



공학석사 학위 논문

Electrochemical Lithium Recovery System Adopting Zinc as Negative Electrode

음극재로 아연을 도입한 전기화학적 리튬회수시스템

2017년 2월

서울대학교 대학원

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Electrochemical Lithium Recovery System Adopting Zinc as Negative Electrode

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Securing lithium resource is an emerging issue owing to widespread use of lithiumion batteries. Currently, over 80 % of lithium is produced by evaporation process from brines located in South America. This process requires a lot of time, additional purifying steps and causes environmental problems. Recently, electrochemical method based on the principle of lithium-ion battery was proposed to meet increased demand for lithium. However, in the electrochemical lithium recovery system, pricey silver is used as negative electrode and its cost is a major hindrance for proceeding to the stage of practical application. Herein, we proposed zinc as alternative material, which is low-priced and has various benefits of being used as a negative electrode. By electrochemical analysis, we demonstrated the suitability of zinc electrode for lithium recovery system in terms of stability, efficiency and the feasibility of system operation. In the zinc-employed system, zinc was reversibly oxidized and reduced

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during the lithium recovery process without side reactions and weight loss, and lithium was selectively recovered with energy consumption of 6.3 Wh per 1 mole of lithium recovery.

Keyword: lithium recovery, lithium manganese oxide, zinc, secondary battery Student number: 2015-21013

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Chapter 1. Introduction

Global lithium consumption has drastically increased because of its versatile applications such as smartphones, electric automobiles, and nuclear fusion reactors. The demand for lithium is likely to continue its upward trend for several years as the growth of electric vehicle market is predicted. Thereby, the possibility of stable supply of lithium resources has become a controversial issue and global competition for securing resources has intensified (Gruber et al., 2011; Legers, 2008; Tahil, 2007). Lithium can be obtained from brines and minerals. Of the two, lithium dissolved in brines accounts for more than 66 % of global lithium reserves and at present, most of lithium is produced (about 83 %) in brines (Tarascon, 2010). The most conventional method for lithium production is lime soda evaporation. It is a simple method which just uses solar energy to evaporate brine water. However, this method is time-consuming and strongly affected by climates such as rainfall, illuminance, and humidity. Also, it requires substantial amount of chemicals and water for purifying lithium. These points make it difficult to supply lithium steadily, and cause environmental problems.

As part of the efforts to alternate the conventional method, some research on the system which electrochemically recovers lithium in brine has reported in recent years (Hirofumi Kanoh et al. (1991); H Kanoh et al., 1993; Lee et al., 2013; Pasta et al., 2012; Rafael Trócoli et al., 2014). Kanoh et al. first proposed this system which is comprised of $\lambda - MnO_2$ and Pt, and showed the possibility of selective lithium

recovery from brines. For more efficient process, system based on the principle of lithium secondary batteries was developed. This system uses LiMn₂O₄ (LMO) or LiFePO₄ (LFP) as lithium-capturing electrode and silver as negative electrode. Lithium-capturing electrode selectively recovers lithium in a few hours, that is, lithium can be obtained consistently without any other purification process. However, the high price of silver is a major hindrance to achieving large scale system and practical application. In addition, silver is unable to be used in the solution which contains sulfate ion, because silver forms Ag₂SO₄ and dissolves in water; this system is applicable to only limited brines. Some candidate materials for replacing Ag electrode such as I^-/I_3^- redox couple, activated carbon, and nickel hexacyanoferrate (NiHCF) have proposed to overcome these drawbacks (J.-S. Kim et al., 2015; S. Kim et al., 2015; R Trócoli et al., 2015). However, there are some other problems which should be considered when using these materials. First, a I^{-}/I_{3}^{-} redox couple is inadequate to aqueous system because organic solvent is used as electrolyte. In the case of activated carbon, not only is its capacity fairly small compared to Ag electrode, but also decrease of process efficiency and pH variation could occur due to side reactions. For NiHCF, cation concentration in recovery solution should be properly adjusted all the time so that NiHCF only react with Na⁺, K⁺, not Li⁺. Also, NiHCF is unfavorable in the aspect of energy consumption because both lithium capturing/releasing step are energy-consuming process. Furthermore, the electrode potential of activated carbon and NiHCF is continuously changed during the process due to the formation of electric double layer or

intercalation of cations. This makes it difficult to set up the working potential range when applying practical process.

