 1st stage, the energy was generated as shown in Figure 6 (a) since the system was discharged in high concentrated solution and charged in diluted solution. This concept was demonstrated at the previous study and the system was called "mixing entropy battery" (La Mantia *et al*., 2011). From this data, 2.3 Wh was generated when 1 mole of lithium ion was recovered. Figure 6 (b) represents the potential vs. charge plot in 2nd stage, and the energy consumption was 3.3 Wh per 1 mole of lithium recovered. In conclusion, the total energy consumption is 1.0 Wh per 1 mole of lithium recovered in the whole process.
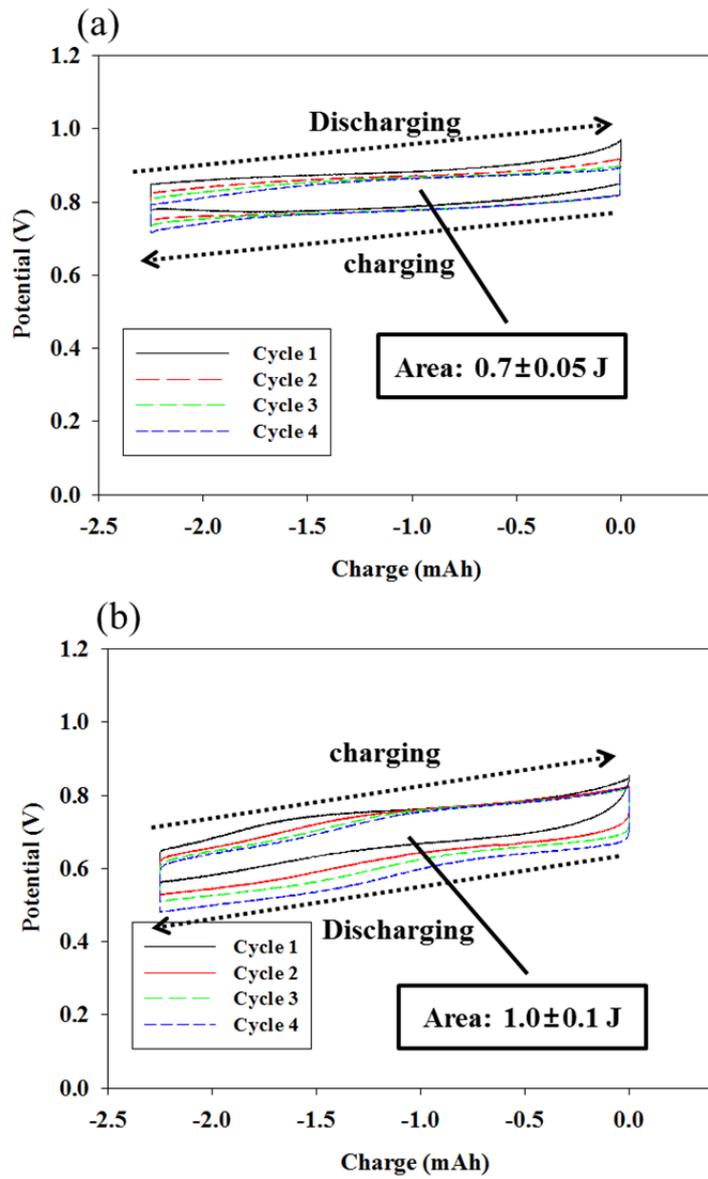
Figure 16. The battery cell voltage (V) vs. charge (Q) at each discharging/charging cycle of two consecutive process ((a) 1st stage and (b) 2nd stage, the charge/discharge current density of 0.5 mA/cm^2).

4.3. Galvanostatic cycling results

Figure 17 (a) & (b) represents the representative galvanostatic cycling performance at a current density of 1 mA/cm^2 in LiCl aqueous solution and their corresponding capacity with cycle number up to 20, respectively as the voltage range varied from zero to 1.0 V. As shown in Figure 4 (a), the voltage profile shows excellent reversibility during discharging and during the several cycles. After 20 cycles, the capacity retention is 87%, and the discharging capacity efficiency still remains 98.5%, as shown in Figure 4 (b). This result indicates that the lithium recovery system from λ-MnO$_2$/Ag cell is reversible and be used repetitively in aqueous solution. The reaction between lithium chloride and λ-MnO$_2$/Ag cell in aqueous solution according to the following equation:

