### LITHIUM EXTRACTION FROM BRINE WITH ION EXCHANGE RESIN AND FERRIC PHOSPHATE

by

#### HIROKI FUKUDA

B.Eng., Waseda University, Japan, 2017

### A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

#### MASTER OF APPLIED SCIENCE

in

# THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES (Materials Engineering)

#### THE UNIVERSITY OF BRITISH COLUMBIA (Vancouver)

July 2019

© Hiroki Fukuda, 2019

The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, a thesis/dissertation entitled:

Lithium extraction from brine with ion exchange resin and ferric phosphate

submitted by	Hiroki Fukuda	in partial fulfillment of the requirements
the degree of	Master of Applied Science	
in	Materials Engineering	
Examining Co	nmittee:	
David Dreising	ger, Materials Engineering	
Supervisor		
David Dixon, I	Materials Engineering	
Supervisory Co	ommittee Member	
Berend Wassir	k, Materials Engineering	
Supervisory Co	ommittee Member	
Daan Maijer (	Chair), Materials Engineering	
Additional Exa	miner	

#### Additional Supervisory Committee Members:

Supervisory Committee Member

Supervisory Committee Member

### Abstract

Lithium is an essential metal for our society. Notably, increasing energy storage system will necessitate much more lithium in the future. This study focused on brine deposit while lithium exists in hard rocks as well. Conventionally, solar evaporation has been used to concentrate lithium from brine, but it takes more than one year. Thus, a more rapid process is desired for the accelerating demand. Here, two types of adsorbent, ion exchange (IX) resin and heterosite ferric phosphate (FP), were studied in order to extract lithium selectively from brine rapidly. First, more than thirty IX resins were tested in lithium chloride solution. Out of the thirty, sulfonate, iminodiacetate and aminomethylphosphonate resins succeeded in extracting lithium with the value of 16.3–32.9 mg-Li/g. However, no resins could adsorb lithium from a mixed brine solution which contains other interfering cations like sodium. An aluminum loaded resin was also tested since some past studies had reported lithium selectivity with this material. Its adsorption density was 6.6 mg-Li/g and was higher than any other resins tested for the mixed brine in this study. Nevertheless, the overall results showed that the IX resins were not so suitable for lithium extraction from a mixed brine. Then, heterosite FP was investigated as an alternative adsorbent. The FP can adsorb lithium selectively with the addition of a reducing agent to form lithium iron phosphate. This study used thiosulfate (TS) and sulfite (SF) individually as a reducing agent. The maximum adsorption density was 45.9 mg-Li/g by SF reduction at 65 °C, which is almost the same as the theoretical value of 46.0 mg-Li/g. The maximum selectivity over sodium was 2541 by SF reduction at 45 °C. Additionally, it was confirmed that the FP could be recycled by persulfate oxidation without degradation. Finally, the kinetics was studied and fit using pseudo first-order and shrinking sphere model. The two models fit the experimental results and indicated that the lithium extraction reaction was chemical reaction controlled. Since the FP method was found to be promising, it is highly recommended that it should be developed further by using natural brine sources.

### Lay Summary

Mobile phones and electric cars always have a battery. Some kinds of battery contain lithium (Li) and are called lithium batteries. As we buy a new mobile phone with better quality and buy an electric car for an eco-friendly lifestyle, Li demand has been increasing. However, with a conventional method using solar heat, it may take more than one year to concentrate lithium from brines, which are saltwater and primary lithium sources. More rapid technologies are required to meet the rapidly increasing demand. This work investigated two extraction techniques using a solid adsorbent with experimental results for speedy lithium recovery. The extraction of lithium was demonstrated as a potential pathway to rapid lithium recovery from saltwater solution.

# Preface

This thesis is original, unpublished, independent work by the author, Hiroki Fukuda.

# **Table of Contents**

Abstract	iii
Lay Summa	aryv
Preface	vi
Table of Co	ntents vii
List of Tabl	es xi
List of Figu	res xiii
Nomenclatu	ıre xxi
Acknowled	gements xxiv
Chapter 1.	Introduction1
Chapter 2.	Literature Review2
2.1. Litl	nium Chemistry
2.1.1.	Electrochemical Properties of Lithium
2.1.2.	Lithium Ion Battery
2.1.3.	Eh-pH Diagram
2.2. Lith	nium Market
2.2.1.	Supply/Demand and Price
2.2.2.	Products and Applications 10
2.3. Lith	nium Deposits
2.3.1.	Overview13
2.3.2.	Ore Deposits
2.3.3.	Brine Deposits

2.4. Pro	ocesses for Lithium Production	19
2.4.1.	Overview	19
2.4.2.	Process of Ore Deposits	20
2.4.3.	Process of Brine Deposits	21
2.4.4.	Process for Lithium Hydroxide Production	31
2.5. Lit	hium Extraction Technologies	33
2.5.1.	Overview	33
2.5.2.	Phosphate Precipitation	35
2.5.3.	Ion Exchange Resin	36
2.5.4.	Al/Mn/Ti-based Adsorbent	42
2.5.5.	Solvent Extraction	43
2.5.6.	Membrane Technologies	44
2.5.7.	Ferric Phosphate Reduction	45
2.6. Su	mmary and Objectives	56
Chapter 3.	Experimental Methods	59
3.1. Pre	eparation	59
3.1.1.	Materials	59
3.1.2.	Apparatus	63
3.2. Pro	ocedures for Lithium Extraction with Ion Exchange Resin	64
3.2.1.	Preparation of Ion Exchange Resin	64
3.2.2.	Lithium Loading Test	67
3.2.3.	Lithium Stripping Test	68
3.3. Pro	ocedures for Lithium Extraction with Ferric Phosphate	69
3.3.1.	Preparation of Ferric Phosphate	69

3.3.2.	Lithium Loading Test	
3.3.3.	Lithium Stripping Test	71
3.3.4.	Acid Digestion	71
3.4. An	alysis Procedures	
3.4.1.	Atomic Absorption Spectroscopy (AAS)	72
3.4.2.	Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).	72
3.4.3.	X-ray Diffraction (XRD)	73
Chapter 4.	Lithium Extraction with Ion Exchange Resins	74
4.1. Lit	hium Recovery from LiCl Solution	74
4.2. Lit	nium Recovery from Brine	76
4.3. Su	nmary	
Chapter 5.	Lithium Extraction with Ferric Phosphate	80
5.1. Pre	paration of Ferric Phosphate	80
5.1.1.	Ferric Phosphate Dihydrate	80
5.1.2.	Lithium Iron Phosphate (Reagent Grade)	81
5.1.3.	Lithium Iron Phosphate (Battery Grade)	
5.2. Sel	ection of Reducing Agents	
5.3. Pro	ducts after Lithium Loading	85
5.3.1.	Thiosulfate Reduction	85
5.3.2.		
010121	Sulfite Reduction	89
5.4. Caj	Sulfite Reduction	89 93
5.4. Caj 5.4.1.	Sulfite Reduction pacity and Selectivity Thiosulfate Reduction	
5.4. Caj 5.4.1. 5.4.2.	Sulfite Reduction pacity and Selectivity Thiosulfate Reduction Sulfite Reduction	

5.6. Rec	cycling of Ferric Phosphate	
5.7. Kir	netics	
5.7.1.	Kinetic Models	
5.7.2.	Thiosulfate Reduction	126
5.7.3.	Sulfite Reduction	131
5.8. Su	mmary	
Chapter 6.	Conclusion	
References		

# List of Tables

Table 2.1 Properties of possible anode materials. <sup>35</sup>	2
Table 2.2 Amount of lithium used in various devices. <sup>35</sup>	11
Table 2.3 Lithium compounds and applications. <sup>35</sup>	11
Table 2.4 Lithium mining sites and resources in tonnes (ores).40	15
Table 2.5 Lithium mining sites and resources in tonnes (brines).40	16
Table 2.6 Lithium minerals. <sup>40</sup>	17
Table 2.7 Analytical values of continental brines. <sup>40</sup>	
Table 2.8 Solubility of chloride salts at 25 °C.44	
Table 2.9 Solubility of hydroxide salts at 25 °C.44	
Table 2.10 Solubility of carbonate salts at 25 °C.44	
Table 2.11 Technologies for lithium extraction from brine and their mechanism	
Table 2.12 Solubility of phosphate salts at 25 °C.44	
Table 2.13 List of functional groups of IX resin studied in this thesis.	
Table 3.1 List of resins tested in this study.	61
Table 3.2 Actual density and swelling ratio of resins.	
Table 3.3 Metal ion concentration in synthetic LiCl solution and brine	67
Table 3.4 Metal ion concentration in eight synthetic solutions.	
Table 3.5 Wavelength for the measured elements.	
Table 5.1 Molarity, molality and mean ionic activity of chloride salts and water a	activity in B1
solution at 25 °C, calculated by Meissner's method <sup>71</sup>	
Table 5.2 k value and activation energy calculated from kinetics in the case of	of thiosulfate

reduction.	
Table 5.3 k value and activation energy calculated from kinetics in t	he case of sulfite
reduction.	

# **List of Figures**

Figure 2.1 Schematic illustration of charge-discharge in lithium ion batteries, Me= Co,	Fe+P,
Mn, Ni+Mn+Co, Ni+Co+Al, Ti, S, etc. <sup>2</sup>	3
Figure 2.2 pH-Eh diagram for Li-H <sub>2</sub> O system at 25 °C, 1 atm, (a) [Li]=1 M or (b) [Li]=	=0.072
M (Drawn by HSC)	5
Figure 2.3 pH-Eh diagram for Li-C-H <sub>2</sub> O system at 25 °C, 1 atm and (a) [Li]=[C]=1 M	or (b)
[Li]=[C]=0.072 M (Drawn by HSC).	7
Figure 2.4 Lithium supply/demand and price and their estimates. <sup>38</sup>	8
Figure 2.5 Annual use of lithium in tonnes in each of the primary lithium usage indu	ıstries
from 2002 to 2020. <sup>39</sup>	10
Figure 2.6 Lithium value chain. <sup>35</sup>	12
Figure 2.7 (a) Resources and (b) Reserves in terms of deposit types in thousands	metric
tonnes Li metal equivalent. <sup>2</sup>	13
Figure 2.8 (a) Resources and (b) Reserves in terms of countries in thousands metric t	tonnes
Li metal equivalent. <sup>3</sup>	14
Figure 2.9 An example of flow chart of Li <sub>2</sub> CO <sub>3</sub> production from ores. <sup>41</sup>	20
Figure 2.10 A simplified flow chart of Li <sub>2</sub> CO <sub>3</sub> production from ores. <sup>42</sup>	21
Figure 2.11 A schematic illustration of lithium production from brines. <sup>43</sup>	22
Figure 2.12 A representative flow of lithium carbonate production from brines. <sup>40</sup>	22
Figure 2.13 Process flow of Salar de Atacama, Chile. <sup>42</sup>	25
Figure 2.14 Process flow of Salar de Hombre Muerto, Argentina. <sup>42</sup>	26
Figure 2.15 Process flow of Salar de Oraroz, Argentina. <sup>42</sup>	27

Figure 2.16 Process flowsheet for lithium recovery in China & Tibet. <sup>42</sup>
Figure 2.17 Process flow of CITIC method. <sup>42</sup>
Figure 2.18 Process flow of POSCO method. <sup>42</sup>
Figure 2.19 Process flow of Bateman method. <sup>42</sup>
Figure 2.20 Chemical structure of SDB copolymer
Figure 2.21 Chemical structure of resin with (a) sulfonate, (b) quaternary ammonium 38
Figure 2.22 A flow sheet of lithium production using solvent extraction by Tenova. <sup>9</sup>
Figure 2.23 Schematic illustrations of heterosite FP structure: (a) oblique view, (b) view along
the c-axis (Drawn by VESTA)
Figure 2.24 Schematic illustrations of triphylite structure: (a) oblique view, (b) view along
the c-axis (Drawn by VESTA)
Figure 2.25 pH-Eh diagram for TS-H <sub>2</sub> O system at 25 °C, 1 atm, [S]=1 M (Drawn by HSC).
Sulfate species (SO4 <sup>2-</sup> and HSO4 <sup>-</sup> ) were excluded in this diagram
Figure 2.26 pH-Eh diagram for PS-H <sub>2</sub> O system at 25 °C, 1 atm, [S]=1 M (Drawn by HSC).
Figure 2.27 pH-Eh diagram for I-H <sub>2</sub> O system at 25 °C, 1 atm, [I]=1 M (Drawn by HSC) 53
Figure 2.28 pH-Eh diagram for SF-H <sub>2</sub> O system at 25 °C, 1 atm, [S]=1 M (Drawn by HSC).
Figure 4.1 Lithium adsorption density of resins in LiCl solution in mg-Li/g-dry resin 75
Figure 4.2 Correlation between results of loading and stripping tests in the case of lithium
chloride solution (A1 solution)
Figure 4.3 Lithium adsorption of resins in brine in mg-Li/g-dry resin. No Data = No
experiment was conducted with brine because of its low capacity in pure LiCl solution77
Figure 4.4 Correlation between results of loading and stripping tests in the case of brine

solution (A2 solution)
Figure 4.5 Lithium adsorption density of the resins which showed higher selectivity in LiCl
solution
Figure 5.1 XRD patterns of ferric phosphate dihydrate calcined at 300, 500 and 600 °C 80
Figure 5.2 XRD patterns of ferric phosphate obtained by calcination of ferric phosphate
dihydrate at 600 °C and samples after lithium loading tests at 20 °C and 65 °C
Figure 5.3 XRD patterns of reagent-grade LFP and delithiated and lithiated ones at 65 $^{ m oC}$ in
comparison with calcined FPD
Figure 5.4 XRD patterns of battery-grade (BG) LFP and delithiated FP by PS oxidation. 83
Figure 5.5 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS
oxidation), and products after loading experiments by cuprous (Cu <sup>+</sup> ) at room temperature
(RoC), by cuprous (Cu <sup>+</sup> ) at 65 °C (65C), by thiosulfate (TS) at 65 °C (65C), by sulfite (SF) at
room temperature (RoC) and by sulfite (SF) at 65 °C (65C). All the loading experiments used
<b>B1 brine solution.</b>
B1 brine solution
B1 brine solution
B1 brine solution.84Figure 5.6 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 25 °C. The loadingexperiments used B1–B8 brine solution.86
B1 brine solution.84Figure 5.6 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 25 °C. The loadingexperiments used B1–B8 brine solution.86Figure 5.7 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS
B1 brine solution.84Figure 5.6 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 25 °C. The loadingexperiments used B1–B8 brine solution.86Figure 5.7 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 45 °C. The loading
B1 brine solution.84Figure 5.6 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 25 °C. The loadingexperiments used B1–B8 brine solution.86Figure 5.7 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 45 °C. The loadingexperiments used B1–B8 brine solution.87
B1 brine solution.84Figure 5.6 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 25 °C. The loadingexperiments used B1–B8 brine solution.86Figure 5.7 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 45 °C. The loadingexperiments used B1–B8 brine solution.87Figure 5.8 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS
B1 brine solution.84Figure 5.6 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 25 °C. The loadingexperiments used B1–B8 brine solution.86Figure 5.7 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 45 °C. The loadingexperiments used B1–B8 brine solution.87Figure 5.8 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 65 °C. The loadingoxidation), and products after loading experiments by thiosulfate (TS) at 65 °C. The loading
B1 brine solution.84Figure 5.6 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 25 °C. The loadingexperiments used B1–B8 brine solution.86Figure 5.7 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 45 °C. The loadingexperiments used B1–B8 brine solution.87Figure 5.8 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 65 °C. The loadingexperiments used B1–B8 brine solution.87Figure 5.8 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PSoxidation), and products after loading experiments by thiosulfate (TS) at 65 °C. The loadingexperiments used B1–B8 brine solution.88

oxidation), and products after loading experiments by sulfite (SF) at 25 °C. The loading
experiments used B1–B8 brine solution
Figure 5.10 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS
oxidation), and products after loading experiments by sulfite (SF) at 45 °C. The loading
experiments used B1–B8 brine solution
Figure 5.11 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS
oxidation), and products after loading experiments by sulfite (SF) at 65 °C. The loading
experiments used B1–B8 brine solution
Figure 5.12 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading
experiments by thiosulfate (TS) at 25 °C (B1–B8 brine solution)
Figure 5.13 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by thiosulfate
(TS) at 25 °C (B1–B3 brine solution)
Figure 5.14 Weight percentage of iron phosphate in solid after loading experiments by
thiosulfate (TS) at 25 °C (B1–B3 brine solution)
Figure 5.15 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading
experiments by thiosulfate (TS) at 45 °C (B1–B8 brine solution)
Figure 5.16 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by thiosulfate
(TS) at 45 °C (B1–B3 brine solution)
Figure 5.17 Weight percentage of iron phosphate in solid after loading experiments by
thiosulfate (TS) at 45 °C (B1–B3 brine solution)
Figure 5.18 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading
experiments by thiosulfate (TS) at 65 °C (B1–B8 brine solution)
Figure 5.19 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by thiosulfate
(TS) at 65 °C (B1–B3 brine solution)

Figure 5.20 Weight percentage of iron phosphate in solid after loading experiments by
thiosulfate (TS) at 65 °C (B1–B3 brine solution)
Figure 5.21 Adsorption density vs. temperature in the case of thiosulfate (TS) reduction (B1–
<b>B4 brine solution). The theoretical maximum of the adsorption density is 46.0 mg/g.</b> 104
Figure 5.22 Weight percentage of lithium iron phosphate in solid vs. temperature in the case
of thiosulfate (TS) reduction (B1–B4 brine solution)105
Figure 5.23 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading
experiments by sulfite (SF) at 25 °C (B2–B7 brine solution)
Figure 5.24 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by sulfite
(SF) at 25 °C (B2 and B3 brine solution)
Figure 5.25 Weight percentage of iron phosphate in solid after loading experiments by sulfite
(SF) at 25 °C (B2 and B3 brine solution)
Figure 5.26 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading
experiments by sulfite (SF) at 45 °C (B2–B7 brine solution)
Figure 5.27 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by sulfite
(SF) at 45 °C (B2 and B3 brine solution)
Figure 5.28 Weight percentage of iron phosphate in solid after loading experiments by sulfite
(SF) at 45 °C (B2 and B3 brine solution)
Figure 5.29 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading
experiments by sulfite (SF) at 65 °C (B2–B7 brine solution)112
Figure 5.30 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by sulfite
(SF) at 65 °C (B2 and B3 brine solution)
Figure 5.31 Weight percentage of iron phosphate in solid after loading experiments by sulfite
(SF) at 65 °C (B2 and B3 brine solution)