Herein, we propose zinc as alternative negative electrode material to complement aforementioned issues. Zinc is a low-cost, large-capacity material, and stable in aqueous solutiotn.

Chapter 2. Literature Review

2.1. Proposal of electrochemical lithium recovery

Electrochemical lithium recovery was first proposed by Kanoh et al. The system was comprised of a spinel-type manganese oxide ($\lambda - MnO_2$), which was prepared by electrochemical extraction of lithium from LiMn₂O₄ (LMO), as lithium-capturing electrode and platinum as counter electrode (Hirofumi Kanoh et al., 1991; H Kanoh et al., 1993). In the solution which contains lithium ions and other cations, when a cathodic sweep was applied to $\lambda - MnO_2$ electrode, lithium was selectively inserted into $\lambda - MnO_2$ structure, and simultaneously, oxygen evolution reaction (OER) occurs at Pt electrode with pH decrease. Reversely, during anodic sweep, lithium which was captured in cathodic sweep is released from LMO electrode with hydrogen evolution reaction (HER) at Pt electrode. They showed the possibility of recovering lithium from brines through using the high selectivity of $\lambda - MnO_2$ for lithium.

2.2. Lithium recovery methods based on the principle

of lithium secondary battery

Despite remarkable selectivity of $\lambda - MnO_2$, there is a limitation in developing electrochemical lithium recovery system to practical application due to some problems caused by using Pt electrode. First, OER at Pt during lithium-releasing result in pH increase, and it makes the lithium recovery process inefficient. Because the potential of OER decreases as pH increases, and it results in easier oxygen evolution. In high pH, OER becomes a competitive reaction of lithium extraction reaction because the potential of OER overlaps with the working potential of λ – MnO₂. Similarly, high energy consumption and pH variation originating from the potential of OER and HER impede effective lithium recovery.

To complement previous lithium recovery method, some research on the novel system which is based on the principle of lithium secondary battery was reported (Lee et al., 2013; Pasta et al., 2012; Rafael Trócoli et al., 2014). In this system, silver electrode substitutes Pt electrode and reacts with chloride ions as follows.

 $Ag + Cl^- \leftrightarrow AgCl + e^-$ (1)

Silver electrode was selected in consideration of its working potential range, as not to be overlapped with the potential of water-splitting reaction.

2.2.1 LiFePO₄/Ag system

The system composed of LiFePO₄ (LFP) as lithium-capturing electrode and Ag as negative electrode was proposed by Pasta et al.. Figure 1 represents schematic diagram of lithium recovery process. First, LFP and Ag electrodes are soaked in brine water, and negative bias is applied to LFP electrode. Lithium ions are selectively inserted into the structure of LFP, and simultaneously chloride ions are captured by Ag electrode (step 1). After that, the electrodes are moved into recovery solution (step 2) and positive bias is applied to LFP (step 3). Lithium which was captured in step 1 is released into recovery solution and chloride-releasing reaction occurs. This is one cycle of electrochemical lithium recovery and repeated by immersing LFP and Ag electrodes into brine water again (step 4). This study confirmed highly selective property of LFP for lithium ions over sodium ions and much better energy efficiency of the system compared to that of previous study. However, Pasta et al. reported that co-intercalation of Mg^{2+} into LFP hinders selective lithium recovery, thus another process to separate Mg^{2+} such as precipitation is necessary.

Contrary to their concern, Trocoli et al. confirmed the high selectivity of LFP for lithium over other cations (Mg²⁺, K⁺, Na⁺). They explain that the highly selective property is attributed to different ionic size of the cations, repulsion force, and for Mg²⁺, kinetics related to the number of nucleation points. Table 1 shows the results after lithium recovery with LFP/Ag system. K_{Li} and η_{Li} in this table are defined as follows:

 $K_{Li} = C_{Li} / \sum c_i$

where c_i is the concentration of all cations in solution, including lithium.