$$2MnO_2 + Ag + LiCl \leftrightarrow LiMn_2O_4 + AgCl \quad (2)$$
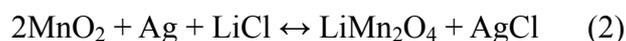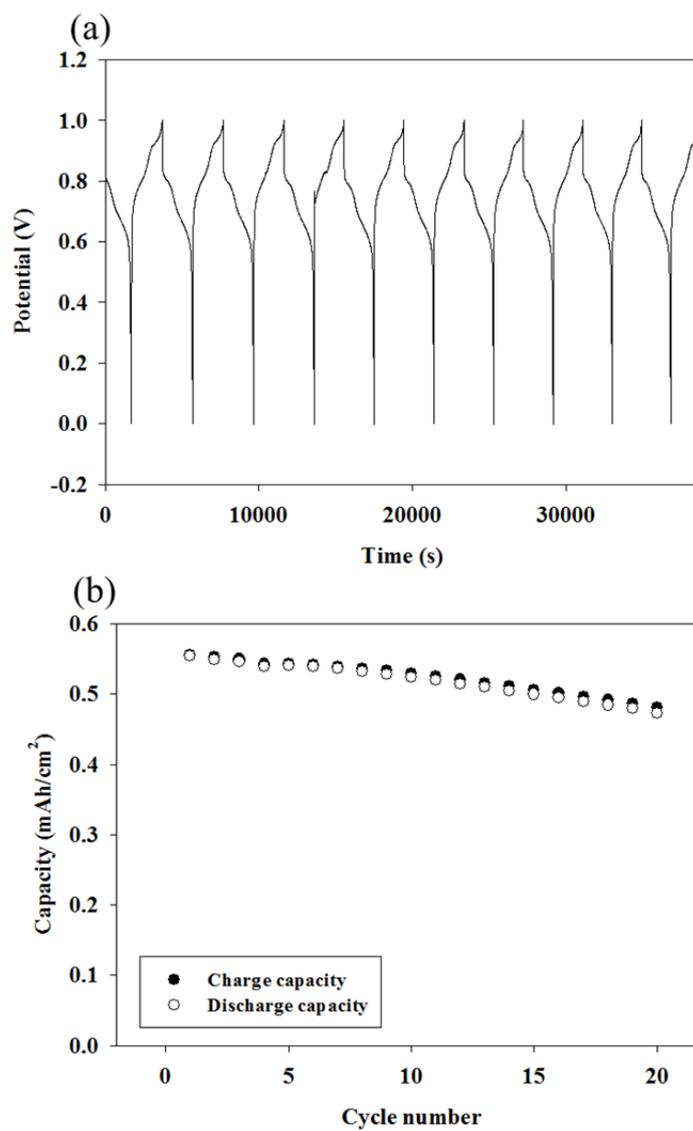
Figure 17. (a) The voltage profile during 10 cycles and (b) their corresponding areal capacity with cycle number in lithium recovery system ($LiMn_2O_4$ and Ag/AgCl system, 1 M LiCl aqueous solution, the charge/discharge current density of 1 mA/cm^2).

Chapter 5. Conclusion

A novel lithium recovery system using rechargeable battery was suggested as spinel $LiMn_2O_4$ positive electrode and silver particles negative electrode was employed. This lithium recovery system successfully demonstrated that lithium can be selectively recovered from salt water which contains various cations, especially magnesium ion, with low energy consumption. Furthermore, it was found that the system is an available lithium recovery process from brine water that the composition of chemical is similar with actual brine lake. This system also has simple construction, easy operation and stable potential in aqueous solution. Compared with conventional process to recovery lithium ion, this system does not need to add chemical compounds for removing magnesium ions, and rapidly condense lithium chloride. The $LiMn_2O_4$ electrode, which is used for positive electrode, is available materials with low cost, environmentally harmless and high charge capacity. However, the redox potential of lithium ion intercalation is close to react with water and this high potential could reduce the efficiency of λ-MnO_2/Ag system. The negative electrode for capturing chloride ions, silver has stable potential, antibacterial properties, and corrosion resistance. However, silver is a precious material and

the electronic conductivity of silver chloride is poor so the primary kinetic of the battery system is limited by silver electrode. Increasing cyclic ability and finding new materials for chloride ion capturing electrode remain as a future study in order to develop this system.

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초록

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이재한

리튬은 유리, 세라믹, 합금, 윤활유, 제약 등 여러 분야의 기술에서 다양하게 사용되고 있으며, 최근 들어 이차전지의 발달로 인해 그 수요는 급증하고 있다. 이러한 리튬의 공급원은 광물(hard mineral), 염수(brine) 또는 해수(seawater)등이며, 현재는 80%이상이 남아메리카에 있는 염호(brine lake)에서 생산되고 있다. 염호에는 리튬 이온이 어느 정도 용해되어 있으나 나트륨, 칼륨, 마그네슘, 그리고 칼슘 이온이 과량 포함되어 있다. 염수에서 리튬을 선택적으로 분리하기 위해 현재 상업적으로 사용되는 공정은 증발법으로, "lime soda evaporation process"라 불린다. 하지만 이러한 증발법은 1 년 이상의 장기간이 걸리고, 비효율적이며, 주위 환경을 파괴하게 된다. 리튬이 포함된 염호에서 더 효율적이고 친환경적으로 리튬을 선택적으로 추출할 수 있는 기술이 필요하며, 본 연구에서는 이차전지의 원리를 이용하여 다양한 이온이 용해되어있는 염수에서 리튬이온을 빠르고

효율적으로 추출하는 친환경적인 기술을 개발하고자 하였다. 리튬추출을 위한 배터리 공정 시스템으로 양극은 spinel 구조의 산화망간리튬($LiMn_2O_4$)을, 음극으로는 은/염화은(Ag/AgCl)을 사용하였으며, 같은 농도(30mM)의 리튬, 나트륨, 칼륨, 마그네슘, 그리고 칼슘이 용해되어 있는 염수에서 실험한 결과, 리튬이온에 대해 높은 선택성을 가지며 효율적이고 빠르게 리튬을 추출할 수 있었다. 나아가 실제 리튬 추출 공정에서의 적용 가능성을 살펴보기 위해, 칠레에 있는 염호의 화학적 조성이 같은 염수에 대해 리튬추출실험을 진행하였다. 이 염수에는 리튬이온에 비해 고농도의 나트륨, 칼륨 마그네슘 이온이 용해되어 있음에도(mole ratio: Na/Li ≈ 15.7, K/Li ≈ 2.2, Mg/Li ≈ 1.9) 배터리 공정을 반복함으로써 고순도의 염화리튬을 효율적으로(1 몰의 리튬 추출 당 에너지 소비: 1.0 Wh) 농축시킬 수 있었다.

주요어: 리튬 추출, 배터리 시스템, $LiMn_2O_4$, 리튬 이온 선택성

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