Figure 5.32 Adsorption density vs. temperature in the case of sulfite (SF) reduction (B2–B4
brine solution). The theoretical maximum of the adsorption density is 46.0 mg/g115
Figure 5.33 Weight percentage of lithium iron phosphate in solid vs. temperature in the case
of sulfite (SF) reduction (B2–B4 brine solution)116
Figure 5.34 Iron (Fe) dissolution and final pH in the case of thiosulfate (TS) reduction (B1–
<b>B8 brine solution).</b> 117
Figure 5.35 Iron (Fe) dissolution and final pH in the case of sulfite (SF) reduction (B1–B8
brine solution)119
Figure 5.36 Adsorption density and iron (Fe) dissolution at pH 4 (uncontrolled) and 7
(controlled with sodium hydroxide) in the case of thiosulfate (TS) reduction (B1 brine
solution)
Figure 5.37 Schematic flowsheet of the ferric phosphate method. Flow of FP and LFP solid
is in orange and flow of brine solution is in blue. FP and LFP are recycled by a continuous
loading and stripping cycle
Figure 5.38 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS
oxidation), and products after two cycles of loading and stripping experiments. The loading
experiments used B1 brine solution at pH 7 controlled by sodium hydroxide and lithium was
loaded by thiosulfate (TS) at 65 °C. The stripping experiments used persulfate to oxidize the
loaded materials
Figure 5.39 Concentration of metal ions in the initial brine solution (B1 brine solution) and
solution after stripping in the first and second cycle of the loading and stripping experiments.
The loading experiments used B1 brine solution at pH 7 controlled by sodium hydroxide and
lithium was loaded by thiosulfate (TS) at 65 °C. The stripping experiments used persulfate
in the second of

In addition to the metal concentration of the stripped ones in the graph, potassium from
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> was also in the solution. 123
Figure 5.40 x in Li <sub>x</sub> FePO <sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of thiosulfate (TS)
reduction (B2 brine solution)
Figure 5.41 Calculation of Pseudo first-order model: "In (1-α) vs. time at 25 °C, 45 °C and
65 °C" and "In k vs1000/RT" in the case of thiosulfate (TS) reduction (B2 brine solution).
α: fraction of reacted, k: reaction rate constant, R: gas constant, T: absolute temperature.
Figure 5.42 Calculation of shrinking sphere model: "1-(1- $\alpha$ ) <sup>1/3</sup> vs. time at 25 °C, 45 °C and
65 °C" and "In k vs1000/RT" in the case of thiosulfate (TS) reduction (B2 brine solution).
a: fraction of reacted, k: reaction rate constant, R: gas constant, T: absolute temperature.
Figure 5.43 Comparison of experimental data and calculated values by Pseudo first-order
model. x in Li <sub>x</sub> FePO <sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of thiosulfate (TS)
reduction (B2 brine solution)
Figure 5.44 Comparison of experimental data and calculated values by shrinking sphere
model. x in Li <sub>x</sub> FePO <sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of thiosulfate (TS)
reduction (B2 brine solution)
Figure 5.45 x in Li <sub>x</sub> FePO <sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of sulfite (SF)
reduction (B2 brine solution)
Figure 5.46 Calculation of Pseudo first-order model: "ln (1-α) vs. time at 25 °C, 45 °C and
65 °C" and "ln k vs1000/RT" in the case of sulfite (SF) reduction (B2 brine solution). $\alpha$ :
fraction of reacted, k: reaction rate constant, R: gas constant, T: absolute temperature. 132
Figure 5.47 Calculation of shrinking sphere model: "1-(1- $\alpha$ ) <sup>1/3</sup> vs. time at 25 °C, 45 °C and

65 °C" and "ln k vs1000/RT" in the case of sulfite (SF) reduction (B2 brine solution). $\alpha$ :
fraction of reacted, k: reaction rate constant, R: gas constant, T: absolute temperature. 133
Figure 5.48 Comparison of experimental data and calculated values by Pseudo first-order
model. x in Li <sub>x</sub> FePO <sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of sulfite (SF) reduction
(B2 brine solution)
Figure 5.49 Comparison of experimental data and calculated values by shrinking sphere
model. x in Li <sub>x</sub> FePO <sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of sulfite (SF) reduction
(B2 brine solution)

# Nomenclature

AAS	Atomic adsorption spectroscopy
ADB	Acrylic-divinylbenzene
AEM	Anion exchange membrane
Ah	Ampere hour
BG	Battery grade
Ce	Equilibrium concentration in solution
Co	Initial concentration in solution
C <sub>R</sub>	Resin concentration in solution
da	Actual denisty
DI	Deionized
dry R	Dry resin
DVB	Divinylbenzene
Е	Electrode potential
E°	Standard electrode potential
ESS	Energy storage system
EV	Electric vehicle
FP	Ferric phosphate
FPD	Ferric phosphate dihydrate
HSC	HSC Chemistry 6.0
ICP-OES	Inductively coupled plasma - optical emission spectroscopy
IX	Ion exchange

K <sub>Li</sub>	Selectivety of lithium to a metal
KLi, solid	Molar ratio of lithium to a metal in solid
KLi, solution	Molar ratio of lithium to a metal in solution
kWh	kilowatt hour
LCE	Lithium carbonate equivalent
LFP	Lithium ferrous (iron) phosphate
LIB	Lithium ion battery
mAh	Milli ampere hour
MFP	Weight of ferric phosphate
MM	Weight of an element in solid
NF	Nanofiltration
ppm	Parts per million
PS	Persulfate
qe	Adsorption density on resin
Qe	Adsorption density on ferric phosphate
Rpm	Revolutions per minute
r <sub>s</sub>	Swelling ratio
SAC	Strong acid cation
SDB	Styrene-divinylbenzene
SF	Sulfite
SFP	Sodium ferrous (iron) phosphate
SHE	Standard hydrogen electrode
SX	Solvent extraction
TS	Thiosulfate

V	Volt
VESTA	Visualization for Electronic and STructual Analysis 3 <sup>1</sup>
wet R	wet resin
XRD	X-ray diffraction
ΔΕ	Electrode potential difference
$\Delta E^{\circ}$	Standard electrode potential difference

### Acknowledgements

I would like to express my special thanks to my supervisor, Dr. David Dreisinger, for his kind guidance and support throughout the Master's program. All of his words lead me to learn a lot about hydrometallurgy and how to do meaningful research works.

I would also like to sincerely thank Dr. Berend Wassink for his kind assistance in my lab work. He always helped me with preparing chemical reagents and experimental equipment and keeping lab work safe. I also thank Jacob Kabel, Eunike Heli for their support of XRD analysis and Kresimir Ljubetic for his support of ICP analysis. This study couldn't be completed without material support from Dow, Purolite, Lanxess, Mitsubishi, Samyang and software support by HSC and VESTA. I would also like to express my gratitude to these groups. I really appreciated the warm support from my group members: Dr. Jianming Lu, Brighty Dutta, Chih Wei Chao, Chulho Song, Eunso Shin, Fei Wang, Jackie Zhou, Junichi Ito, Mariam Melashvili, Maryam Mohammadi, Maryam Rasouli, Roselyn Yeboah. My research life was fruitful and enjoyable. This thesis was supported by my thesis committee of Dr. David Dixon, Dr. Berend Wassink, and Dr. David Dreisinger and the chairperson Dr. Daan Maijer. I would like to thank the committee for their kind review.

Finally, I would like to express my special thanks to my family and friends in Canada and Japan. Thanks to all the support from you, I was able to complete the Master's program.

### **Chapter 1. Introduction**

Lithium is one of the critical metals in today's world, and the demand for lithium is now sharply increasing due to the accelerating use of energy storage systems containing lithium ion batteries. While lithium is obtained from mineral ores or brines, lithium from brines is now getting more attention since brines are known to have more reserves than ores.<sup>2</sup> Brines containing lithium exist mainly in the "lithium triangle" of Argentina, Bolivia and Chile in South America.<sup>3,4</sup> There are also a lot of medium size or small size of brines deposits around the world including oilfield brines and geothermal brines. Since brines which contains a higher concentration of lithium have been preferentially mined in the past decades, conventional solar evaporation processes, which require vast areas and an enormous amount of time, have been utilized as a major method to concentrate and recover lithium. However, new processes now need to be developed in order to meet the accelerating demand by mining brines with a lower concentration of lithium. To recover lithium efficiently from low concentration resources, new processes should be more rapid, lithiumselective, and small-scale than the solar evaporation process. Therefore, some researchers have proposed new rapid processes such as ion exchange resin<sup>5-8</sup>, solvent extraction<sup>9,10</sup>, inorganic absorbent such as aluminum oxide<sup>11-16</sup>, manganese oxide<sup>17-20</sup>, titanium oxide<sup>21,22</sup> and ferric phosphate<sup>23-25</sup>, phosphate precipitation<sup>26,27</sup>, nanofiltration<sup>28-30</sup>, membrane electrolysis<sup>31-34</sup>. Some of them are now used commercially or under a pilot test. However, there is no established process other than solar evaporation. This thesis focused on two processes out of the available options: ion exchange resin and ferric phosphate adsorption.

## **Chapter 2.** Literature Review

### 2.1. Lithium Chemistry

### 2.1.1. Electrochemical Properties of Lithium

Lithium is one of the alkali metals with an atomic number of 3 and an atomic weight of 6.941. It is reactive as with the other alkali metals and is generally dealt with in the form of salts or compounds such as lithium carbonate  $Li_2CO_3$ . From the electrochemical point of view, lithium has the lowest oxidation-reduction potential with the standard electrode potential of -3.05 V as shown in Equation (2.1) and **Table 2.1**.

$$Li^+ + e^- = Li \quad E^\circ = -3.05 \text{ V vs. SHE}$$
 (2.1)

	Standard electrode potential	Density	Capacity density	
	E° (vs. SHE) [V]	[g/cm <sup>3</sup> ]	[Ah/kg]	[Ah/dm <sup>3</sup> ]
Li	-3.05	0.53	3860	2060
Na	-2.71	0.97	1170	1130
Al	-1.66	2.70	2980	8050
Zn	-0.76	7.14	820	5860
Fe	-0.44	7.85	960	7550
Cd	-0.40	8.65	480	4120
Pb	-0.13	11.4	260	2940

Table 2.1 Properties of possible anode materials.<sup>35</sup>

Lithium also has a very low density with 0.53 g/cm<sup>3</sup>, which enables batteries to have higher

capacity per unit weight. For the above two reasons, lithium is very useful for battery development.

#### 2.1.2. Lithium Ion Battery

Lithium ion battery (LIB) is one of the most important lithium products. This thesis doesn't focus on the chemistry of lithium ion batteries, but it is essential to know this topic as a "lithium researcher". Therefore, this section only summarizes chemical reactions at the anode and cathode when the charge and discharge occur.



Figure 2.1 Schematic illustration of charge-discharge in lithium ion batteries, Me= Co, Fe+P, Mn, Ni+Mn+Co, Ni+Co+Al, Ti, S, etc.<sup>2</sup>

When a battery is charged, the following reactions in Equation (2.2) occur. Lithium metal oxide at the anode provides carbon at the cathode with electrons via lithium ion electrolyte.

Cathode: LiMeO 
$$\rightarrow$$
 Li<sub>1-x</sub>MeO + xLi<sup>+</sup> + xe<sup>-</sup>  
Anode: C<sub>6</sub> + xLi<sup>+</sup> + xe<sup>-</sup>  $\rightarrow$  Li<sub>x</sub>C<sub>6</sub> (2.2)

When a battery is discharged, the reactions in Equation (2.3) occur. Carbon at the cathode supplies

electrons to lithium metal oxide at the anode. Lithium moves into and out of the electrode materials.

Cathode: 
$$\operatorname{Li}_{1-x}\operatorname{MeO} + x\operatorname{Li}^+ + xe^- \to \operatorname{LiMeO}$$
  
Anode:  $\operatorname{Li}_x C_6 \to x\operatorname{Li}^+ + C_6 + xe^-$  (2.3)

There have been various metals used in lithium ion batteries such as Co, Fe+P, Mn, Ni+Mn+Co, Ni+Co+Al, Ti. Moreover, lithium sulfur (Li+S) batteries are currently being focused on by many researchers.<sup>36</sup> The cathode reaction of LiS batteries is Equation (2.4).

$$2\mathrm{Li}^{+} + \mathrm{S} + 2\mathrm{e}^{-} \to \mathrm{Li}_{2}\mathrm{S} \tag{2.4}$$

Although the electronic conductivity of sulfur is lower than other cathode materials, it has a higher theoretical capacity (1675 mAh/g) than that of other available cathode materials for lithium ion batteries such as lithium cobalt oxide (-140 mAh/g). There are various problems for practical use, but this is why lithium sulfur batteries are now eliciting much interest.

#### 2.1.3. Eh-pH Diagram

To understand the aqueous chemistry of lithium, an Eh-pH diagram is one of the essential tools. **Figure 2.2** is an Eh-pH diagram for the Li-H<sub>2</sub>O system when (a)  $[Li^+]=1$  M and (b)  $[Li^+]=0.072$  M. Almost all the experiments in this thesis used the condition of  $[Li^+]=0.072$  M(=500 mg/L) because this value is close to the concentration in South American brines. These figures show that lithium exists as lithium ion (Li<sup>+</sup>) in almost all the range of pH and Eh regardless of the concentration.



Figure 2.2 pH-Eh diagram for Li-H<sub>2</sub>O system at 25 °C, 1 atm, (a) [Li]=1 M or (b)

[Li]=0.072 M (Drawn by HSC).

From **Figure 2.3 (a)**, it is clear that lithium can be recovered from aqueous solution as Li<sub>2</sub>CO<sub>3</sub>, which is the standard commercial product of lithium for the battery market. However, when the concentration is reduced to 500 mg/L or 0.072 M, lithium carbonate is not precipitated unless an over-addition of carbonate is used (**Figure 2.3 (b)**). This result confirms that it is necessary to preconcentrate lithium in brines prior to precipitation of lithium carbonate.



Figure 2.3 pH-Eh diagram for Li-C-H<sub>2</sub>O system at 25 °C, 1 atm and (a) [Li]=[C]=1 M or

(b) [Li]=[C]=0.072 M (Drawn by HSC).

### 2.2. Lithium Market

#### 2.2.1. Supply/Demand and Price

The lithium market is expanding. It is a new market without a clear history unlike the copper market. It is therefore more difficult to predict supply/demand and price of lithium in a today's rapidly fluctuating market.<sup>37</sup> While there are several reports from some companies, the data by BMO Capital Markets is cited here in Figure 2.4.



1. Carbonate price forecasts are BMO estimates

2. For hydroxide prices, assumed \$2,000/t historical hydroxide-to-carbonate premium

3. Demand forecast is BMO base case

Figure 2.4 Lithium supply/demand and price and their estimates.<sup>38</sup>

According to the graph, there won't be a supply deficit by 2025, although, around 2015, there was a concern of lithium shortage. The price of lithium carbonate and hydroxide are expected to drop and then increase gradually over time. At first glance, it seems that there is no problem in the lithium market because, according to the current estimates, a sufficient amount of lithium would be supplied to the lithium market and the price would be stable. However, this topic is controversial since the lithium market is unique, and it's not easy to predict future demand.

First of all, it takes some time for lithium to be supplied into the market, especially from brine deposits. Since the process used for brine deposits is mainly solar evaporation, which normally takes at least one year to concentrate lithium, the market can be affected by the supply situation in the past few years. In other words, a certain amount of lithium should be prepared beforehand to meet the demand in the next few years. On the other hand, the demand side of the market is rapidly changing, and the future demand is unclear at least in the current situation. Some automobile companies announced a sales target for EVs and the lithium market reacted so as to prepare for those targets, but there has been less demand because EVs are not yet common among consumers due to the restriction of infrastructure and available models. It is more complicated than expected to keep the lithium market in balance by predicting supply and demand. This is one of the reasons that the price of lithium compounds hit the highest point in 2018. In the early 2010s, the market was thought to become short of lithium soon due to EVs production, and the price rose rapidly though the supply finally managed to meet the demand. This means there is a possibility that lithium demand will catch and surpass its supply in the near future while the current estimates show the opposite situation. For example, China, which is one of the biggest markets for EVs in the world, has started to head toward becoming an EV society by making laws to restrict the emission of greenhouse gases. It is uncertain how fast EVs will spread to the world. To maintain the supply of lithium, a process is needed to make lithium compounds quickly. The slow response time for the use of long-term solar evaporation of brines is not sufficient to meet rapidly escalating demand for lithium chemicals. This is the reason that a lot of researchers are working on rapid lithium recovery technologies.

### 2.2.2. Products and Applications

Lithium is utilized in various ways. **Figure 2.5** shows the changes in lithium uses from 2003 to 2020. According to the graph, lithium use has been increasing because the demand for lithium batteries has been dramatically increasing. Almost half of the lithium produced was consumed for lithium batteries in 2019. The rapid increase in demand in the current period (**Figure 2.4**) due to lithium battery production is expected to continue.



Figure 2.5 Annual use of lithium in tonnes in each of the primary lithium usage industries from 2002 to 2020.<sup>39</sup>

Rockwood Holdings, Inc. report about 23 kg-LCE (lithium carbonate equivalent) of lithium is needed for one EV while only about 3 g is needed for one cellphone as shown in **Table 2.2**.<sup>35</sup> For instance, Tesla, Inc. made a plant, called Tesla Gigafactory 1, to make lithium ion battery EVs in a larger scale than ever before.