 $\eta_{Li} = FC_{Li} V\!/\!Q$

where F is the Faraday constant, V is the volume of the recovery cell (350 $\,\mu L),$ and

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Q the total charge flow during the first step.



Figure 1. 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., 2012).

	0.05	0.5	5	Original solution
Li [mM]	74 ± 5	99 ± 23	52 ± 4	42
K [mM]	0.002 ± 0.002	$2 0.002 \pm 0.002$	0.002 ± 0.002	108
Mg [mM]	0.002 ± 0.002	$2 0.85 \pm 0.004$	0.1 ± 0.1	74
Na [mM]	0.008 ± 0.004	$4 0.93 \pm 0.004$	17 ± 1	793
K _{Li/Na}	29000	106	3	0.053
K _{Li/K}	36000	49500	26000	0.388
K _{Li/Mg}	9000	116	520	0.567
K _{Li} [%]	99.98	97.86	74.27	4.13
η_{Li} [%]	69.4	92.9	48.8	-
E [Wh mo	I ⁻¹] 4.0	2.8	29.5	-

Table 1. Concentration of recovery solution after measurements with Atacama brinesat different currents, coefficient of lithium selectivity, purity, and energyconsumption (Rafael Trócoli et al., 2014).

2.2.2 $\lambda - MnO_2/Ag$ system

Another research for improving the selectivity for lithium over magnesium was reported in 2013 by Lee et al.. In this study, $\lambda - MnO_2$ was used as lithiumcapturing electrode and silver electrode as negative electrode. Similar to the previous study about lithium recovery system based on the principle of lithium-ion battery, when negative bias is applied to $\lambda - MnO_2$ electrode, lithium ions are selectively intercalated into the structure of $\lambda - MnO_2$, and chloride ions are captured by silver electrode, forming AgCl. This process corresponds to the discharging step of lithium secondary battery, it is spontaneous reaction, that is, electric energy is generated during lithium-capturing. Reversely, lithium-releasing occurs when the negative bias is exerted to lithium manganese oxide electrode, and AgCl electrode is reduced to Ag. It coincides with the charging step which is energy-consuming process. To examine the selective property of $\lambda - MnO_2$, 4 cycles of lithium recovery process was operated in the solution which contains equal concentrations (30 mM) of LiCl, NaCl, KCl, MgCl₂, and CaCl₂ (Figure 2). As Figure 2 illustrates, lithium was selectively recovered and extracted except for magnesium in the first discharging step. No other significant feature was found, and the phenomenon was concluded as the concentration decrease of magnesium in the first discharging step is not attributed to electrochemical insertion. In addition, the feasibility of lithium recovery was demonstrated with the experiment in the solution of which composition is similar to actual brine located in Chile. Despite of the high concentrations of other cations (Na⁺,

 K^+ , Mg^{2+}), high-purity LiCl solution was obtained with consecutive lithium recovery process by consuming 1.0 Wh of energy per one mole lithium recovery.



Figure 2. (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⁺: •, Mg²⁺: •, Ca²⁺: \checkmark) (Lee et al., 2013).

2.3 Research on alternatives to Ag in lithium recovery

With electrochemical lithium recovery method which is based on the principle of lithium secondary battery, lithium can be obtained consistently in short time, without chemical treatment, and environmentally friendly. However, the negative electrode in this system, silver, is one of the biggest obstacle to practical application due to its high cost. In addition, there are several problems with silver electrode. Operation of the system is limited in brines which contain sulfate ions, because silver forms silver sulfate and dissolves in water. Some research on finding an alternative material for substituting Ag was introduced.