Usage	Lithium used in LCE	
Cellphone	3 g	
Laptop	30 g	
Plug-in hybrid car (16 kWh)	9 kg	
EV (25 kWh)	23 kg	

Table 2.2 Amount of lithium used in various devices.<sup>35</sup>

Other than lithium batteries, ceramics and the lubricant industry are the primary lithium consumers. Aluminum production and pharmaceuticals also use lithium as one of their critical components though the total consumption is not so large. For those industries, various kinds of lithium compounds are prepared. **Table 2.3** shows key products and key applications of lithium, and **Figure 2.6** illustrates a lithium value chain.<sup>35</sup>

Table 2.3 Lithium compounds and applications.<sup>35</sup>

Key product	Key applications
Lithium carbonate	Lithium ion batteries, Glass ceramics, Cement, Aluminum
Lithium hydroxide	Lithium ion batteries, Grease, CO2 adsorption, Mining
Lithium metal	Lithium batteries, Pharmaceuticals, Aluminum alloy
Butyl-lithium	Elastomers, Pharmaceuticals, Agrochemicals

Lithium carbonate and hydroxide are the main lithium products used in lithium ion batteries, glass ceramics and lubricants, which, in total, occupy more than 50 percent of the lithium use. Lithium carbonate is used for most glass products because it decreases the viscosity and melting point of glass. In the ceramics industry, lithium hydroxide is used for lithium grease. Lithium greases

adhere well to metal over a wide range of temperature. Lithium carbonate is also useful for aluminum production since lithium can lower the melting point of the molten electrolyte of aluminum and increase the electrical conductivity in the electrolysis cell. This helps decrease costs and energy for aluminum production. When welding steel alloys, lithium may be used to reduce the melting temperature and lower the surface tension. Some other lithium compounds also enhance electrical conductivity in some metal processes. Interestingly, as some environmental concerns are increasing, lithium hydroxide is applied to adsorption of one of the greenhouse gases, carbon dioxide. Lithium metal and lithium organic compounds like butyl-lithium are also critical products for life science such as pharmaceuticals.



Figure 2.6 Lithium value chain.<sup>35</sup>

Though more explanation will be provided later, it should be noted here that lithium carbonate is firstly produced from ores and brines in most cases, from which other compounds are produced
such as lithium hydroxide and lithium metal.

# 2.3. Lithium Deposits

### 2.3.1. Overview

It is vital to review lithium deposit types before discussing the separation science and technology of lithium because separation technology is dependent on lithium deposit type.





**Figure 2.7** is the estimate of the global lithium resources and reserves based on data summarized in 2015.<sup>2</sup> According to the graph, lithium deposit types are divided into two. Brines constitute about 58% of global resources and 82% as reserves while ore minerals about 37% and 17% respectively.



Figure 2.8 (a) Resources and (b) Reserves in terms of countries in thousands metric tonnes Li metal equivalent.<sup>3</sup>

**Figure 2.8** shows that more than half of the resources are in the lithium triangle of Argentina, Bolivia and Chile in South America and almost 80 percent of the estimated reserves are in the triangle as well.<sup>3</sup> These data indicate that brines would be expected to be a more abundant lithium source in the future if technologies are developed which can extract lithium from brine more rapidly and economically.

**Table 2.4** and **Table 2.5** show some ore-type and brine-type mining sites respectively.<sup>40</sup> Ore-type deposits mainly exist in the US, Canada, Australia and China. Some deposits are in Africa and Europe, but they are not major ones. Australia and China are still expanding the operation of lithium production from pegmatites.

Deposit types		Mining Sites	Li [t]
		North Carolina Former operations	230,000
		North Carolina Undeveloped	2,600,000
		Barraute, Quebec	90,000
		Bernic Lake, Manitoba	18,600
		Others, Canada	147,000
		Bikita, Zimbabwe	56,700
		Manono, Zaire	2,300,000
	Pegmatites	Greenbushes, Western Australia	1,500,000
Ores		Mount Marion, Western Australia	19,800
		Mount Catlin, Western Australia	20,000
		Koralpa, Austria	100,000
		Larritta, Finland	14,000
		Various, Russia	1,000,000
		Brazil, Minas Gerais & Ceara	85,000
		China	750,000
	Hectorites	McDermitt Caldera Oregon/Nevada	2,000,000
	Jadarite	Jadar, Serbia	850,000

 Table 2.4 Lithium mining sites and resources in tonnes (ores).40

Of course, brine-type deposits are mainly found in the lithium triangle as shown in **Table 2.5**. It is also known that some geothermal and oilfield brines in the US, such as the Smackover formation, have the potential for lithium production. That is why there are now many interests in the methods

of how to extract lithium from oilfield brines.

Deposit types		Mining Sites	Li [t]
		Silver Peak, Nevada	40,000
		Salar de Uyuni, Bolivia	8,900,000
		Salar de Hombre Muerto, Argentina	850,000
	Continental	Salar de Rincon, Argentina	1,400,000
	Brines	Salar de Oraroz, Argentina	300,000
Brines		Salar de Atacama, Chile	6,900,000
		Salar de Maricunga,Chile	200,000
		China & Tibet	2,600,000
	Geothermal		1 000 000
	Brines	Brawley, Southern Cantornia	1,000,000
	Oilfield Brines	Smackover Formation USA	750,000

Table 2.5 Lithium mining sites and resources in tonnes (brines).<sup>40</sup>

## 2.3.2. Ore Deposits

As shown in **Table 2.4**, pegmatite is the most common lithium ore type, which contains some lithium minerals such as spodumene, while there are some other ores such as hectorite. **Table 2.6** summarizes some lithium minerals with the theoretical and practical amount of lithium contained.

Minoral	Composition	Li <sub>2</sub> O [wt%]		
Winerar	Composition	Theoretical	Practical	
Petalite	LiAlSi <sub>4</sub> O <sub>10</sub>	4.9	3.0-4.5	
Spodumene	LiAlSi <sub>2</sub> O <sub>6</sub>	8	1.5–7.0	
Amblygonite	(Li,Na)AlPO4(F,OH)	10	8–9	
Lepidolite	K(Li,Al) <sub>3</sub> (Al,Si,Rb) <sub>4</sub> O <sub>10</sub> (F,OH) <sub>2</sub>	4.1	3–4	
Eucryptite	LiAlSiO4	11.9	5	
Hectorite	Na <sub>0.3</sub> (Mg,Li) <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	-	0.3–0.7	
Jadarite	LiNaSiB <sub>3</sub> O <sub>7</sub> OH	-	-	
Igneous rock	-	-	1–35 ppm	
Carbonate rocks	-	-	8 ppm	
Shales and clay	-	-	70 ppm	
Seawater	-	-	0.18 ppm	

**Table 2.6 Lithium minerals.**<sup>40</sup>

Many pure minerals contain several percent of lithium, while the amount of lithium found in natural minerals is smaller because the minerals are not pure. Usually, the concentration in hard rock deposits is higher than brine deposits.

### 2.3.3. Brine Deposits

As shown in **Table 2.5**, continental brines in South America are the main brine-type deposits that are exploited, while a few geothermal brines or oilfield brines are also commercialized. Continental brines contain at most 0.05–2% of lithium. Some analytical data of

brines are provided below in **Table 2.7**.<sup>40</sup> Continental brines generally contain 5–12% of sodium, and some other ions such as magnesium, sulfate, boron, potassium as shown in the table. Calcium is also found in continental brines. Sodium and potassium may be partially recovered via evaporation as chloride salts before lithium recovery. Magnesium and calcium are precipitated as carbonates by soda ash addition before the lithium concentration gets high enough to be coprecipitated as a carbonate. It is necessary to remove sulfate and boron because they disturb lithium production in the following process. Sulfate precipitates with sodium as sodium sulfate when brine temperature is low. Boron is an unfavorable impurity in lithium products and must be removed.

Driver	Evaporation	Li [%]	Mg [%]	SO <sub>4</sub> [%]	B [%]	K [%]
Brines	[mm/y]		(Mg/Li)	(SO <sub>4</sub> /Li)	(B/Li)	(K/Li)
Salars de Atacama	2200		0.96	1.65	0.05	2.36
(Chile, SQM)	3200	0.15	(6.4)	(11.0)	(0.3)	(15.7)
Salars de Atacama	2200	0.16	1.02	1.76	0.05	1.97
(Chile, Chemetall)	3200	0.16	(6.4)	(11.0)	(0.3)	(12.3)
Salars del Hombre Muerto	2400	0.069	0.097	0.952	0.034	0.61
(Argentina, FMC)	2400		(1.4)	(13.8)	(0.5)	(8.8)
Great Salt Lake		0.004		2	0.006	0.65
(Utah, USA)	-		-	(500.0)	(1.5)	(162.5)
SilverPeak	760 1200	0.016	0.028	0.494	0.008	0.53
(Nevada, USA, Chemetall)	/00-1200	00-1200 0.016		(30.9)	(0.5)	(33.1)

 Table 2.7 Analytical values of continental brines.40

Drings	Evaporation	Li	Mg [%]	SO <sub>4</sub> [%]	B [%]	K [%]
Brines	[mm/y]	[%]	(Mg/Li)	(SO <sub>4</sub> /Li)	(B/Li)	(K/Li)
Dead Sea		0.000		0.07	0.003	0.6
(Israel/Jordan)	-	0.002	-	(35.0)	(1.5)	(300.0)
Rincon	1500 2100	0.04	0.344	1.228	0.12	0.75
(Argentina, Admiralty)	1300–2100	0.04	(8.6)	(30.7)	(3.0)	(18.8)
Uyuni	1200 2200	0.025	0.651	0.854	0.08	1.6
(Bolivia, Gerve-)	1200–2200	0.035	(18.6)	(24.4)	(2.3)	(45.7)
West Taijnar	2600 2100	0.025	1.538	3.45	0.038	0.84
(China, Qinhai Citic Group)	2000–3100		(61.5)	(138.0)	(1.5)	(33.6)
East Taijnar	2600-3100	0.05	1.87	2.2	0.022	0.38
(China, Qinhai Lithium)			(37.4)	(44.0)	(0.4)	(7.6)
Zhabuye	Zhabuye		0.03	2.228		
(China, Zhabuye Lithium)	2300	0.13	(0.2)	(17.1)	-	-
Dongxiung Cuo	2200	0.025	0.008	0.571		
(China, Sterling)	2300	0.035	(0.2)	(16.3)	-	-

 Table 2.7 Analytical values of continental brines,<sup>40</sup> cont'd.

# 2.4. Processes for Lithium Production

### 2.4.1. Overview

As explained in **2.3**, ore and brine deposits are the primary resources of lithium. In most cases, when making products, especially for lithium ion batteries, those deposits are processed and refined into lithium carbonate. If necessary, lithium carbonate is then converted into lithium

hydroxide. In this section, therefore, the following three processes are explained with some practical examples.

- 1) Process from ore deposits to lithium carbonate
- 2) Process from brine deposits to lithium carbonate
- 3) Process from lithium carbonate to lithium hydroxide

### 2.4.2. Process of Ore Deposits

Ores firstly go through mineral processing like grinding and sieving to get lithium mineral concentrates. The lithium concentration of the concentrates is slightly higher than brine but is still low. In order to extract lithium from the concentrates, there is a common method decomposing ores by using sulfuric acid. **Figure 2.9** and **Figure 2.10** present the process schematically and in a simplified flow chart.



Figure 2.9 An example of flow chart of Li<sub>2</sub>CO<sub>3</sub> production from ores.<sup>41</sup>



Figure 2.10 A simplified flow chart of Li<sub>2</sub>CO<sub>3</sub> production from ores.<sup>42</sup>

First, the concentrates are roasted and reacted with sulfuric acid in a rotary kiln at high temperature (-1100 °C). Lithium sulfate  $(\text{Li}_2\text{SO}_4)$  is extracted into water and the solution is recovered by filtration followed by neutralization for impurity rejection. Li<sub>2</sub>CO<sub>3</sub> can be obtained by adding soda ash.

#### 2.4.3. Process of Brine Deposits

A schematic illustration of the brine process is shown in **Figure 2.11**, and a representative flow chart is in **Figure 2.12**, which is drawn based on a report by JOGMEC, 2010<sup>40</sup>.



Figure 2.11 A schematic illustration of lithium production from brines.<sup>43</sup>



Figure 2.12 A representative flow of lithium carbonate production from brines.<sup>40</sup>

First, brine containing around 0.2% of lithium is pumped up from wells. Then in evaporation ponds, brine is concentrated by solar heat for about one year so that lithium concentration finally gets to 4–6%. During the evaporation, some sodium and potassium are removed as chloride salts by making use of a solubility different as shown in **Table 2.8**.

Compounds	Solubility [g/100 g-H <sub>2</sub> O]
LiCl	84.5
NaCl	36.0
KCl	35.5
MgCl <sub>2</sub>	56.0
CaCl <sub>2</sub>	81.3

Table 2.8 Solubility of chloride salts at 25 °C.44

 Table 2.9 Solubility of hydroxide salts at 25 °C.44

Compounds	Solubility [g/100 g-H <sub>2</sub> O]
LiOH	12.5
NaOH	100
КОН	120.8
Mg(OH) <sub>2</sub>	0.00069
Ca(OH) <sub>2</sub>	0.160

Boron and magnesium removal follow the evaporation. Magnesium is rejected by adding a base to precipitate magnesium hydroxide. During this step, magnesium and calcium precipitates and are removed from brine as hydroxides. Other monovalent cations remain in solution because of the difference of the solubility of their hydroxide in **Table 2.9**.

Lithium carbonate is finally precipitated by adding soda ash Na<sub>2</sub>CO<sub>3</sub> and then dried. As magnesium and calcium are removed beforehand, only lithium precipitates as lithium carbonate. Some sodium and potassium ions remain in solution, but these species can be ignored due to the solubility difference of their carbonate salts in **Table 2.10**. This lithium carbonate is a product itself and can be a source of other lithium compounds like lithium hydroxide LiOH.

Compounds	Solubility [g/100 g-H <sub>2</sub> O]
Li <sub>2</sub> CO <sub>3</sub>	1.3
Na <sub>2</sub> CO <sub>3</sub>	30.7
K <sub>2</sub> CO <sub>3</sub>	111.4
MgCO <sub>3</sub>	0.18
CaCO <sub>3</sub>	0.00066

Table 2.10 Solubility of carbonate salts at 25 °C.44

This section introduces seven practical cases below. **Figure 2.13** is the process flow of Salar de Atacama, Chile. After the evaporation step, boron is removed by SX and magnesium is precipitated by lime.



Figure 2.13 Process flow of Salar de Atacama, Chile.<sup>42</sup>

**Figure 2.14** is the process flow of Salar de Hombre Muerto, Argentina. This process uses an adsorption method onto alumina at a certain pH and temperature to enhance lithium concentration before evaporation because of low concentration in brines.



Figure 2.14 Process flow of Salar de Hombre Muerto, Argentina.<sup>42</sup>

**Figure 2.15** is the process flow of Salar de Oraroz, Argentina. In this process, magnesium removal is performed in the first place to increase the lithium concentration before evaporation because of low concentration in brines. Besides, crude lithium carbonate is first recovered and then redissolved and refined to remove impurities efficiently.



Figure 2.15 Process flow of Salar de Oraroz, Argentina.<sup>42</sup>

**Figure 2.16** shows the process flowsheet for lithium recovery in China and Tibet. This method firstly removes sulfate by natural cooling because sulfate inhibits evaporation and lithium cannot be concentrated sufficiently as a result.



Figure 2.16 Process flowsheet for lithium recovery in China & Tibet.<sup>42</sup>

**Figure 2.17** is the process flow of CITIC method (CITIC Group Corporation Ltd., formerly the China International Trust Investment Corporation, is a state-owned investment company of the People's Republic of China). This method is similar to the process of Salar de Atacama, Chile (**Figure 2.13**), but it removes boron by hydrochloric acid treatment, whose process is not clearly explained in the literature. Spray drying and kiln processing are used to concentrate lithium more efficiently.



Figure 2.17 Process flow of CITIC method.<sup>42</sup>

**Figure 2.18** is the process flow of POSCO method (POSCO, formerly Pohang Iron and Steel Company, is a multinational steel-making company headquartered in Pohang, South Korea). This process does not use evaporation in an ideal case and precipitates and removes magnesium hydroxide and calcium carbonate by adding sodium hydroxide and sodium carbonate. After the removal, lithium phosphate is precipitated by adding sodium phosphate, and the precipitates are redissolved by phosphoric acid. Membrane electrolysis makes lithium hydroxide from the lithium

phosphate solution and CO<sub>2</sub> addition forms lithium carbonate form.



Figure 2.18 Process flow of POSCO method.<sup>42</sup>

**Figure 2.19** is the process flow of Bateman method. This process doesn't use evaporation either in an ideal case. Membrane electrolysis and solvent extraction are used to enhance lithium concentration in lithium chloride solution.



Figure 2.19 Process flow of Bateman method.<sup>42</sup>

As mentioned above, there are different optimum methods to recover lithium from brine with different characteristics. Additionally, it is generally said that favorable conditions for lithium extraction are (1) High Li concentration, (2) Low Mg and B concentration, (3) Low SO<sub>4</sub> concentration, and (4) High K concentration. Conditions (1) and (2) directly lead to lower cost. Condition (3) makes it easier to separate lithium from brines while (4) increases profit with greater amounts of byproducts.

#### 2.4.4. Process for Lithium Hydroxide Production

Lithium hydroxide is an essential product for the production of lithium ion batteries. Although there are some methods proposed to make LiOH directly from brines, this section only mentions a method using lithium carbonate because there are few direct processes which are feasible. Lithium hydroxide solution is firstly produced by Equation (2.5).

$$Li_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2LiOH$$
(2.5)

Then, lithium hydroxide monohydrate LiOH $\cdot$ H<sub>2</sub>O is crystallized from the mother solution by evaporation as shown in Equation (2.6).

$$\text{LiOH} + \text{H}_2\text{O} \rightarrow \text{LiOH} \cdot \text{H}_2\text{O} \downarrow$$
(2.6)

In order to precipitate and crystallize higher grade of lithium hydroxide monohydrate for lithium ion batteries, it is important to prepare a higher concentration of lithium hydroxide solution with a higher grade of lithium carbonate.<sup>45</sup> There are also various processes proposed using membrane electrodialysis to get lithium hydroxide solution.

# 2.5. Lithium Extraction Technologies

## 2.5.1. Overview

For the past several decades, a combination of solar evaporation and carbonation has been mainly utilized to produce pure lithium compounds. However, this combination can be applied only to brine that has a relatively high concentration of lithium, roughly more than 500 mg/L. The evaporation method also takes approximately one year to concentrate lithium and subsequently precipitate lithium carbonate. Thus, other rapid processes have been considered and studied recently as shown in Table 2.11.<sup>46</sup> This section reviews those technologies by considering some practical examples.

Technology		Mechanism	Developer
		Lithium-containing solutions in ponds	
		are concentrated by solar heating so that	
Solar		lithium carbonate can precipitate after	Conventional
evaporation	<b>*</b>	adding soda ash (sodium carbonate).	
	111 23 23	$2\text{LiCl} + \text{Na}_2\text{CO}_3 \rightarrow \text{Li}_2\text{CO}_3 + 2\text{NaCl}$	
		In place of soda ash, phosphoric acid is	
Phosphate		used to precipitate lithium.	POSCO <sup>26,27</sup>
precipitation		$3\text{LiCl} + \text{H}_3\text{PO}_4 \rightarrow \text{Li}_3\text{PO}_4 + 3\text{HCl}$	

Table 2.11 Technologies for lithium extraction from brine and their mechanism.

Technology	Mechanism	Developer
	Lithium ions are absorbed into aluminum hydroxide's	
Ion exchange	layers formed in ion exchange resins.	Dowr <sup>5–7</sup>
resin	$LiCl+NaCl \cdot 2Al(OH)_3 \cdot nH_2O$	Dow
	$\rightarrow$ NaCl+LiCl · 2Al(OH) <sub>3</sub> · nH <sub>2</sub> O	
Aluminum	Lithium ions are absorbed by the same mechanism as the	FMC <sup>11–13</sup>
based	ion exchange resin adsorption. The adsorbent in the form	Simbol <sup>14,15</sup>
adsorbent	of powder or granulated beads.	Eramet <sup>16</sup>
Manganese	Lithium ions are adapthed into lower of monophers	
based	cuide such as IL Mr. O and Mr.O	JOGMEC <sup>20</sup>
adsorbent	$0x1de such as H_{1.6}WH_{1.6}O_4  and \lambda-WHO_2.$	
Titanium based	Lithium ions are adsorbed into layers of titanium oxide	Noomotols <sup>22</sup>
adsorbent	such as H <sub>2</sub> TiO <sub>3</sub> .	incometais

Table 2.11 Technologies for lithium extraction from brine and their mechanism, cont'd.

Technology	Mechanism	Developer
Solvent extraction	Organic $\widehat{\Box}$ Lithium ions are extracted to an oil phase from a water phase.Aqueous $R-H_{sol}+LiCl_{aq} \rightarrow R-Li_{sol}+HCl_{aq}$	Tenova <sup>9,10</sup>
Nanofiltration	Lithium ions are concentrated by making use of the differences in ion rejection ratios and water flow rejection through a membrane	MGX <sup>29</sup>
Membrane electrolysis	Magnesium and calcium ions are removed as hydroxide. $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $\downarrow$ $Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$ $Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2$	Research underway <sup>34</sup>
Ferric phosphate reduction	Lithium ions are selectively extracted to form lithium ferrous phosphate by ferric phosphate reduction by thiosulfate. $2FePO_4+2LiCl+2Na_2S_2O_3$	Research underway <sup>23–</sup> 25

Table 2.11 Technologies for lithium extraction from brine and their mechanism, cont'd.

## 2.5.2. Phosphate Precipitation

Phosphate precipitation is a newly invented technology to replace the carbonation step in the solar evaporation process as shown in **Figure 2.18**. Phosphoric acid is added to precipitate lithium from brine as Equation (2.7).

$$3\text{LiCl} + \text{H}_{3}\text{PO}_{4} \rightarrow \text{Li}_{3}\text{PO}_{4} + 3\text{HCl}$$

$$(2.7)$$

While this method needs extra processes to convert lithium phosphate into lithium carbonate or hydroxide,<sup>47</sup> it has succeeded in shortening the solar evaporation step by precipitating lithium phosphate whose solubility, 0.027 g per 100g of H<sub>2</sub>O, is much lower than lithium carbonate's solubility, 1.3 g per 100g of H<sub>2</sub>O, at ambient temperature (**Table 2.12**).

Compounds	Solubility [g/100 g-H <sub>2</sub> O]
Li <sub>3</sub> PO <sub>4</sub>	0.027
Na <sub>3</sub> PO <sub>4</sub>	14.4
K <sub>3</sub> PO <sub>4</sub>	105.8
Mg3(PO4)2	-
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	0.00012

Table 2.12 Solubility of phosphate salts at 25 °C.44

POSCO currently has projects to recover lithium from brine or battery recycling with this method.<sup>26,27</sup> However, it is doubtful that phosphate precipitation can be applied to low-concentration brines because this method still partially uses solar evaporation in practical cases.

### 2.5.3. Ion Exchange Resin

IX resin is a widely used material for water softening, water purification and metal separation. IX resins commonly consist of a polymer matrix and functional groups introduced into

the matrix. Most commercial IX resins use styrene-divinylbenzene (SDB) as their matrix. SDB forms a three-dimensional structure by styrene polymer chains and divinylbenzene (DVB) crosslinks (**Figure 2.20**). Here, DVB is called a crosslinking agent.



Figure 2.20 Chemical structure of SDB copolymer.

The number of crosslinks partially determines how small the micropores in resin are and how hard resin is. The more crosslinking, the smaller the micropores and the harder the resin. The percentage of DVB amount is usually calculated as an index of the degree of crosslinking with Equation (2.8).

Crosslinkage = DVB [%] = 
$$\frac{\text{Mass of DVB}}{\text{Mass of total monomer}} \times 100$$
 (2.8)

Also, a porous-type resin can be manufactured by using a special polymerization method, while otherwise, SDB resin is usually gel-type. As for functional groups, sulfonate (R-SO<sub>3</sub><sup>-</sup>H<sup>+</sup>) and quaternary ammonium (R-NR<sub>3</sub><sup>+</sup>OH<sup>-</sup>) are commonly used as a strong acid - and strong base - exchanger, respectively. They are introduced on the copolymer matrix by chemical reaction as illustrated in **Figure 2.21**. In the figure, R-SO<sub>3</sub><sup>-</sup> and R-NR<sub>3</sub><sup>+</sup> are called fixed ion because they cannot move freely in a resin, and H<sup>+</sup> and OH<sup>-</sup> are called counter ion, which makes a neutral pair with the fixed ion.



Figure 2.21 Chemical structure of resin with (a) sulfonate, (b) quaternary ammonium.

However, there are many other types of resins. Some have special functional groups on them, and others contain additional chemical compounds on functional groups. Keeping this in mind, IX resin for lithium extraction is next reviewed.

Although IX resins are conventional adsorbents to recover metal ions from solutions, lithium is much more difficult to adsorb selectively than other metal ions such as copper ions. The reason is that, in brine, a much higher concentration of sodium, potassium, calcium and magnesium ions are present (sometimes 100 times as high as lithium concentration in mol/L), and these ions have a higher affinity to cation exchange resins. Despite the unfavorable conditions for ion exchange resins, Dow Chemical in the US invented aluminum loaded resins which can take lithium selectively from brine by the reaction in Equation (2.9),<sup>5–7</sup> although the approach remains challenging for practical use.

$$LiCl+NaCl \cdot 2Al(OH)_{3} \cdot nH_{2}O \rightarrow NaCl+LiCl \cdot 2Al(OH)_{3} \cdot nH_{2}O$$
(2.9)

Some other investigations have looked at solvent impregnated resins that extract lithium into resins loaded with an organic phase. S. Nishihama et al., for example, studied 1-phenyl-1,3-tetradecanedione ( $C_{11}$ ph $\beta$ DK) / tri-n-octylphosphine oxide (TOPO) impregnated resin to separate lithium ions from sodium and potassium ions.<sup>8</sup> Solvent impregnated resin method is one of the

most promising ways to recover lithium because of its high selectivity, but the gradual extraction of solvent from the resin, which makes the resin more difficult to be reused, remains problematic especially in oil and gas wastewater which can contain some organic phases.

The two special types of ion exchangers above are not believed to be in commercial use. However, some commercial IX resins with unique functional groups may be candidates for lithium extraction as well. **Table 2.13** lists the functional groups of cation exchange resins and chelating resins which were surveyed in this study. It was not sure that these functional groups are effective for selective lithium extraction, but commercial resins of these functional groups were tested for lithium recovery and the results are discussed in Chapter 4.

Name	Chemical structure	Note
Sulfonate	$HC = \begin{bmatrix} -H_2 & 0 \\ -H_2 & -H_2 \\ -H_1 & -H_2 \\ -H_1 & -H_2 \\ -H_2 & -H_$	Commonly used as cation exchange resin
Phosphonate + Sulfonate	$\begin{array}{c}   \\ CH_2 \\ HC \\ H$	Selective for antimony, bismuth and iron

Table 2.13 List of functional groups of IX resin studied in this thesis.

Name	Chemical structure	Note
Iminodiacetate	$HC - CH_2 - CH$	Selective for copper, cobalt, nickel and zinc
Aminomethylphosphonate (Aminophosphonate)	$H_{C}^{CH_{2}} \xrightarrow{CH_{2}} H_{N}^{CH_{2}} \xrightarrow{CH_{2}} M^{2+}$	Selective for lead, copper, zinc, nickel, iron, antimony and bismuth
Bispicolylamine	$HC - CH_2 - N - M_2^{2+} N - CH_2 - N - M_2^{2+} - N - CH_2 - N - M_2^{2+} - N - CH_2 $	Selective for copper and nickel
Hydroxypropylpicolylamine	$H_{C}^{CH_{2}}$	Selective for copper and nickel

Table 2.13 List of functional groups of IX resin studied in this thesis, cont'd.

Name	Chemical structure	Note
Thiouronium (Isothiouronium)	$HC - CH_2 - SHN - NH_2 - M^2 + M^2$	Selective for mercury and precious metals
Thiourea	$H_{C}^{C} H_{2} H_{C}^{C} H_{2}^{C} H_{2}^{C$	Selective for mercury and precious metals
Thiol	$H_{C}^{CH_{2}}$	Selective for mercury and precious metals
N- methylglucamine	$H_{C}^{CH_{2}}$	Selective for borate (boron)
Amidoxime	$HC \xrightarrow{CH_2} CH_2 \xrightarrow{NH_2} HC \xrightarrow{HC} CH_2 \xrightarrow{C} C \xrightarrow{N-O} \xrightarrow{I} \xrightarrow{I} \xrightarrow{I} \xrightarrow{I} \xrightarrow{I} \xrightarrow{I} \xrightarrow{I} I$	Selective for uranyl (uranium) and precious metals

## Table 2.13 List of functional groups of IX resin studied in this thesis, cont'd.

Name	Chemical structure	Note
Polyamine	$H_{1}^{CH_{2}}$	Selective for divalent heavy metals such as mercury, iron, copper, zinc
Amphoteric		
(Quaternary amine	$HC - CH_2 - N^+ X - CH_2 - C' - C$	Effective for salts removal
+ Carboxylate)	н <sub>3</sub> с ом	

Table 2.13 List of functional groups of IX resin studied in this thesis, cont'd.

### 2.5.4. Al/Mn/Ti-based Adsorbent

Some metal oxides/hydroxides also can adsorb lithium. They have a higher selectivity for lithium than ion exchange resins although it takes more time than ion exchange resins to complete extraction because lithium needs to be intercalated into the layers of the metal oxides/hydroxides.

Aluminum-based adsorbents are typically LiCl/Al(OH)<sub>3</sub> compounds, which have a similarity to the aluminum-loaded resin. The loading mechanism is the same as well. Since the aluminum-loaded resin only has adsorption sites on the surface of the resin, and the aluminum-based adsorbent has adsorption sites along its whole surface, the latter generally has a higher capacity. Some companies, FMC, Simbol and Eramet, have their patents for aluminum adsorbents.<sup>11–16</sup>

A manganese-based adsorbent was first reported by K. Ooi et al.<sup>18,19,48</sup> and had high selectivity for lithium, raising interest among many researchers. Some papers were published after the first report; however, the adsorption mechanism is essentially the same as the aluminum adsorbents. The manganese-based adsorbent is now being tested with the Uyuni salt lake in Bolivia

by Japan Oil, Gas and Metals National Corporation (JOGMEC).<sup>20</sup>

A titanium-based adsorbent also has comparable capacity for lithium recovery according to the study by R. Chitrakar et al.,<sup>21</sup> and Neometals used a similar kind of titanium-based absorbent to extract lithium directly from brine.<sup>22</sup> Furthermore, the three adsorbents are granulated for practical operation in columns, and they are currently being studied in terms of their optimal binder and the method of granulation. In spite of the potential of the three adsorbents, there are still few practical operations; only a few pilot tests have been carried out.

#### 2.5.5. Solvent Extraction

Solvent extraction is another promising method for lithium recovery.<sup>49</sup> Lithium ion is extracted and stripped by the reaction between aqueous and organic phase (Equation (2.10)).

Loading: 
$$\text{Li}_{aq}^{+} + \text{HL}_{org} \rightarrow \text{H}_{aq}^{+} + \text{LiL}_{org}$$
  
Stripping:  $\text{LiL}_{org} + \text{H}_{aq}^{+} \rightarrow \text{Li}_{aq}^{+} + \text{HL}_{org}$ 
(2.10)

The symbol L refers to the lithium extractant. Several extractants have been developed to satisfy each condition for each metal. For example, hydroxyoxime extractants from BASF and Solvay are very famous for copper SX from dilute leach solutions. Solvent extraction technology shows higher selectivity for lithium over other monovalent ions such as sodium and potassium ions. On the other hand, other divalent ions, such as magnesium and calcium ions, should be removed and lithium should be pre-concentrated before the solvent extraction step to maintain the efficiency of the process.

As for a practical case, Tenova, an Italian company, is now testing an SX process in Israel.<sup>9,10</sup> **Figure 2.22** is a flow sheet of the process. This process uses SX to extract lithium and separate sodium and potassium after calcium and magnesium removal. The extracted lithium is

directly conveyed to electrolysis to make lithium hydroxide solution from lithium sulfate.



Figure 2.22 A flow sheet of lithium production using solvent extraction by Tenova.<sup>9</sup>

### 2.5.6. Membrane Technologies

Membrane technology is also expected to play an essential role in lithium extraction. Somrani et al.<sup>28</sup> studied nanofiltration and low pressure reverse osmosis for lithium ion separation from brine. Although temperature and pressure control are required, the membrane process can be applied to low concentrations of lithium, such as lithium in oil and gas wastewater. Furthermore, while fouling is a huge concern, as discussed in other membrane applications, the membrane process can be applied to a variety of brines or wastewaters when conditions are adequately determined and controlled. MGX has reported success in lithium extraction from oilfield produced wastewater.<sup>29,30</sup> Besides nanofiltration, some researchers have investigated membrane electrolysis.

Nieto et al.<sup>34</sup> studied the removal of magnesium and calcium by making hydroxide ions by membrane electrolysis.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2.11}$$

With an anode of a titanium mesh coated with an iridium-based mixed metal oxide  $(IrO_2/TiO_2; 65/35\%)$ , a cathode of a stainless steel wire mesh with a stainless steel current collector and an in-between anion exchange membrane, hydroxide ions are produced on the cathode side by Equation (2.11).

$$\frac{\text{Mg}^{2+} + 2\text{OH}^{-} \rightarrow \text{Mg(OH)}_{2}}{\text{Ca}^{2+} + 2\text{OH}^{-} \rightarrow \text{Ca(OH)}_{2}}$$
(2.12)

Then, with the reactions in Equation (2.12), the produced hydroxides precipitate magnesium and calcium ions in brine. This technology is novel because it does not need to use either base like sodium hydroxide or carbonate salts like soda ash in order to remove both ions from brine.

### 2.5.7. Ferric Phosphate Reduction

This technology uses the redox couple of ferric phosphate (FP) and lithium ferrous (or iron) phosphate (LFP), which is inspired by the mechanism of a rechargeable battery cell of lithium iron phosphate. LFP is one of the most popular cathode materials for LIBs because of low cost, performance and safety. The practical capacity is typically 140–160 mAh/g while the theoretical capacity is 170 mAh/g. When FP is reduced in aqueous solution by a reducing agent or an external potential, lithium ions in the solution are selectively adsorbed into FP with the formation of LFP. According to the existing researches, it is known that only the reversible couple of "heterosite-structure FP" and "olivine-structure LFP" can take up and release lithium selectively due to their unique structure. Therefore, the structures of heterosite FP and olivine LFP are firstly reviewed

here before getting into the detail of this technology.

FP has several structures. The most common form adopts  $\alpha$ -quartz structure, and two orthorhombic phases and one monoclinic phase are also known. One of the orthorhombic FPs is heterosite FP. This structure is named after heterosite (Fe<sup>3+</sup>,Mn<sup>3+</sup>)PO<sub>4</sub>. Heterosite FP is in orthorhombic lattice system, *Pbnm* (No. 62) space group with lattice parameters of *a*=4.76 Å, *b*=9.68 Å, *c*=5.82 Å.<sup>50</sup> **Figure 2.23** is the structure of heterosite FP drawn by VESTA. The figures clarify that, among PO<sub>4</sub> tetrahedra along the c-axis, there are octahedral spaces for some cations being inserted.



Figure 2.23 Schematic illustrations of heterosite FP structure: (a) oblique view, (b) view along the c-axis (Drawn by VESTA).