2.3.1 $\lambda - MnO_2$ /activated carbon system

As an alternative material for Ag electrode, activated carbon was proposed by Kim et al.. Activated carbon is low-cost, stable material, and applicable to any solution regardless of anion species (S. Kim et al., 2015). It is widely used as supercapacitor and electric double layer capacitor (EDLC) thanks to its large surface area. Figure 3 shows the system configuration and overview. Electrodes for this system are $\lambda -$ MnO₂ and activated carbon. In discharging step, negative/positive bias is applied to $\lambda -$ MnO₂/activated carbon, respectively, so lithium ions are selectively captured in $\lambda -$ MnO₂, and anions such as chloride, sulfate ions are adsorbed to activated carbon. In charging step, positive bias is exerted to $\lambda -$ MnO₂ and negative bias is applied to activated carbon. It should be noted that an anion exchange membrane is placed

on the surface of the activated carbon electrode, so that lithium which was captured in $\lambda - MnO_2$ during discharging step is not recaptured by activated carbon. It makes anion-releasing reaction occur with negative bias, not lithium-capturing. It was confirmed that lithium is selectively recovered with low-energy consumption and the system operated with great stability. However, the capacity of activated carbon is relatively small, compared to the battery materials.



Figure 3. Schematic diagram of the lithium recovery process (S. Kim et al., 2015).

2.3.2 I^-/I_3^- redox couple as an alternative to Ag

Reversibility of I^-/I_3^- redox couple has been confirmed in Li-I batteries and dyesensitized solar cells. Kim et al. proposed I^-/I_3^- redox couple as an alternative electrode to Ag electrode, and lithium iron phosphate as lithium-capturing electrode (J.-S. Kim et al., 2015). They chose LFP thanks to its appropriate working potentials within stable windows of water at all pHs (Figure 4a). The schematic diagram of this system is represented in Figure 4d. Iodine solution of 0.5M in acetonitrile and Pt were used as electrolyte and electrode for I^-/I_3^- redox couple, respectively. Total reaction during thee lithium recovery process is given as follows:

$$3I^- + 2Li^+ + 2FePO_4 \leftrightarrow I_3^- + 2LiFePO_4$$
 (2)

Many attempts to improve the electrochemical lithium recovery such as carbon coating and polydopamine coating was done in this study (Figure 4b, c). However, I^-/I_3^- redox couple which is introduced to substitute Ag electrode still seems not that suitable for lithium recovery system because it is used in organic electrolyte which is inadequate in aqueous system, and the noble metal, Pt, is still used in the system.



Figure 4. Overall strategy for selective Li capture from the ocean. (a) Electrochemical stability window of water at different pHs and operating windows of various LIB electrode materials. (b) Surface modification of **LFePO**₄ (LFP) and **FePO**₄ (FP). Synthesized pristine LFP (left), carboncoated FP (c-FP, middle), and polydopamine (pD)-coated c-FP (pD-c-FP, right). (c) Structural preference of FP during Li or Na ion captures. Basic structures of LFP (olivine), FP (olivine), and FeNaPO₄ (maricite). (d) Cell configuration. Li ions are captured (left) or released (right) depending the polarity of the applied bias (J.-S. Kim et al., 2015).

2.3.3 LFP/Nickel hexacyanoferrate system

Nickel hexacyanoferrate (NiHCF) which is an analogue of Prussian blue is an abundant, environmentally-benign material. Recently, study on Prussian blue derivatives as positive electrode material for sodium ion battery and potassium ion battery has been introduced. Trocoli et al. proposed NiHCF as a substitute for Ag electrode in electrochemical lithium recovery. LFP was used as lithium-capturing electrode, and Figure 5 illustrates lithium recovery procedure in this system. In the first step, lithium is selectively intercalated in FePO₄ which is charged state of LFP, and simultaneously, NiHCF is oxidized as releasing cations. Overall reaction of lithium recovery is as follows:

$$Fe^{III}PO_4 + M_{1/n}KNiFe^{II}(CN)_6 + LiCl \leftrightarrow$$

$$\text{LiFe}^{\text{II}}\text{PO}_4 + \text{KNiFe}^{\text{III}}(\text{CN})_6 + 1/n\text{MCl}_n$$
 (3)

where n is the valence state of the cation in the hexacyanoferrate. In the second step, LFP/NiHCF electrodes were moved to recovery solution. In this study, brine and seawater which are abundant in lithium production sites were used as recovery solution. In the third step which is lithium-releasing process, reverse reaction of lithium-capturing step occurs; NiHCFe^{III} is reduced as capturing M^{n+} in recovery solution. Therefore, low Li⁺ affinity of NiHCF should be confirmed so that lithium which is released by LFP is not recaptured by NiHCF. By analyzing cyclic voltammetry, it turned out that NiHCF has Na⁺, K⁺ affinity rather than other cations (Li⁺, Mg²⁺, Ca²⁺). Therefore, after lithium recovery with LFP/NiHCF

system, the concentration of Li⁺ in recovery solution was increased and those of Na⁺, K⁺ were decreased. It seemed that lithium was recovered more efficiently and rationally with LFP/NiHCF system. However, in this system, the concentration of Na⁺, K⁺ in recovery solution should be properly controlled in every cycle so that lithium is not captured by NiHCF electrode. Eventually, it is hard to concentrate and purify LiCl solution. In addition, energy is consumed in both lithium capturing/releasing step because of the working potential of NiHCF overlaps with that of LFP.



Figure 5. Li exchange recovery process based on LFP and NiHCF electrodes using Atacama brine or sea water as recovery solution (R Trócoli et al., 2015).

Chapter 3. Methods

3.1 Lithium recovery system description

Figure 6 shows two steps of lithium recovery system with LMO and zinc electrode (LMO-Zn system). The reactor of this system is divided into two compartments by anion exchange membrane (AEM; ASTOM Co.). LMO electrode which is used as positive electrode is immersed in one compartment, and zinc foil as negative electrode is dipped in the other compartment which is filled with ZnCl₂ solution whose concentration is above 1.8 M. Figure 6a shows discharging step; when applying negative bias to $\lambda - MnO_2$ electrode, lithium ions in brine are selectively captured into $\lambda - MnO_2$ structure and simultaneously zinc metal is oxidized to zinc ions. These reactions occur spontaneously, that is, electrical energy is generated. The overall reaction is as follows.

$$\lambda - \mathrm{MnO}_2 + \mathrm{Li}^+ + \frac{1}{2}\mathrm{Zn}_{(s)} \leftrightarrow \mathrm{Li}\mathrm{Mn}_2\mathrm{O}_4 + \frac{1}{2}\mathrm{Zn}^{2+}$$
(4)

In charging step, LMO electrode is moved to charging solution and releasing Li⁺ the solution when negative bias is exerted to LMO electrode, therby we could obtain high-purity lithium solution, at the same time, zinc ions are reduced to zinc metal (Figure 6b). This step is energy consuming process (The reverse reaction of Equation (4)). Charge neutrality of this system is balanced by transfer of anions through AEM. As reported by Pourbaix diagram of zinc, redox reactions between Zn^{2+} and Zn^{0} are reversible when zinc is in the solution whose pH is below 6 (Delahay et al., 1951). Above pH 6, Zn^{0} is oxidized to $Zn(OH)_{2}$ which is hardly soluble in water and acts





Figure 6. Schematic diagrams of lithium recovery process in LMO-Zn system. (a) Discharging step; lithium ions are captured selectively in brine water and zinc oxidation occurs. (b) Charging step; lithium ions are released in recovery solution and zinc reduction occurs.

as insulating material. When zinc salt dissolves in aqueous solution, the solution become acidic. The higher concentration of Zn^{2+} makes the solution more acidic because, as the aquo complex of zinc becomes less hydrated, protonating power increases (Duffy & Ingram, 1978). pH variation with the concentration of $ZnCl_2$ is referred to Table 2.

Concentration of ZnCl ₂ (M)	1.0	1.5	1.8	2.0
рН	5.09	4.95	4.71	4.38

Table 2. Relationship between the concentration of $ZnCl_2$ aqueous solution and their pH.

3.2 Electrode fabrication

3.2.1 LMO electrode

The fabrication method of LMO electrode is as follows. LiMn₂O₄ (Sigma Aldrich), carbon black (Timcal), polytetrafluoroethylene (Sigma Aldrich) were mixed in weight ratio 8:1:1 with ethanol. The resulting mixture was roll-pressed to 300 μ m thickness, and dried in vacuum oven at 80 °C for 12 h to evaporate the solvent. The dried electrode was cut into 2.5 cm×4 cm, and attached to a titanium foil with carbon paste (CANS). Lithium from LMO electrode was extracted by electrochemical method to form $\lambda - MnO_2$ phase which is available to capture lithium ions in brine. In the LMO-Zn system, constant current of 0.5 mA/cm² was applied to LMO until the cell voltage reaches 1.93 V. The electrolyte on the side of LMO was 0.1 M CaCl₂.