LFP is generally known with the mineral name of triphylite and has only one structure,

which is the olivine structure. This structure is named after olivine  $(Mg^{2+}, Fe^{2+})_2SiO_4$ , a common mineral on the earth. Like olivine, triphylite or LFP is in orthorhombic lattice system, *Pbnm* (No. 62) space group with lattice parameters of a=4.71 Å, b=10.38 Å, c=6.05 Å.<sup>51</sup> This means that heterosite FP and olivine LFP have almost the same structure. With the parameters, the illustrations of triphylite structure can be drawn by VESTA in Figure 2.24. By comparing Figure 2.24 with Figure 2.23, it is shown that olivine LFP is structured by the octahedral spaces of heterosite FP being occupied by lithium ions. When the transformation between FP and LFP occurs by lithium insertion and desertion, the unit-cell volume expands only by 6.5%.<sup>52</sup> This stability is an advantage of LFP as a battery material. On the other hand, it also has a structural drawback. Since there are only one-dimensional pathways for lithium ion migration (c-axis direction), LFP/FP has lower conductivity than other cathode materials with two- or three-dimensional pathways. This phenomenon was reported and discussed by some researchers in terms of diffusion coefficient. activation energy and migration energy.<sup>53–56</sup> When the structure is reviewed in detail, the strong P-O covalent bonds of PO<sub>4</sub> tetrahedra keep oxygen from being released, which contributes to high resistance to thermal ignition.<sup>57</sup> This is also why the FP/LFP couple is preferable as a cathode material of LIB in terms of safety. The P-O covalent bonds additionally weaken covalent bonds of the iron ion and lower the  $Fe^{3+}/Fe^{2+}$  redox potential, which makes the  $Fe^{3+}/Fe^{2+}$  couple easier to be oxidized and reduced even in the solid phase of FP or LFP.<sup>58</sup> Thanks to those unique structures, the FP/LFP redox couple can absorb and release lithium selectively and repeatedly.

When it comes to methods to make LFP powders, they can be synthesized by both solidstate and solution-based methods<sup>59</sup>. Standard solid-state methods are mechano-chemical activation, carbo-thermal reduction and microwave heating. They are simple ways to obtain well-crystallized structure, but typically consume so much time and energy and often result in poor purity. On the other hand, solution-based methods can usually obtain high purity and can control particle sizes for the homogeneous property. Solution-based methods include hydrothermal synthesis, sol-gel synthesis, spray pyrolysis, co-precipitation and microemulsion drying.



Figure 2.24 Schematic illustrations of triphylite structure: (a) oblique view, (b) view along the c-axis (Drawn by VESTA).

Coming back to the lithium extraction technology, the ferric phosphate reduction method is not used in practical sites currently, but its research has been underway in recent years. While LFP is widely used in rechargeable batteries, it is only recently that the FP/LFP redox couple has started to be used to recover lithium selectively from brine. X. Liu et al. firstly proposed an electrochemical cell with FP/LFP electrodes for lithium extraction from brine.<sup>31,32</sup> With an external potential applied, lithium ions are extracted from catholyte brine, and lithium ions are stripped
from anode LFP into anolyte like NaCl solution as shown in Equation (2.13).

Cathode: 
$$FePO_4 + Li^+ + e^- \rightarrow LiFePO_4$$
  
Anode:  $LiFePO_4 \rightarrow FePO_4 + Li^+ + e^-$  (2.13)

The electrochemical cell consumes electrical energy.

As an alternative, Intaranont et al.<sup>23–25</sup> used thiosulfate ( $S_2O_3^{2-}$ , TS) as a reducing agent to promote the redox reaction of FP/LFP. As in Equation (2.14), thiosulfate is oxidized to tetrathionate by reducing FP particles into LFP particles. The reduction potential of FP/LFP is 3.45 V vs. Li/Li<sup>+ 60</sup> and 0.40 V vs. SHE<sup>23</sup>, while S<sub>4</sub>O<sub>6</sub><sup>2-</sup>/S<sub>2</sub>O<sub>3</sub><sup>2-</sup> reduction potential is -0.015 V vs. SHE from HSC database. It is clear that the overall reaction is favorable because the potential difference is positive.

Cathodic: 
$$FePO_4 + Li^+ + e^- \rightarrow LiFePO_4$$
  
Anodic:  $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$   
Overall:  $2FePO_4 + 2Li^+ + 2S_2O_3^{2-} \rightarrow 2LiFePO_4 + S_4O_6^{2-}$   
 $\Delta E^0 = 0.40 V vs.SHE$  (2.14)  
 $E^0 = -0.015 V vs.SHE$  (2.14)

**Figure 2.25** is an Eh-pH diagram for the TS-H<sub>2</sub>O system. As there is no potent oxidizing agent in the experimental system of this research, the diagram considers the gentle oxidation into tetrathionate ( $S_4O_6^{2-}$ ) and possible acid decomposition of Equation (2.15).



Figure 2.25 pH-Eh diagram for TS-H<sub>2</sub>O system at 25 °C, 1 atm, [S]=1 M (Drawn by HSC). Sulfate species (SO4<sup>2-</sup> and HSO4<sup>-</sup>) were excluded in this diagram.

$$Na_{2}S_{2}O_{3} + 2HCl \rightarrow 2NaCl + S \downarrow + SO_{2} \uparrow + H_{2}O$$

$$(2.15)$$

Conversely, Intaranont et al.<sup>23–25</sup> prepared FP for the lithium extraction by the delithiation of LFP with persulfate ( $S_2O_8^{2-}$ , PS) in Equation (2.16). The reduction potentials of  $S_2O_8^{2-}/SO_4^{2-}$  is 1.94 V vs. SHE from HSC database. This reaction is also favorable from a thermodynamic point of view.

Cathodic: 
$$S_2O_8^{2^-} + 2e^- \rightarrow 2SO_4^{2^-}$$
  
Anodic:  $\text{LiFePO}_4 \rightarrow \text{FePO}_4 + \text{Li}^+ + e^-$   
Overall:  $2\text{LiFePO}_4 + S_2O_8^{2^-} \rightarrow 2\text{FePO}_4 + 2\text{Li}^+ + 2SO_4^{2^-}$   $\Delta E^0 = 1.54\text{V vs.SHE}$  (2.16)

Figure 2.26 is an Eh-pH diagram for the PS(persulfate)-H<sub>2</sub>O system. Both the reaction equation

and the diagram prove that the reduction potential of persulfate is high enough to oxidize LFP to FP.



Figure 2.26 pH-Eh diagram for PS-H<sub>2</sub>O system at 25 °C, 1 atm, [S]=1 M (Drawn by HSC).

With the reducing and oxidizing reactions, Intaranont et al.<sup>23–25</sup> studied the lithium extraction from brine and reported the following points.

- Heterosite-FePO<sub>4</sub> was chosen as FP adsorbent due to its unique structure, where Li<sup>+</sup> can be inserted to form olivine-structured LFP.<sup>61</sup>
- 2) Heterosite-FePO<sub>4</sub> can be obtained by the delithiation of LFP with the use of potassium PS ( $K_2S_2O_8$ ) as an oxidizing agent.<sup>62</sup>
- 3) The delithiation rate was dependent on the molar ratio of PS:LFP, while it took 2

hours at most to convert 99% of LFP to FP in the case of the minimum theoretical reaction ratio of 1:2.

- 4) Sodium TS ( $Na_2S_2O_3$ ) completed the lithiation of FP into LFP.
- 5) The kinetics of the lithiation could be explained by a surface-reaction limited model.
- 6) The lithiation rate was first-order proportional to both lithium and thiosulfate concentrations, and an overall second order rate constant was around  $0.03 \text{ min}^{-1} \text{ M}^{-2}$ .
- 7) The maximum adsorption capacity was 46 mg-Li/g-solid, which is comparable with that of any other types of adsorbents except some manganese-based adsorbents with the capacity of 38–40 mg-Li/g-solid<sup>63–66</sup>.
- The extractions of other ions such as sodium, potassium and magnesium from a brine solution were less than 4 mg/g-solid.

In place of thiosulfate, other reducing agents have been studied by some researchers. Iodide (I<sup>-</sup>) is one of them. Kuss et al.<sup>67</sup> successfully converted FP into LFP with lithium iodide in acetonitrile, which is an organic solvent. Intaranont tried to use the same reaction of iodide in aqueous solution as shown in Equation (2.17). The potential of  $I_2/I^-$  couple is from HSC database.

Cathodic: 
$$FePO_4 + Li^+ + e^- \rightarrow LiFePO_4$$
  
Anodic:  $2I^- \rightarrow I_2 + 2e^-$   
Overall:  $2FePO_4 + 2Li^+ + 2I^- \rightarrow 2LiFePO_4 + I_2$   
 $\Delta E^0 = -0.22 V vs.SHE$   
(2.17)

Since the overall reaction is thermodynamically unfavorable, the reaction was aided with the zinciodine reaction of Equation (2.18).<sup>24</sup>

$$I_2 + Zn \rightarrow ZnI_2 \tag{2.18}$$

However, the author found that the reaction was incomplete although a high concentration of iodide was used and iodine was removed from aqueous phase to a solid phase of zinc iodide in

order to promote the overall reaction in Equation (2.17) by following Le Chatelier's principle.



Figure 2.27 pH-Eh diagram for I-H<sub>2</sub>O system at 25 °C, 1 atm, [I]=1 M (Drawn by HSC).

**Figure 2.27** is an Eh-pH diagram for I-H<sub>2</sub>O system. Triiodide ( $I_3^-$ ) is a byproduct of the  $I_2/I^-$  couple formed by the following reaction. Regardless of the presence of triiodide, the diagram clearly shows that the reduction potential of iodine/iodide couple is above that of FP/LFP couple.

$$\mathbf{I}_2 + \mathbf{I}^- \to \mathbf{I}_3^- \tag{2.19}$$

The same author studied sodium nitrite (NaNO<sub>2</sub>), formaldehyde (CH<sub>2</sub>O), formic acid (HCOOH), and sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) as alternative reducing agents and found that sulfite was the most suitable. It is reported that sulfite fully converted FP to LFP.<sup>24</sup> Equation (2.20) shows the

reactions which are considered to occur. The potential of the sulfate/sulfite couple at each pH is calculated from data in HSC.

Cathodic: 
$$FePO_4 + Li^+ + e^- \rightarrow LiFePO_4 \quad E^0 = 0.40 \text{ V vs.SHE}$$
  
Anodic :  
 $HSO_3^- + H_2O \rightarrow SO_4^{2-} + 3H^+ + 2e^-$   
 $E^0 = -0.34, -0.52 \text{ V vs.SHE} (pH = 5,7)$   
 $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$   
 $E^0 = -0.64 \text{ V vs.SHE} (pH = 9)$  (2.20)  
Overall :  
 $2FePO_4 + 2Li^+ + HSO_3^- + H_2O \rightarrow 2LiFePO_4 + SO_4^{2-} + 3H^+$   
 $\Delta E^0 = 0.74, \ 0.92 \text{ V vs.SHE} (pH = 5,7)$   
 $2FePO_4 + 2Li^+ + SO_3^{2-} + H_2O \rightarrow 2LiFePO_4 + SO_4^{2-} + 2H^+$   
 $\Delta E^0 = 1.04 \text{ V vs.SHE} (pH = 9)$ 

The advantage of sulfite over thiosulfate as a reducing agent is that sulfite needs an only half dosage of thiosulfate since SF reacts with FP with the ratio of one to two while TS does with the ratio of one to one. **Figure 2.28** is an Eh-pH diagram for SF-H<sub>2</sub>O system. The diagram considers the acid decomposition of sulfite into sulfur dioxide in Equation (2.21).

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + SO_2 \uparrow + H_2O$$
(2.21)



Figure 2.28 pH-Eh diagram for SF-H<sub>2</sub>O system at 25 °C, 1 atm, [S]=1 M (Drawn by HSC).

According to the equation and diagram, the potential difference is dependent on pH and, in the range of neutral pH, it is around 1 V. This difference is more than twice that of the thiosulfate case,  $\Delta E^{\circ}=0.42$  V. At the same time, it should be noted that, under an uncontrolled pH condition, the potential difference decreases as the reaction produces protons.

As for an oxidizing agent, hydrogen peroxide is an alternative to persulfate. LFP would be oxidized by the following reaction in (2.22). The potential of hydrogen peroxide is from HSC database. The potential difference  $\Delta E^{\circ}=1.44$  V is comparable to that of persulfate  $\Delta E^{\circ}=1.54$  V. However, it's not promising because it can only be used as an oxidizing agent in acid solution,<sup>24</sup> where ferric phosphate is partially dissolved into solution.

Cathodic: 
$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
  
Anodic:  $LiFePO_4 \rightarrow FePO_4 + Li^+ + e^-$   
Overall:  $2LiFePO_4 + H_2O_2 + 2H^+ \rightarrow 2FePO_4 + 2Li^+ + 2H_2O$   $\Delta E^0 = 1.44V$  vs. SHE (2.22)

## 2.6. Summary and Objectives

This chapter firstly focused on lithium chemistry from a scientific point of view. Second, the lithium market was reviewed in order to grasp supply and demand in the future. Lithium production was then reviewed from types of deposit to processes and technologies. Out of the technologies reviewed, this thesis focused on ion exchange resin and ferric phosphate reduction. The following summarizes the development of each technology and objectives for this research.

Ion exchange resin probably has the longest history as a rapid lithium recovery process. Although this method is a conventional method to recover metal ions from solutions, lithium is much more challenging to adsorb selectively than other metal ions. The reason is that, in brine, a much higher concentration of sodium, potassium, calcium and magnesium ions are present (sometimes 100 times as high as lithium concentration in mol/L), and these ions have a stronger affinity than lithium to general cation exchange resins. Despite the unfavorable conditions for ion exchange resins, in the 1980s, Dow Chemical in the US invented aluminum-loaded resins which can adsorb lithium selectively from brine.<sup>5–7</sup> However, as the invention needs some special conditions to be carried out and the selectivity is not so high, it has not yet been applied to a practical situation. Since then, there are fewer promising reports about lithium-selective ion exchange resins for brine while a lot of new types of resins have been developed like chelating resins. Therefore, this thesis tested a wide variety of commercial resins from various producers and summarized the current situation of ion exchange resins around lithium extraction from brine.

Ferric phosphate is a relatively new adsorbent for lithium extraction from brine. While

lithium iron phosphate is widely used in rechargeable batteries, it is only recently that the ferric phosphate (FP)/lithium iron phosphate (LFP) redox couple is used to recover lithium selectively from brine. X. Liu et al. used an electrochemical cell with FP/LFP electrodes for lithium extraction from brine.<sup>31,32</sup> Furthermore, as an electrochemical cell consumes electrical energy, Intaranont et al. used sodium thiosulfate as a reducing agent to promote the redox reaction of FP/LFP to load lithium from a mixed salt brine.<sup>23–25</sup> To be sure, this method using a reducing agent showed excellent lithium selectivity over other cations such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, but more studies should be carried out and it is necessary to develop a scientific understanding in order to apply the process into a practical site. Therefore, in this thesis, lithium extraction by FP/LFP redox reaction promoted by reducing agents was studied from the following points of view.

- 1) What kind of material is the best to make heterosite FP?
- 2) Which reducing agent is favorable?
- 3) How much are the capacity and selectivity?
- 4) How do temperature and pH have an impact on the process?
- 5) Is it possible to recycle ferric phosphate?
- 6) How long does it take to extract lithium? (Kinetics)

Overall, this study investigated the possibility of the use of ion exchange resin and ferric phosphate method for lithium extraction from brine. Especially, the points which distinguish this work from the other works are as follows.

- a) Many kinds of commercial IX resins were screened for lithium extraction from brine
- b) Some precursor materials were compared for the formation of heterosite FP

- c) Some reducing agents were investigated and compared for the FP reduction into LFP
- d) Lithium extraction by the sulfite reduction was investigated in detail for the first time
- e) Effects of temperature and pH on the FP method were well investigated for the first time
- f) Simplified kinetic models were developed for the FP method at different temperature

This thesis consists of 6 chapters. After an explanation of the experimental methods, Chapter 4 and Chapter 5 discuss the experimental results of lithium extraction by ion exchange resin and ferric phosphate respectively. Finally, Chapter 6 concludes all the discussions and mentions challenges and outlook for future works.

## **Chapter 3. Experimental Methods**

## 3.1. Preparation

This work required preparation of synthetic solutions from various salts, measurement of pH and the testing of many ion exchange materials and ferric phosphate substrates. The chemical materials, sources of ion exchange materials obtained, and experimental and analytical equipment used are summarized below

#### 3.1.1. Materials

All the experiments in this study were carried out with the following materials unless otherwise noted. IX resins are listed in **Table 3.1** with their characteristics.

- Buffer, Reference Standard pH 10.00 ± 0.01 at 25 °C (Color Coded Blue), VWR Analytical BDH®
- Buffer, Reference Standard pH  $4.00 \pm 0.01$  at 25 °C, VWR Analytical BDH®
- Buffer, Reference Standard pH 7.00 ± 0.01 at 25 °C (Color Coded Yellow), VWR Chemical BDH®
- Calcium chloride hexahydrate, BioUltra, ≥99.0% (calc. based on dry substance, KT), Sigma Aldrich
- Calcium Standard for AAS, TraceCERT®, 1000 mg/L Ca in nitric acid, Sigma Aldrich
- Copper(I) chloride, reagent grade, 97%, Sigma Aldrich
- Hydrochloric acid 1.0 N, VWR Chemical BDH®
- Hydrochloric acid 36.5 38.0% ACS, VWR Chemicals BDH®
- Iron(III) phosphate dihydrate, Fe 29%, Sigma Aldrich

- Lithium chloride, anhydrous, free-flowing, Redi-Dri<sup>™</sup>, ACS reagent, ≥99%, Sigma Aldrich
- Lithium iron phosphate (LiFePO4) powder, 500g/bag, LIB-LFP-500G, MSE supplies
- Lithium iron(II) phosphate, powder, <5 µm particle size (BET), >97% (XRF), Sigma Aldrich
- Lithium Standard for AAS, TraceCERT®, 1000 mg/L Li in nitric acid, Sigma Aldrich
- Magnesium chloride hexahydrate ACS, Amresco
- Magnesium Standard for AAS, TraceCERT®, 1000 mg/L Mg in nitric acid, Sigma Aldrich
- Nitric acid 68 70%, ARISTAR® ACS, VWR Chemicals BDH®
- Phosphorus Standard for AAS, TraceCERT®, 1000 mg/L P in H2O, Sigma Aldrich
- Potassium chloride 99.0-100.5% ACS, VWR Chemicals BDH®
- Potassium Persulfate (Crystalline Powder/Certified), Fisher Chemical
- Potassium Standard for AAS, TraceCERT®, 1000 mg/L K in nitric acid, Sigma Aldrich
- Sodium chloride ≥99.0% ACS, VWR Chemicals BDH®
- Sodium hydroxide 1.0 N, VWR Chemical BDH®
- Sodium Standard for AAS, TraceCERT®, 1000 mg/L Na in nitric acid, Sigma Aldrich
- Sodium Sulfite Anhydrous (Crystalline/Certified ACS), Fisher Chemical
- Sodium Thiosulfate Anhydrous (Certified), Fisher Chemical

No	Manufacturor	Manufacturar Nama Structura		Matrix	Functional	Ionic	
110.	wanuracturer	Ivanie	Structure		group	form	
1	Dow	XE 832	Gel	SDB	Aluminum loaded	-	
2	Dow	AMBERLITE IR120 plus	Gel	SDB	Sulfonate	Na <sup>+</sup>	
3	Lanxess	LEWATIT MonoPlus S 108	Gel	SDB	Sulfonic acid	Na <sup>+</sup>	
4	Purolite	PUROLITE C100	Gel	SDB	Sulfonic acid	Na <sup>+</sup>	
5	Mitsubishi	DIAION SK1B	Gel	SDB	Sulfonic acid	Na <sup>+</sup>	
6	Samyang	TRILITE SCR-B	Gel	SDB	Sulfonate	Na <sup>+</sup>	
7	Lanxess	LEWATIT MonoPlus SP 112	Macroporous	SDB	Sulfonic acid	Na <sup>+</sup>	
8	Purolite	PUROLITE C150	Macroporous	SDB	Sulfonic acid	Na <sup>+</sup>	
9	Purolite	PUROLITE C160	Macroporous	SDB	Sulfonic acid	Na <sup>+</sup>	
10	Purolite	PUROMET MTC1500	Macroporous	SDB	Sulfonic acid	Na <sup>+</sup>	
11	Mitsubishi	DIAION PK216	Macroporous	SDB	Sulfonic acid	Na <sup>+</sup>	
12	Mitsubishi	DIAION PK228	Macroporous	SDB	Sulfonic acid	Na <sup>+</sup>	
13	Samyang	TRILITE CMP28	Macroporous	SDB	Sulfonate	Na <sup>+</sup>	
					Phosphonic acid		
14	Purolite	Purolite	Purolite PUROMET MTS9570	Macroporous	SDB	and	Na <sup>+</sup>
					Sulfonic acid		
15	Dest		Macroporous	SDB	Iminodiacetic	NL +	
15	Dow	AMBEKLITE IKU/481			acid	ina	

### Table 3.1 List of resins tested in this study.

No.	Manufacturer	anufacturer Name Structure Matrix		Matrix	Functional group	Ionic
						form
	-	LEWATIT		675 F		
16	Lanxess	MonoPlus TP 207	Macroporous	SDB	Iminodiacetic acid	Na⁺
17	Tanaaa	LEWATIT	Management	CDD	Turing dia setiense i d	NI.+
1/	Lanxess	MonoPlus TP 208	Macroporous	SDB	Iminodiacetic acid	Na
10		PUROMET			<b>T</b> · <b>T</b> · · · <b>T</b>	NT +
18	Purolite	MTS9300	Macroporous	SDB	Iminodiacetic acid	INa
19	Mitsubishi	DIAION CR11	Macroporous	SDB	Iminodiacetate	Na <sup>+</sup>
	AMBERLITE	M			$N_{e}^{+}$	
20	Dow	IRC747	Macroporous	SDB	Aminometnyipnosphonate	Ina
- 21	21 Lanxess	LEWATIT	M	SDB	Aminomethylphosphonic	$Nc^+$
21		MonoPlus TP 260	Macroporous SDI		acid	INa
		PUROMET				
22	Purolite	MTS9500	Macroporous	SDB	Aminophosphonic acid	Na <sup>+</sup>
22	Lauran	LEWATIT MDS TP	Management	CDD	Dis vised lawing	$\mathrm{H}_2\mathrm{SO}_4$
23	Lanxess	220	Macroporous	SDB	Bis-picolylamine	salt
		PUROMET			D	
24	Purolite	MTS9600	Macroporous	SDB	Bispicolylamine	FB/SO <sub>4</sub>
25	Dow	DOW XUS 43605	Macroporous	SDB	Hydroxypropylpicolylamine	-
26	Dow	DOW XUS 43600	Macroporous	SDB	Thiouronium	-

No.	Manufacturer	Name	Structure N		Functional group	Ionic	
						form	
27	Lanxess	LEWATIT MonoPlus TP 214	Macroporous	SDB	Thiourea	-	
28	Purolite	PUROMET MTS9140	Macroporous	SDB	Thiourea	-	
29	Purolite	PUROMET MTS9200	Macroporous	SDB	Isothiouronium	$\mathrm{H}^{+}$	
20	D			Dalariana	N-	Free	
30	Dow	AMBERLITE IRA/45	Macroporous	Polystyrene	methylglucamine	Base	
		DIALON CREAS	M	GDD	N-methyl	Free	
31	Witsubisiii	DIAION CRB05	Macroporous	500	glucamine	Base	
22	Duralita	Duralita DUROMET MTS0100	Macroporous		Amidovima	Free	
32	Fulonte	PUROMET MTS9100	Macroporous	ADB	Amidoxime	Base	
33	Purolite	PUROMET MTS9240	Macroporous	SDB	Thiol	$\mathrm{H}^{+}$	
24	Mitsubishi			SDD	Delvernine	Free	
54		DIAION CR20		506	Polyannie	Base	
	Mitsubishi	Mitsubishi D	Mitsubishi DIAION AMP03	Gel		Quaternary amine	Innor
35					SDB	and	milei
					Carboxylate	Salt	

Table 3.1 List of resins tested in this study, cont'd.

## 3.1.2. Apparatus

All the experiments in this study were carried out with the following apparatus unless otherwise noted.

- Electric furnace: Exciton
- pH meter: Oakton ION 700
- Shaker: Lab-Line Orbit Environ-Shaker 3527
- Water bath shaker: Thermo Scientific SWB 25
- AAS: Varian AA240
- ICP-OES: Agilent ICP-OES 5110
- XRD: Rigaku Multiflex 2kW

## 3.2. Procedures for Lithium Extraction with Ion Exchange Resin

#### 3.2.1. Preparation of Ion Exchange Resin

Before a series of lithium extraction experiments with IX resins, all the resins obtained from the companies were pretreated. The resins were washed with deionized (DI) water several times to remove impurities on their surface and immersed into DI water so that they were fully hydrated. Then, they were vacuum filtered for just 30 seconds. These resins were directly used.

After washing and before experiments, actual density and swelling ratio of the resins were measured for later calculation of the experimental results. Actual density  $d_a$  was calculated from the volume and mass of the resins as follows.

Actual density 
$$d_a$$
 [g-wet R/mL-wet R] =  $\frac{\text{Mass of wet resins [g-wet R]}}{\text{Volume of wet resins [mL-wet R]}}$  (3.1)

The volume was measured by a 10 mL graduated cylinder. The resins were put into the cylinder with DI water and tapped so that they were fully packed. After vacuum filtration for 30 seconds, all the packed resins were weighed using an electronic scale. Next, the swelling ratio  $r_s$  was

calculated with wet volume and dry mass in Equation (3.2).

Swelling ratio 
$$r_s [mL-wet R/g-dry R] = \frac{Volume of wet resins [mL-wet R]}{Mass of dry resins [g-dry R]}$$
 (3.2)

Dry mass was obtained after the weighed wet resins were dried at 60–65 °C in an oven for 12 hours. These measurements were repeated three times, and the average was used for subsequent experiments and calculation. The values of each resin are listed in **Table 3.2**.

No.	Resin	da [g-wet R/L-wet R]	rs [mL-wet R/g-dry R]
1	XE832	825	1.89
2	AMBERLITE IR120 plus	854	2.24
3	LEWATIT MonoPlus S 108	841	2.05
4	PUROLITE C100	814	2.21
5	DIAION SK1B	848	2.13
6	TRILITE SCR-B	829	2.18
7	LEWATIT MonoPlus SP 112	810	2.61
8	PUROLITE C150	800	2.27
9	PUROLITE C160	839	1.98
10	PUROMET MTC1500	799	2.50
11	DIAION PK216	818	2.29
12	DIAION PK228	826	1.90
13	TRILITE CMP28	841	1.83
14	PUROMET MTS9570	751	3.62

Table 3.2 Actual density and swelling ratio of resins.

No.	Resin	da [g-wet R/L-wet R]	rs [mL-wet R/g-dry R]	
15	AMBERLITE IRC748i	720	3.99	
16	LEWATIT MonoPlus TP 207	740	3.41	
17	LEWATIT MonoPlus TP 208	749	3.49	
18	PUROMET MTS9300	763	2.93	
19	DIAION CR11	713	3.89	
20	AMBERLITE IRC747	745	3.97	
21	LEWATIT MonoPlus TP 260	768	3.40	
22	PUROMET MTS9500	749	3.63	
23	LEWATIT MDS TP 220	735	3.02	
24	PUROMET MTS9600	707	2.98	
25	DOW XUS 43605	696	3.22	
26	DOW XUS 43600	725	2.23	
27	LEWATIT MonoPlus TP 214	735	3.25	
28	PUROMET MTS9140	686	3.19	
29	PUROMET MTS9200	718	2.93	
30	AMBERLITE IRA743	699	2.90	
31	DIAION CRB05	730	2.71	
32	PUROMET MTS9100	791	2.14	
33	PUROMET MTS9240	730	2.62	
34	DIAION CR20	668	3.35	
35	DIAION AMP03	703	2.84	

### Table 3.2 Actual density and swelling ratio of resins, cont'd.

#### 3.2.2. Lithium Loading Test

Lithium loading test was performed to see how much lithium could be extracted from a brine solution. First of all, two types of synthetic solution were prepared with DI water and reagents. The first was a lithium chloride (LiCl) solution and the other was a brine containing chloride of lithium, sodium, potassium, magnesium and calcium. **Table 3.3** shows the concentration of each metal ion in both solutions and they were labeled as A1 and A2 solution respectively. The concentration was determined roughly by referring to that of saline lakes in South America.<sup>68–70</sup>

		Li	iCl	Brine		
	Species	(A1) mg/L mol/L 500 0.07		(A2)		
				mg/L	mol/L	
_	Li			500	0.07	
	Na	-	-	90000	3.91	
	K	-	-	6000	0.15	
	Mg	-	-	2500	0.10	
	Ca	-	-	2000	0.05	

Table 3.3 Metal ion concentration in synthetic LiCl solution and brine.

The washed wet resins were contacted with both solutions in batch tests. A 300 mL volume of LiCl solution or brine was prepared in an Erlenmeyer flask. Initial pH before putting IX resins was always around 6 at ambient temperature. Before adding the resin, 0.1 mL of the solution was taken by a syringe filter for AAS analysis of initial concentration. Then, 1.5 mL of the wet resins were added to the solution, which gave the dosage of 5 mL-wet R/L. Since it was hard to measure such

a small volume of resins with a graduated cylinder, the volume was converted into weight by the actual density prepared in the last section so that 1.5 mL of resins could be taken by weight on an electronic balance. With the flask covered with parafilm, it was shaken for 24 hours on the shaker at 220 rpm at an ambient temperature of around 20 °C. After 24 hours, 0.1 mL of the solution was taken again for AAS analysis of final concentration. Both samples for AAS analysis were diluted 200 times in solution with 1% of hydrochloric acid (HCl) and 3.81 g/L of potassium chloride (KCl). After AAS analysis, adsorption density  $q_e$  [mg-Li/g-dry R] was calculated as follows:

Adsorption density q<sub>e</sub> [mg-Li/g-dry R] = 
$$\frac{C_o [mg-Li/L] - C_e [mg-Li/L]}{\frac{C_R [mL-wet R/L]}{r_s [mL-wet R/g-dry R]}}$$
(3.3)

where  $C_0$ : initial lithium concentration in solution before loading,  $C_e$ : equilibrium (or final) lithium concentration in solution after loading,  $C_R$ : resin concentration in solution and  $r_s$ : swelling ratio.

#### **3.2.3.** Lithium Stripping Test

Lithium stripping test was carried out after the loading test to see how much lithium could be recovered from resins back into solution. First, all the resins after 24-hour loading were washed with DI water three times. The washed Li-loaded resins were used for a batch-style stripping test. They were put into 20 mL of 1 M HCl and shaken for 12 hours on the shaker at 220 rpm and ambient temperature. After 12 hours, 0.1 mL of the solution was taken for AAS analysis. The sample for AAS analysis was treated in the same way as described for the loading experiments. Adsorption density q<sub>e</sub> [mg-Li/g-dry R] was calculated as follows:

Adsorption density q<sub>e</sub> [mg-Li/g-dry R] = 
$$\frac{C_{e} \text{ [mg-Li/L]}}{\frac{C_{R} \text{ [mL-wet R/L]}}{r_{s} \text{ [mL-wet R/g-dry R]}}}$$
(3.4)

where Ce: equilibrium lithium concentration in solution after stripping, CR: resin concentration in

solution and rs: swelling ratio.

## **3.3.** Procedures for Lithium Extraction with Ferric Phosphate

#### 3.3.1. Preparation of Ferric Phosphate

Ferric phosphate powder was prepared in two different ways before a series of lithium extraction experiments because there is no commercial reagent of ferric phosphate. One was dehydration of ferric phosphate dihydrate (FePO<sub>4</sub>·2H<sub>2</sub>O, FPD) and the other was oxidation of battery-grade lithium iron phosphate (LiFePO<sub>4</sub>, LFP). First, the dehydration of FPD was done by calcination. FPD powder was put into a crucible and calcined for 2 hours at 300–600 °C in the electric furnace. Second, oxidation of LFP was treated chemically by potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) in aqueous solution. Equation (3.5) is the oxidation reaction and LFP and PS react in the ratio of 2:1.

$$2\text{LiFePO}_4 + \text{K}_2\text{S}_2\text{O}_8 \rightarrow 2\text{FePO}_4 + \text{Li}_2\text{SO}_4 + \text{K}_2\text{SO}_4 \tag{3.5}$$

Here in this experiment, in order to oxidize LFP completely, LFP and PS were reacted in the ratio of 1:1. Specifically, 370 mL of 0.2 M PS solution was prepared in an Erlenmeyer flask and 0.2 M of LFP powder (11.67 g/370 mL) was put into the solution. Then, it was shaken on the shaker for 24 hours at 220 rpm and ambient temperature. After 24 hours, the powder was vacuum filtered and dried at 60–65 °C for further experiments and XRD analysis and acid digestion as well. The solution was also recovered and diluted 100 times in solution with 2% of nitric acid (HNO<sub>3</sub>) for ICP analysis

#### 3.3.2. Lithium Loading Test

A lithium loading test was performed to see how much lithium could be extracted from solution onto ferric phosphate. First, eight kinds of synthetic solution were prepared with DI water and reagents as shown in **Table 3.4**. In order to study the effects of other ions on lithium extraction, solutions with each metal ion, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, were separately prepared in addition to brines. Each of the solutions was labeled as B1 to B8 respectively.

					8	J			
	Brine (B1)		Brine	Brine	LCI	NaCl	KC1	MaCl	CaCl
a .			w/o Ca	w/o Na Ca		NaCI	KCI (DC)	MgCl <sub>2</sub>	
Species			(B2)	(B3)	(B4)	(B2)	(B6)	(B7)	(B8)
	mg/L	mol/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Li	694	0.10	694	694	694	-	-	-	-
Na	45980	2.00	45980	_*	-	45980	-	-	-
K	5865	0.15	5865	5865	-	-	5865	-	-
Mg	2431	0.10	2431	2431	-	-	-	2431	-
Ca	2004	0.05	-	-	-	-	-	-	2004

Table 3.4 Metal ion concentration in eight synthetic solutions.

\*There was still some concentration of sodium from reducing agents (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub>).

The prepared FP was tested for these eight solutions by batch testing. A 100 mL volume of each solution was prepared in a plastic bottle. Before adding FP powder, 0.1 mL of the solution was taken by a syringe filter for ICP analysis of initial concentration. The initial pH before adding a reducing agent and LFP was always around 6 at ambient temperature. A reducing agent was

added and dissolved into the solution. The dosage of sodium thiosulfate and sodium sulfite was 15.8 g/L (=0.1 mol/L) and 12.6 g/L (=0.1 mol/L) respectively. Then, 0.75 g of FP was added, which gave the dosage of 7.5 g/L or 0.05 mol/L. A lid was placed on the bottle and it was shaken for 24 hours on the water bath shaker at 100 rpm at 25, 45 or 65 °C. The pH was uncontrolled or controlled at 5, 7 or 9 with sodium hydroxide. During the 24 hour experiment, 0.1 mL samples of the solution were taken several times at a certain time for ICP analysis. All the samples for ICP analysis were diluted 1000 times in solution with 2% of nitric acid (HNO<sub>3</sub>). After 24 hours, the powder was washed with DI water three times, vacuum filtered and dried at 60–65 °C for stripping experiments or for XRD analysis or acid digestion.

#### 3.3.3. Lithium Stripping Test

A lithium stripping test was carried out after each loading test to see how much lithium could be recovered from LFP back into solution. The dried powder after loading was used for batch-style stripping test. A stripping method is same as that of preparation of FP, but the volume of solution was varied. A mass of 0.63 g of LFP was put into 20 mL of 0.2 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (LFP:PS=1:1) and shaken for 24 hours on the shaker at 220 rpm and ambient temperature. After 24 hours, the powder and solution were recovered and treated for XRD and digestion/ICP analysis in the same way above.