3.2.2 Zinc electrode

Zinc foil (Alfa Aesar) was cut to the same as LMO electrode without any other fabrication process

3.2.3 Ag electrode

Ag electrode was fabricated as follows. Silver powder (Sigma Aldrich), carbon black (Timcal), polytetrafluoroethylene (Sigma Aldrich) were mixed in weight ratio 8:1:1 with ethanol. The resulting mixture was roll-pressed to 300 μ m thickness, and dried in vacuum oven at 80 °C for 12 h to evaporate the solvent. The dried electrode was cut and attached to a titanium foil with carbon paste (CANS).

3.3 Electrochemical analysis

3.3.1 Cyclic voltammetry of zinc

Cyclic voltammetry was performed by using potentiostat (PARSTAT 2273, Princeton Applied Research) in a potential range -0.8 V - -1.9 V, and scan rate of 5 mVs⁻¹. Zinc foil, Ag/AgCl electrode, and Ag/AgCl (KCl sat.) were used as working, counter, and reference electrode, respectively.

3.3.2 Lithium recovery with LMO-Zn system

Lithium recovery process was carried out galvanostatically with batter cycler (WBCS3000, WonATech, Korea) in 1.38 V – 1.93 V range. Solutions on the side of LMO electrode were 50mL of Atacama brine and 0.1 M CaCl₂ in discharging and charging step, respectively. Zinc-side solution was 1.8 M ZnCl₂, and distance between LMO and zinc was 5 cm. Ion concentrations in charging solution were measured by ion chromatography (DX-120, DIONEX).

3.3.3 Cyclability test

For the long-term stability test, $\pm 1.0 \text{ mA/cm}^2$ was applied repeatedly for 100 times to LMO-Zn two electrode system between 1.38 V and 1.93 V. The solutions on the side of LMO and zinc were Atacama brine and 3.2 M ZnCl₂. XRD patterns of zinc were obtained with Rigaku D-MAX2500.

Chapter 4. Results & Discussion

4.1 Cyclic voltammetry of zinc

Prior to performance evaluation of LMO-Zn system, we tested the characteristic of zinc electrode using cyclic voltammetry (Figure 7). CVs were performed in two different solutions to compare the redox reaction properties. One is 1.8 M ZnCl₂ aqueous solution which is used in lithium recovery process, and the other is NaCl aqueous solution of same concentrations. Red solid line in Figure 8 shows cyclic voltammogram of the zinc electrode in 1.8 M NaCl solution. In the range of -0.8 V -1.0 V electrode potential, oxidation of zinc metal to zin ions occurs. Afterwards, a cathodic peak caused by reduction of Zn^{2+} which is oxidized in -0.8 V -1.0 V was observed between -1.0 V and -1.2 V. Any other redox reaction did not happen until -1.8 V, and then in more negative potential, hydrogen evolution reaction (HER) results in exponential cathodic current. In accordance with the standard reduction potential, it is expected that HER (0 V vs. SHE) occurs prior to Zn^{2+} reduction reaction (-0.76 V vs. SHE). However, the exchange current density for HER of zinc electrode is small enough so that HER is observed in more negative potential range than Zn²⁺ reduction reaction (Beverskog & Puigdomenech, 1997). Blue dashed line is a cyclic voltammogram of zinc electrode in 1.8 M ZnCl₂ solution. From Nernst equation (Equation (5)),



Figure 7. Cyclic voltammograms (the scan rate of 5 mV s^{-1} within -0.8 V - -1.9 V) of the zinc electrode in 1.8 M NaCl aqueous solution (red solid line), and in 1.8 M ZnCl₂ aqueous solution (blue dashed line).