#### 3.3.4. Acid Digestion

In order to analyze an exact ratio of elements in the solid, FP or LFP powder was digested with concentrated HCl. In a small beaker, 0.01 g of FP or LFP was reacted with 5 mL of 38% HCl and 5 mL of DI water for an hour under a fume hood. After one hour, all the solution was filtered,

collected in a 100 mL volumetric flask and diluted in 2% HNO<sub>3</sub> for ICP analysis. Based on the analysis results of acid digestion, adsorption density Q<sub>e</sub> [mg/g-FP] was calculated as follows for each element:

Adsorption density Q<sub>e</sub> [mg/g-FP]=
$$\frac{m_{M} [mg]}{m_{FP} [g]}$$
 (3.6)

where  $m_M$ : weight of an element in solid after loading,  $m_{FP}$ : weight of ferric phosphate used for loading. The selectivity of lithium over other ions  $K_{Li}$  [-] was also calculated as follows:

Selectivity 
$$K_{Li}$$
 [-]= $\frac{K_{Li,solid} \text{ [mol-Li/mol-M]}}{K_{Li,solution} \text{ [mol-Li/mol-M]}}$  (3.7)

where  $K_{Li,solid}$ : molar ratio of lithium over each metal in solid after loading,  $K_{Li,solution}$ : molar ratio of lithium over each metal in solution after loading.

## 3.4. Analysis Procedures

#### 3.4.1. Atomic Absorption Spectroscopy (AAS)

The aqueous samples were diluted with a solution of 1% HCl and 3.81 g/L KCl and were directly analyzed by AAS. Since AAS can measure only one element at the same time, in this study, AAS was used to measure the concentration of lithium (Li) only. The measurement was carried out at a wavelength of 670.9 nm, which is the most sensitive peak of Li.

## 3.4.2. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)

The aqueous samples were diluted with 2% HNO<sub>3</sub> and were directly analyzed by ICP. ICP was used to measure the concentration of lithium (Li), sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), iron (Fe), phosphorus (P) at the same time. The wavelength for each element

was set as follows in Table 3.5.

Element	Wavelength [nm]
Li	670.78
Na	589.59
K	766.49
Mg	280.27
Ca	396.85
Fe	259.94
Р	213.62

Table 3.5 Wavelength for the measured elements.

#### 3.4.3. X-ray Diffraction (XRD)

The dried solid samples were analyzed by XRD to determine their crystal structure. Samples were ground in a mortar and pestle if required. The samples were mounted and smoothed on a glass plate and analyzed by x-ray diffraction at 40 kV and 40 mA with Cu-Kα.

# Chapter 4. Lithium Extraction with Ion Exchange Resins

## 4.1. Lithium Recovery from LiCl Solution

First of all, all the resins listed in **Table 3.1** were tested in lithium chloride solution (A1 solution) in order to check the capacity of each resin. Lithium capacity of each resin is summarized in **Figure 4.1**. Overall, functional groups of sulfonate, iminodiacetate and aminophosphonate showed better performance than the others with the capacity of around 20–30 mg/g. Only resins with relatively high capacity from XE 832 to PUROMET MTS9500 were tested in the next experiment with brine solution (A2 brine solution).



Figure 4.1 Lithium adsorption density of resins in LiCl solution in mg-Li/g-dry resin.

**Figure 4.2** is a graph of the weight of lithium stripped vs. that of lithium loaded. There is a good correlation between the results from the loading and the stripping. This is evidence of the accuracy of AAS measurement of the solution after both loading and stripping.



Figure 4.2 Correlation between results of loading and stripping tests in the case of lithium chloride solution (A1 solution).

## 4.2. Lithium Recovery from Brine

Lithium capacity of each resin is summarized in **Figure 4.3**. The resins generally have poor selectivity (and lithium loading) when exposed to brine solution with high salinity. Only the aluminum loaded resin (XE 832) maintained a reasonable lithium capacity. Furthermore, the aluminum loaded resin showed a higher capacity in the brine compared to the simple solution of lithium chloride. It is indicated that the high concentration of other ions increases the activity of lithium ions and promotes lithium loading (calculation of activity is carried out in Chapter 5).



Figure 4.3 Lithium adsorption of resins in brine in mg-Li/g-dry resin. No Data = No experiment was conducted with brine because of its low capacity in pure LiCl solution.

**Figure 4.4** is a graph of the weight of lithium stripped vs. that of lithium loaded in the case of brine solution (A2 solution). There is no correlation between the results from the loading and the stripping. That is because lithium uptake was so small that measurement error would overlap the

difference between initial and final concentration in the loading experiment (samples were diluted 200 times when analyzed). Therefore, the adsorption density shown in **Figure 4.3** was calculated from the results of the stripping experiment.



Figure 4.4 Correlation between results of loading and stripping tests in the case of brine solution (A2 solution).

## 4.3. Summary

Out of the resins listed in **Table 3.1**, the resins with functional groups of sulfonate, iminodiacetate and aminophosphonate had better performance in contact with lithium chloride solution (A1 solution). However, these resins could not recover lithium selectively from a brine

solution (A2 solution) except the aluminum loaded resin (XE 832). While XE 832 is worth investigating furthermore under various condition, the results indicated that the use of ion exchange materials is not so suited to recover lithium from brine solutions. Therefore, the attention of this study turned to iron phosphate based adsorbents.



Figure 4.5 Lithium adsorption density of the resins which showed higher selectivity in LiCl

solution.

# Chapter 5. Lithium Extraction with Ferric Phosphate

## 5.1. Preparation of Ferric Phosphate

#### 5.1.1. Ferric Phosphate Dihydrate

Ferric phosphate dihydrate (FPD) was calcined at temperatures of 300, 500 and 600 °C. The as-received FPD was amorphous. After calcining at 300 and 500 °C, there was no crystalline material left; just amorphous FPD. Crystal ferric phosphate (FP) was obtained at 600 °C. However, the structure was different from heterosite FP (suitable for Li extraction). The calcine had another structure of ferric phosphate:  $\alpha$ -quartz type.



Figure 5.1 XRD patterns of ferric phosphate dihydrate calcined at 300, 500 and 600 °C.

After the loading test, there was no change in the FP structure, and lithium was not extracted.



Figure 5.2 XRD patterns of ferric phosphate obtained by calcination of ferric phosphate dihydrate at 600 °C and samples after lithium loading tests at 20 °C and 65 °C.

#### 5.1.2. Lithium Iron Phosphate (Reagent Grade)

Reagent grade lithium iron phosphate was studied by delithiation by oxidation with potassium persulfate and then attempted relithiation by reduction with thiosulfate. It was confirmed by AAS analysis that lithium could be wholly extracted from LFP by PS oxidation. However, according to XRD results in **Figure 5.3**, the structure of oxidized FP was not well-crystallized heterosite FP. In addition, the delithiated FP couldn't extract lithium even from LiCl solution when reduced by TS. This is mainly because the reagent grade LFP has low electronic conductivity<sup>59</sup> and could not carry the electronic current during the reduction reaction.



Figure 5.3 XRD patterns of reagent-grade LFP and delithiated and lithiated ones at 65 °C in comparison with calcined FPD.

#### 5.1.3. Lithium Iron Phosphate (Battery Grade)

LFP battery grade was converted to heterosite FP by PS oxidation. The complete extraction of lithium was confirmed by AAS analysis of solution after delithiation (100% of the lithium from LFP was extracted into solution). Typically, in order to get carbon coated and obtain high electronic conductivity, battery-grade LFP is synthesized in the presence of carbon black whose surface area is high<sup>59</sup>. Therefore, it is indicated that the successful result is due to the carbon coating.



Figure 5.4 XRD patterns of battery-grade (BG) LFP and delithiated FP by PS oxidation.

In summary, it was not possible to prepare ferric phosphate from FPD and reagent-grade LFP while persulfate oxidation of battery-grade LFP successfully made heterosite FP, which can be used for lithium extraction. Therefore, ferric phosphate used as a lithium adsorbent in the following experiments was prepared from battery-grade LFP by persulfate oxidation.

## 5.2. Selection of Reducing Agents

Some experiments were carried out to compare a selection of reducing agents to determine which is preferable for lithium extraction. Three agents were tested: cuprous (Cu<sup>+</sup>), thiosulfate (TS) and sulfite (SF). Cuprous was experimentally studied because no literature uses cuprous as a reducing agent for the FP method.



Figure 5.5 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS oxidation), and products after loading experiments by cuprous (Cu<sup>+</sup>) at room temperature (RoC), by cuprous (Cu<sup>+</sup>) at 65 °C (65C), by thiosulfate (TS) at 65 °C (65C), by sulfite (SF) at room temperature (RoC) and by sulfite (SF) at 65 °C (65C). All the loading experiments used B1 brine solution.

First, reduction by cuprous was not successful while it dissolves well in brine with a high concentration of chloride as chloride complex. XRD patterns in **Figure 5.5** show that it could not
reduce FP into LFP completely. Also, it left an unfavorable material called Botallackite  $(Cu_2(OH)_3Cl)$ . This result indicates that cuprous ions were oxidized immediately in solution by air before reacting with FP.

Second, thiosulfate successfully reduced FP into LFP. There is an XRD pattern of LFP produced by thiosulfate reduction at 65 °C only in **Figure 5.5** and it cannot promote the reaction entirely at ambient temperature, but it surely had the potential for lithium recovery.

Third, sulfite is also a promising reducing agent. While it is a problem that sulfite ions make unfavorable salts with calcium called Hannebachite (CaSO<sub>3</sub> $\cdot$ 0.5H<sub>2</sub>O), this reagent can recover lithium efficiently even at ambient temperature if there is no calcium in solution. In **Figure 5.5**, XRD patterns of LFP produced by sulfite reduction clarified that it could make LFP at room temperature and the higher temperature. Therefore, this study investigated thiosulfate and sulfite as a reducing agent for the reaction of lithium extraction in the following discussion.

### 5.3. Products after Lithium Loading

The work reported above confirmed that heterosite FP could be made using thiosulfate and sulfite as reducing agents. This section starts to discuss details of the ferric phosphate based lithium extraction method. As a first step, the capacity and selectivity of this method were studied by contacting FP with solutions containing metal ions other than lithium by checking XRD patterns in the case of thiosulfate and sulfite separately.

#### 5.3.1. Thiosulfate Reduction

**Figure 5.6** shows XRD patterns after thiosulfate reduction at 25 °C in B1–B8 brine solution. There is a bit of change of FP into LFP in the case of B1–B3 solution. However, there is

no change in the case of the lithium chloride solution (B4). This may be because higher salinity may be required to facilitate the reduction reaction of FP. The experiments with FP in contact with sodium, potassium, magnesium and calcium ions at 25 °C did not show evidence of change in structure.



Figure 5.6 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS oxidation), and products after loading experiments by thiosulfate (TS) at 25 °C. The loading experiments used B1–B8 brine solution.

**Figure 5.7** shows XRD patterns after thiosulfate reduction at 45 °C in B1–B8 brine solution. In the case of B1–B3 solution, FP was almost wholly converted to LFP. In the case of lithium chloride solution (B4), there is a more substantial change in the pattern at 45 °C than 25 °C, but some FP was still in the final product. Again, a new material is not formed from FP in contact with sodium, potassium, magnesium and calcium ions at 45 °C.



Figure 5.7 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS oxidation), and products after loading experiments by thiosulfate (TS) at 45 °C. The loading experiments used B1–B8 brine solution.

**Figure 5.8** shows XRD patterns after thiosulfate reduction at 65 °C in B1–B8 brine solution. FP was utterly reduced to LFP in B1–B4 solution while sodium iron phosphate (NaFePO<sub>4</sub>, SFP) was produced from FP and sodium ions at 65 °C. Potassium, magnesium and calcium ions did not make any compounds with FP even at 65 °C.



Figure 5.8 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS oxidation), and products after loading experiments by thiosulfate (TS) at 65 °C. The loading experiments used B1–B8 brine solution.

#### 5.3.2. Sulfite Reduction

**Figure 5.9** shows XRD patterns after sulfite reduction at 25 °C in B1–B8 brine solution. Firstly, B1 and B8 brine solution, which contains calcium ions, produced the salts of calcium and sulfite. This means that it is difficult to separate lithium from calcium by sulfite reduction. That's why this study won't discuss sulfite reduction in B1 and B8 solution from the next section. There are more significant LFP patterns than those observed for thiosulfate at 25 °C in the case of B2–B4 solution, but the pattern of FP remains. There was no significant change in the pattern when FP was in contact with sodium, potassium and magnesium ions in salt solutions at 25 °C.



Figure 5.9 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS oxidation), and products after loading experiments by sulfite (SF) at 25 °C. The loading experiments used B1–B8 brine solution.

**Figure 5.10** shows XRD patterns after sulfite reduction at 45 °C in B1–B8 brine solution. Hannebachite was also formed at 45 °C in B1 and B8 brine solution. In the case of B2–B4 solution, LFP was completely produced without FP remaining. Sodium, potassium and magnesium ions do not interact with FP even at 45 °C.



Figure 5.10 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS oxidation), and products after loading experiments by sulfite (SF) at 45 °C. The loading experiments used B1–B8 brine solution.

**Figure 5.11** shows XRD patterns after sulfite reduction at 65 °C in B1–B8 brine solution. The calcium salt was formed again at 65 °C in B1 and B8 brine solution. In the case of B2–B4 solution, LFP was produced entirely without FP remaining. Sodium iron phosphate (SFP) was formed in B5 solution only. Solutions containing potassium and magnesium ions at 65 °C did not change the structure of the solid.



▲ Hannebachite (CaSO<sub>3</sub> $\cdot$ 0.5H<sub>2</sub>O) ■ NaFePO<sub>4</sub>

Figure 5.11 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS oxidation), and products after loading experiments by sulfite (SF) at 65 °C. The loading experiments used B1–B8 brine solution.

## 5.4. Capacity and Selectivity

The previous section reported on lithium extraction by checking XRD patterns of the products. It is confirmed that FP was appropriately reduced into LFP under most of the conditions, while there were some differences due to temperature and a reducing agent. Notably, it turned out that it was not useful to add sulfite as a reducing agent in B1 and B8 solution containing calcium ions. Based on the discussion in the last section, this section will discuss capacity and selectivity.

#### 5.4.1. Thiosulfate Reduction

**Figure 5.12** shows the adsorption density of each metal on FP after thiosulfate reduction at 25 °C in B1–B8 brine solution. In the case of B2 brine solution, the adsorption density of lithium was 12.5 mg/g and the other metals were also adsorbed with the density of several milligrams per gram of FP.



Figure 5.12 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading experiments by thiosulfate (TS) at 25 °C (B1–B8 brine solution).

When lithium adsorption density is compared between B1 and B4 solution, the adsorption density was much higher in B1 case than B4 case, although they contained the same molarity or molality of lithium. The reason why this phenomenon was observed is probably an effect of the activity of lithium. Since B1 solution was composed of a high concentration of chloride salts of other cations, the activity of each chloride salts must be different from its molality. To evaluate the difference, the mean ionic activity of each chloride salts was calculated by Meissner's method<sup>71</sup>. **Table 5.1** shows the calculated values of the mean ionic activity. It is found that activity of lithium chloride, 0.432 mol/kg-H<sub>2</sub>O, is four times as high as its molality, 0.100 mol/kg-H<sub>2</sub>O. Therefore, it's reasonable to mention that the adsorption density was higher because lithium activity was increased by the high concentration of other chloride salts and the reaction of lithium insertion got

easier to proceed.

Species	Molarity	Molality	Mean ionic activity
	[mol/L]	[mol/kg-H <sub>2</sub> O]	[mol/kg-H2O]
LiCl	0.100	0.100	0.432
NaCl	2.00	2.09	1.60
KC1	0.150	0.152	0.358
MgCl <sub>2</sub>	0.100	0.101	0.246
CaCl <sub>2</sub>	0.0500	0.0503	0.193
Water activity [-]	0.875		

Table 5.1 Molarity, molality and mean ionic activity of chloride salts and water activity in

**B1** solution at 25 °C, calculated by Meissner's method<sup>71</sup>.

**Figure 5.13** shows the selectivity of lithium over the other metals after thiosulfate reduction at 25 °C in B1–B3 brine solution. Selectivity over sodium was 428 in B2 brine solution while 18 in B3 brine solution because lithium was not adsorbed well in B3 solution and because the initial concentration of sodium was not so high in B3 solution. Selectivity over potassium, magnesium and calcium was lower than that over sodium because the initial concentration of those ions was not so high as that of sodium ions.



Figure 5.13 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by thiosulfate (TS) at 25 °C (B1–B3 brine solution).

**Figure 5.14** shows the weight percentage of FP in solid after thiosulfate reduction at 25 °C in B1–B3 brine solution when assuming each metal would make metal iron phosphate. FP was not all changed to LFP at 25 °C in 24 hours. Even in solution B2, the percentage was 27.8%. The amount of LFP produced in B3 solution, which contains lower total dissolved solids (TDS) than B1 or B2, was smaller. This indicates that high TDS may promote the reaction of lithium recovery in some ways.



Figure 5.14 Weight percentage of iron phosphate in solid after loading experiments by thiosulfate (TS) at 25 °C (B1–B3 brine solution).

**Figure 5.15** shows the adsorption density of each metal on FP after thiosulfate reduction at 45 °C in B1–B8 brine solution. Adsorption density of lithium at 45 °C was more than three times as high as that at 25 °C with the value of 44.5 mg/g in the case of B2 solution. The adsorption density of the other metals also got a little bit larger.



Figure 5.15 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading experiments by thiosulfate (TS) at 45 °C (B1–B8 brine solution).

**Figure 5.16** shows the selectivity of lithium over the other metals after thiosulfate reduction at 45  $^{\circ}$ C in B1–B3 brine solution. Selectivity over sodium was 1430 in B2, which is also more than three times as high as that at 25  $^{\circ}$ C.



Figure 5.16 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by thiosulfate (TS) at 45 °C (B1–B3 brine solution).