$$E = E^{\circ} + \frac{RT}{nF} ln \frac{\{Zn^{2+}\}}{\{Zn_{(s)}\}}$$
(5)

in 1.8 M ZnCl₂ solution, the reduction potential is positively shifted compared to that of NaCl solution, so that zinc is oxidized up to -0.955 V. In more negative potential range, cathodic current corresponding to reduction of Zn²⁺ was observed. Cathodic current is much bigger in high-concentrated Zn²⁺ solution than in NaCl solution; these results imply Zn²⁺ reduction is more preferred reaction than HER. Considering the extent of current density used in lithium recovery system (0.5 mAcm⁻² – 1.0 mAcm⁻²), zinc electrode is oxidized and reduced reversibly in the range of -0.952 V – -0.957 V without side reactions such as HER.

4.2 Lithium recovery with LMO-Zn system

The performance of LMO-Zn system was evaluated during three cycles of discharge and charging steps. Artificial brine whose chemical composition is similar to Salar de Atacama in Chile (Table. 3) was used as discharging solution. For quantative measurement of extracted Li⁺, charging step proceeded in 0.1 M CaCl₂ aqueous solution because Atacama brine hardly contains calcium so that Ca²⁺ was used as internal standard for ion chromatography. Figure 8 corresponds to concentration changes of cations in charging solution when the discharging-charging cycles was repeated three times with current density of 0.5 mAcm⁻². Li⁺, Na⁺, K⁺, Mg²⁺ are extracted up to 40.3 mM, 11.0 mM, 2.2 mM, 4.8 mM, respectively, during 3 cycles. This result is attributed to the preference of insertion into $\lambda - MnO_2$ spinel

Ions	mg/L	M (mol/L)
Li ⁺	1,500	0.21
Na ⁺	76,000	3.3
К+	18,500	0.46
Mg ²⁺	9,600	0.4
S04 ²⁻	16,500	0.172
Cl ⁻	160,400	4.5

Table 3. Chemical composition of Salar de Atacama, Chile (Tahil, 2007).



Figure 8. Selective lithium recovery in the presence of other cations, the concentration changes in recovery solution during the 3 cycles of discharging-charging (the discharge-charge current density of 0.5 mA cm^{-2}).

structure; insertion of lithium is energetically favorable than that of other ions. In consideration of high concentration of other cations in Atacama brine, especially Na⁺, selectivity with regard to Li⁺ is remarkable.

Figure 9 shows discharging-charging voltage profile of LMO-Zn system with respect to the charge which was delivered during the cycles, and from the Equation (6), energy consumption per cycle was calculated by the circular integration of the plot.

$$W = -\oint_c \Delta E dq \tag{6}$$

where W is the energy (J), ΔE is the cell voltage, and q is the charge (C).

6.3 Wh is required to recovery 1 mole of Li⁺.

Figure 10 exhibits how the lithium recovery ratio, namely selectivity, is affected when different current densities were applied in discharging-charging cycles. Lithium recovery ratio was defined as follows:

Lithium recovery ratio =
$$\frac{C_{Li^+}}{C_T}$$
 (7)

Where C_{Li^+} is Li^+ concentration in charging solution, C_T is the concentration of total cations (Li⁺, Na⁺, K⁺, Mg²⁺) which were extracted in charging solution. Lithium recovery ratio decreases as more intensive current density is applied. With higher intensity of electric field, other cations as well as Li⁺ gain enough energy to insert into LMO structure.



Figure 9. Voltage profile vs. capacity during the 3 cycles of discharging-charging (the discharge-charge current density of 0.5 mA an^{-2}). Area between charging-discharging curves shows the consumed energy.



Figure 10. Effect of current density on lithium recovery ratio (**Li**⁺ concentration over total cation concentration).

4.3 Cyclability test

To demonstrate the cyclability and stability of LMO-Zn system, 100 cycles of discharging-charging step with the current density of 1 mA/cm² was repeated in LMO-Zn cell. The electrolytes on the side of LMO and zinc electrode were Atacama brine, ZnCl₂ solution, respectively. Zinc electrode was 1675 mg, and the concentration of ZnCl₂ solution was 3.2 M in order to minimize the osmotic pressure between the compartments. Figure 11 represents capacity retention of LMO-Zn cell during the cycles. After 100 cycles, the system retained a 73 percent of its capacity. In concentrated brine, capacity decrease which is inevitable feature of the lithium-ion storage materials due to the structural stress caused by the intercalation of lithium is assumed to be intensified by the insertion of other cations which have bigger ionic radius. It could be improved by operating the system with lower current density, that is, higher lithium selectivity. Zinc electrode was repeatedly oxidized and reduced during 100 cycles and its weight was increased to 1701 mg. Tiny, bumpy particles which are products of Zn^{2+} reduction were widely formed on the zinc foil. To investigate whether reversible redox reaction between Zn²⁺and Zn⁰ occurs, the particles were scraped from zinc foil and analyzed by Xray diffraction (Figure 12). Peaks for zinc metal were clearly detected, and some peaks assumed for simonkolleite and beta-ZnOHCl which are unstable compounds in low pH were also obatined. Generally, simonkolleite and beta-ZnOHCl are obtained by cathodical reaction in high pH, because they are unstable compounds in

low pH. This result might be attribute to the dissolved oxygen in the solution, and could explain the reason of weigh increase of zinc electrode. The compounds would dissolve with simple acid treatment, as a result, zinc electrode showed great stability during long-term operation.



Figure 11. Capacity retention of LMO-Zn cell during 100 cycles of dischargingcharging (LMO in Atacama brine, zinc in 3.2 M $ZnCl_2$ aqueous solution, the discharge-charge current density of 1 mA am^{-2}).



Figure 12. X-ray Diffraction patterns of the particles which was formed on zinc foil as the result of \mathbf{Zn}^{2+} reduction (ICSD collection code : 64990, 34904, 15900 for zinc, simonkolleite, and beta-ZnOHCl, respectively).

Chapter 5. Conclusion

This study verifies the suitability of zinc, which is inexpensive and environmentallybenign material, as an alternative for negative electrode in electrochemical lithium recovery system. By storing high concentration of $ZnCl_2$ in the solitary compartment, zinc is reversibly oxidized and reduced without side reactions and electrode potential variation. When constructing the two-electrode system with $LiMn_2O_4$ as lithium-capturing electrode and zinc as negative electrode (LMO-Zn system), lithium was selectively recovered from the solution which contains high concentration of impurities with the energy consumption of 6.3 Wh per 1 mole lithium recovery. Stability of the system was examined through 100 cycles of discharging-charging, and 73 % of capacity retained without loss of zinc. Above all, LMO-Zn system is a step forward for practical application thanks to the properties of zinc; low-cost, constant electrode potential, and large capacity.

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음극재로 아연을 도입한 전기화학적

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리튬이온배터리 사용량의 증가로 인해 리튬자원 확보문제가 이슈가 되고 있다. 현재 대부분의 리튬은 남아메리카에 위치한 염수로부터 생산되고 있는데, lime soda evaporation 이라는 증발법을 이용하여 얻어진다. 하지만 이 공정은 리튬을 생산하는데 오랜 시간이 걸리고, 정제과정이 필요하며, 환경적인 문제를 유발한다. 최근 이러한 문제점들을 극복하기 위해 전기화학적으로 리튬을 회수하는 연구가 진행되었다. 하지만 이 시스템에서 음전극으로 이용되는 은 전극의 높은 가격이 실제 공정 적용에의 걸림돌이 되고 있다. 본 연구에서는 값싸고, 용량이 큰 아연을 음전극으로 사용하여 리튬회수시스템의 구동 가능성을 확인하고, 아연전극이 음전극으로 적합한지에 대한 특성분석을 진행하였다. 아연 전극을 도입한 리튬회수시스템에서 1 몰의 리튬을 회수할 때 6.3 Wh 의

에너지가 소모됨을 확인하였고, 염수에서 리튬이온이 선택적으로 회수되는 것을 확인하였다. 또한, 회수공정동안 아연전극이 손실없이 가역적인 산화환원반응을 한다는 것을 확인하였다.

주요어: 리튬회수, 리튬망간옥사이드, 아연, 이차전지 학번: 2015-21013