**Figure 5.17** shows the weight percentage of FP in solid after thiosulfate reduction at 45 °C in B1–B3 brine solution. The weight percentage was 90.5% in the case of B2 solution. Although FP did not remain in the case of B1 and B2 solution, less than 10% of the products were impurities. In B3 solution, FP was still left even at 45 °C.



Figure 5.17 Weight percentage of iron phosphate in solid after loading experiments by thiosulfate (TS) at 45 °C (B1–B3 brine solution).

**Figure 5.18** shows the adsorption density of each metal on FP after thiosulfate reduction at 65 °C in B1–B8 brine solution. Adsorption density of lithium at 65 °C was 44.6 mg/g in the case of B2 solution. This value is almost the same as the value at 45 °C because it is so close to a theoretical value of 46.0 mg/g. Additionally, as it is indicated in the last section that sodium iron phosphate was produced at 65 °C, the adsorption density of sodium was much higher than that at 25 °C and 45 °C, especially in B5 solution.



Figure 5.18 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading experiments by thiosulfate (TS) at 65 °C (B1–B8 brine solution).

**Figure 5.19** shows the selectivity of lithium over the other metals after thiosulfate reduction at 65 °C in B1–B3 brine solution. Selectivity over sodium was 570 in B2, which is much lower than that at 45 °C because of SFP formation. In the case of B3 solution, there was no sodium adsorbed and so a small amount of potassium adsorbed. That is why the selectivity over sodium and potassium was respectively N/A and 1159.



Figure 5.19 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by thiosulfate (TS) at 65 °C (B1–B3 brine solution).

**Figure 5.20** shows the weight percentage of various forms of FP in solid after thiosulfate reduction at 65 °C in B1–B3 brine solution. The weight percentage was 89.6% LFP in the case of B2 solution, which is almost the same value as that at 45 °C. No FP was remaining in every case. Although there were impurities more than 10% of the products in B1 and B2 cases, impurities in B3 solution were only 3.3%. That is because there was no calcium ion and few sodium ions from sodium thiosulfate in B3 solution.



Figure 5.20 Weight percentage of iron phosphate in solid after loading experiments by thiosulfate (TS) at 65 °C (B1–B3 brine solution).

**Figure 5.21** is a graph of adsorption density vs. temperature in the case of thiosulfate reduction in B1–B4 brine solution. According to the graph, adsorption density is higher at a higher temperature. Though the experimental values are almost the same as the theoretical value at 65 °C, they are lower at 25 °C and 45 °C.



Figure 5.21 Adsorption density vs. temperature in the case of thiosulfate (TS) reduction (B1–B4 brine solution). The theoretical maximum of the adsorption density is 46.0 mg/g.

**Figure 5.22** is a graph of weight percentage of lithium iron phosphate in solid vs. temperature in the case of thiosulfate reduction in B1–B4 brine solution. The weight percentage is higher at a higher temperature though the experimental values are around 90% even at 65 °C because of the presence of impurities like sodium and calcium.



⊙TS Brine (B1) ⊙TS Brine w/o Ca (B2) ⊙TS Brine w/o Na Ca (B3) ⊙TS Li (B4)

Figure 5.22 Weight percentage of lithium iron phosphate in solid vs. temperature in the case of thiosulfate (TS) reduction (B1–B4 brine solution).

### 5.4.2. Sulfite Reduction

**Figure 5.23** shows the adsorption density of each metal on FP after sulfite reduction at 25 °C in B2–B7 brine solution. In the case of B2 brine solution, the adsorption density of lithium was 28.6 mg/g. This value is more than twice as that of thiosulfate case at 25 °C. In contrast to the case of thiosulfate, lithium adsorption density is not lower in low TDS solution like B3 and B4. This fact suggests that thiosulfate is not an effective reductant for lithium loading under low TDS condition.



Figure 5.23 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading experiments by sulfite (SF) at 25 °C (B2–B7 brine solution).

**Figure 5.24** shows the selectivity of lithium over the other metals after sulfite reduction at 25 °C in B2 and B3 brine solution. The selectivity of lithium over sodium was 1503 in the B2 brine solution, which is more than three times that achieved with thiosulfate as the reductant. This means that sulfite is better than thiosulfate at 25 °C when calcium doesn't exist.



Figure 5.24 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by sulfite (SF) at 25 °C (B2 and B3 brine solution).

**Figure 5.25** shows the weight percentage of FP in solid after sulfite reduction at 25 °C in the B2 and B3 brine solution. It is clear that FP was not all changed to LFP at 25 °C, but the value is 62.6% in the B2 solution case and more extensive than that of the thiosulfate case.



Figure 5.25 Weight percentage of iron phosphate in solid after loading experiments by sulfite (SF) at 25 °C (B2 and B3 brine solution).

**Figure 5.26** shows the adsorption density of each metal on FP after sulfite reduction at 45 °C in B2–B7 brine solution. In B2 case, adsorption density of lithium at 45 °C was 45.2 mg/g, which is so close to the theoretical value. Again, in contrast to the case of thiosulfate, lithium adsorption density is not lower in B3 and B4 case than in B2 case, which indicates a difference between thiosulfate and sulfite.



Figure 5.26 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading experiments by sulfite (SF) at 45 °C (B2–B7 brine solution).

**Figure 5.27** shows the selectivity of lithium over the other metals after sulfite reduction at 45 °C in B2 and B3 brine solution. Selectivity over sodium was 2541 in B2, which is close to twice as that at 25 °C and that of the thiosulfate case at 45 °C.



Figure 5.27 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by sulfite (SF) at 45 °C (B2 and B3 brine solution).

**Figure 5.28** shows the weight percentage of FP in solid after sulfite reduction at 45 °C in B2 and B3 brine solution. The weight percentage was 93.3% in the case of B2 solution. Although FP didn't remain in the case of B1 and B2 solution, less than 10% of the products were impurities.



Figure 5.28 Weight percentage of iron phosphate in solid after loading experiments by sulfite (SF) at 45 °C (B2 and B3 brine solution).

**Figure 5.29** shows the adsorption density of each metal on FP after sulfite reduction at 65 °C in B2–B7 brine solution. Adsorption density of lithium at 65 °C was 45.9 mg/g in the case of B2 solution. Due to SFP formation, the adsorption density of sodium was much higher at 65 °C in B5 solution.



Figure 5.29 Adsorption density of Li, Na, K, Mg, Ca on ferric phosphate after loading experiments by sulfite (SF) at 65 °C (B2–B7 brine solution).

**Figure 5.30** shows the selectivity of lithium over the other metals after sulfite reduction at 65 °C in B2 and B3 brine solution. Selectivity over sodium is 1056 in B2, which is lower than that at 45 °C because of SFP formation. On the other hand, selectivity over potassium is higher than that at 45 °C. This indicates that SFP formation may be disturbed adsorption of potassium.



Figure 5.30 Selectivity of lithium over Na, K, Mg, Ca after loading experiments by sulfite (SF) at 65 °C (B2 and B3 brine solution).

**Figure 5.31** shows the weight percentage of FP in solid after sulfite reduction at 65 °C in B2 and B3 brine solution. The weight percentage was 92.6% in the case of B2 solution. Impurities were less than 10% in both cases, and both products have a higher purity than the products after thiosulfate reduction.



Figure 5.31 Weight percentage of iron phosphate in solid after loading experiments by sulfite (SF) at 65 °C (B2 and B3 brine solution).

**Figure 5.32** is a graph of adsorption density vs. temperature in the case of sulfite reduction in B2–B4 brine solution. According to the graph, adsorption density is higher at a higher temperature. The experimental values reached the theoretical value at 45 °C, which means sulfite is better than thiosulfate in the absence of calcium.



Figure 5.32 Adsorption density vs. temperature in the case of sulfite (SF) reduction (B2–B4 brine solution). The theoretical maximum of the adsorption density is 46.0 mg/g.

**Figure 5.33** is a graph of weight percentage of iron phosphate in solid vs. temperature in the case of sulfite reduction in B2–B4 brine solution. The weight percentage is higher at a higher temperature. Though the experimental values are larger than 90% even at 45 °C and of course at 65 °C, which again means sulfite can reduce FP to LFP better compared to thiosulfate in the absence of calcium.



Figure 5.33 Weight percentage of lithium iron phosphate in solid vs. temperature in the case of sulfite (SF) reduction (B2–B4 brine solution).

### 5.5. Effect of pH

This section will investigate whether pH influences the ferric phosphate method. The relation between pH change and iron dissolution is firstly discussed, and then the prevention of iron dissolution by controlling pH and the pH effect on lithium capacity of ferric phosphate are discussed. This section focuses on only the case of 65 °C because pH change and iron dissolution were observed at 65 °C and it was confirmed that almost no iron was extracted at 25 °C and 45 °C by either method of reduction.

**Figure 5.34** shows iron dissolution from FP and the final pH of a solution in the case of thiosulfate reduction at 65 °C.



Figure 5.34 Iron (Fe) dissolution and final pH in the case of thiosulfate (TS) reduction (B1– B8 brine solution).

According to the graph, almost 40% of iron extracted from FP and the pH went down to 4–5 in B1–B4 solution while sodium thiosulfate solution itself is neutral at around 7.

$$2\text{FePO}_4 + 2\text{LiCl} + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{LiFePO}_4 + \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaCl}$$
(5.1)

However, as shown in Equation (5.1), there is no acid produced to lower pH and no iron dissolution by the thiosulfate reduction. Ferric phosphate would not dissolve even at 65 °C and at pH 4. Therefore, it is appropriate to guess another reaction which produces proton and dissolves ferric phosphate. The reaction should be involved in thiosulfate because this phenomenon occurred in the thiosulfate case only. Based on these considerations, it is assumed that ferric phosphate is reduced to ferrous sulfate by tetrathionate with the following reaction.

$$14\text{FePO}_{4} + S_{4}O_{6}^{2-} + 10H_{2}O \rightarrow 14\text{Fe}^{2+} + 14PO_{4}^{3-} + 4SO_{4}^{2-} + 20H^{+}$$
(5.2)

At the same time, there is a possibility that oxygen oxidizes tetrathionate.

$$2S_4O_6^{2-} + 7O_2 + 6H_2O \rightarrow 8SO_4^{2-} + 12H^+$$
(5.3)

Both oxygen and ferric can be an oxidant, and it depends on a condition how much oxygen or ferric or both contribute to the oxidation. For example, Druschel et al.<sup>72</sup> suggested, based on their experimental results, that the overall reaction of tetrathionate oxidation at low pH was as follows.

$$S_4O_6^{2-} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 4SO_4^{2-} + 3Fe^{2+} + 9H^+$$
 (5.4)

On the other hand, when ferric phosphate dissolves into solution as ferrous sulfate, phosphate ions are neutralized by water and release hydroxide ions, which increase pH. This reaction contradicts the pH decrease observed while it may be because the amount of protons released from the reaction above is much more than that of hydroxides.

$$\mathrm{PO}_{4}^{3-} + \mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{HPO}_{4}^{2-} + \mathrm{OH}^{-}$$
(5.5)

For these reasons, the reaction system of the FP method is so complicated. That's why, to investigate the reactions above more in detail, it is necessary to analyze phosphate ions by ICP and polythionate species by ion chromatography (IC).

**Figure 5.35** shows iron dissolution from FP and the final pH of a solution in the case of sulfite reduction at 65 °C. The graph shows that the pH decreased to 4–5 in the sulfite case while sodium sulfite solution itself is a little bit alkaline at around 9. There is much less iron dissolution than observed in the thiosulfate experiments.

$$2\text{FePO}_4 + 2\text{LiCl} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{LiFePO}_4 + \text{Na}_2\text{SO}_4 + 2\text{HCl}$$
(5.6)

The decrease in pH can be explained by Equation (5.6). The reduction by sulfite produces proton as a byproduct, and the small amount of iron dissolution is attributed to the pH decline.



Figure 5.35 Iron (Fe) dissolution and final pH in the case of sulfite (SF) reduction (B1–B8 brine solution).

In order to prevent iron dissolution in the thiosulfate case, another experiment was conducted with B1 solution by thiosulfate reduction at controlled pH 7. **Figure 5.36** compares lithium adsorption density and iron dissolution at pH 4 with that at pH 7. Setting pH at 7 was effective to keep iron phosphate from dissolving. At the same time, controlling pH didn't have any effects on the adsorption density of lithium.



Figure 5.36 Adsorption density and iron (Fe) dissolution at pH 4 (uncontrolled) and 7 (controlled with sodium hydroxide) in the case of thiosulfate (TS) reduction (B1 brine solution).

When it comes to delithiation of LFP, the oxidation reaction in Equation (5.7) occurs. It is readily found out that the reaction does not dissolve ferric phosphate.

$$2\text{LiFePO}_4 + \text{K}_2\text{S}_2\text{O}_8 \rightarrow 2\text{FePO}_4 + \text{Li}_2\text{SO}_4 + \text{K}_2\text{SO}_4 \tag{5.7}$$

While potassium persulfate solution itself is acidic at around 3.9, it is confirmed by ICP analysis that almost no iron eluted.

# 5.6. Recycling of Ferric Phosphate

The previous sections discussed details of the ferric phosphate recovery method by using FP obtained from new battery-grade LFP. However, FP and LFP should be recycled to use this
method more efficiently in practical situations as shown in Figure 5.37.





**Figure 5.38** shows XRD patterns of solid after the loading and stripping in the first and second cycle by thiosulfate reduction at 65 °C and at pH 7 in the B1 brine solution. In both the first and the second cycle, well crystallized LFP and FP were obtained after the loading and stripping respectively.



Figure 5.38 XRD patterns of battery-grade (BG-) LFP and BG-FP (delithiated LFP by PS oxidation), and products after two cycles of loading and stripping experiments. The loading experiments used B1 brine solution at pH 7 controlled by sodium hydroxide and lithium was loaded by thiosulfate (TS) at 65 °C. The stripping experiments used persulfate to oxidize the loaded materials.

**Figure 5.39** shows metal concentration in solution after stripping in the first and second cycle by persulfate oxidation with a solid concentration of 10 wt%. Lithium concentration in

solution after stripping was seven times as the concentration in the initial brine in both the first and the second cycle. Sodium was almost completely rejected.



Figure 5.39 Concentration of metal ions in the initial brine solution (B1 brine solution) and solution after stripping in the first and second cycle of the loading and stripping experiments. The loading experiments used B1 brine solution at pH 7 controlled by sodium hydroxide and lithium was loaded by thiosulfate (TS) at 65 °C. The stripping experiments used persulfate to oxidize the loaded materials and it was carried out with a solid concentration of 10 wt%. In addition to the metal concentration of the stripped ones in the graph, potassium from K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was also in the solution.

Potassium concentration is a little bit higher than the concentration in the initial brine because of potassium persulfate. However, as **Table 2.10** shows, the solubility of potassium carbonate is almost 100 times as that of lithium carbonate and they can be separated by carbonate

precipitation. Alternatively, further concentration and refining would help them separate. Therefore, the ferric phosphate method can recycle the adsorbent (FP) without degradation.

## 5.7. Kinetics

Finally, this section discusses the kinetics of the reactions by both thiosulfate and sulfite. Two models are utilized here. One is the pseudo first-order model and the other is shrinking sphere model. While, as mentioned, the reactions in the system of the FP method are so complicated, kinetic models are simplified here. Only one parameter  $\alpha$ , reacted fraction of FP, is included in the kinetic models, and temperature is considered by Arrhenius formula. However, the other factors, such as the concentration of lithium, thiosulfate, sulfite and particle size distribution of FP powder and pH, are ignored for simplification. Furthermore, while the two models assume that the reactions of the FP method are normal chemical reactions, they are also electrochemical redox reactions. That's why it is also possible to consider kinetics by the Butler-Volmer equation and the Tafel equations if the reactions are electron transfer controlled. Here, this study hands over the electrochemical consideration of kinetics to future works.

#### 5.7.1. Kinetic Models

To begin with, the theory of the two models are reviewed in the following.<sup>72</sup> Pseudo firstorder model is described as Equation (5.8).

$$\frac{d\alpha}{dt} = -k\alpha$$

$$\alpha = 1 - e^{-kt}$$
(5.8)

where  $\alpha$  is fraction reacted, k is reaction rate constant, and t is time. By taking the natural logarithm, the equation changes to Equation (5.9) and k is obtained as a slope of plots of  $\ln(1-\alpha)$  vs. time.

$$\ln(1-\alpha) = -kt \tag{5.9}$$

Furthermore, k is described by Arrhenius formula as shown in Equation (5.10).

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$
(5.10)

where A: frequency factor, Ea: activation energy, R: gas constant, T: absolute temperature. By taking the natural logarithm again,  $E_a$  is obtained as a slope of plots of ln k vs. -1000/RT.

The shrinking sphere model is described as Equation (5.11).

$$-\frac{dV}{dt} = kS = k(4\pi r^{2})$$
  
$$-\frac{dV}{dt} = k(4\pi) \left(\frac{3V}{4\pi}\right)^{\frac{2}{3}} = k(4\pi) \left(\frac{3}{4\pi}\right)^{\frac{2}{3}} V^{\frac{2}{3}} = k'V^{\frac{2}{3}}$$
  
$$-\frac{dV}{dt} = k'V^{\frac{2}{3}}$$
 (5.11)

where V: volume of a particle, t: time, k: reaction rate constant, S: surface area of the particle, r: radius of the particle, k'= $k(4\pi)(3/4\pi)^{2/3}$ . In the calculation of experimental results, initial radius r<sub>o</sub> was set at 1.5 µm, which is D50 of the battery-grade LFP. The following equations are derived by integrating the reaction above.

$$V_{o}^{\frac{1}{3}} - V^{\frac{1}{3}} = \frac{k't}{3}$$

$$1 - \left(\frac{V}{V_{o}}\right)^{\frac{1}{3}} = \frac{k'}{3V_{o}^{\frac{1}{3}}}t$$

$$1 - (1 - \alpha)^{\frac{1}{3}} = k''t$$
(5.12)

where V<sub>o</sub>: initial volume of the particle,  $\alpha$ : fraction reacted (=1-V/V<sub>o</sub>), k''=k'/(3V<sub>o</sub><sup>1/3</sup>). From the last equation, k'' is obtained as a slope of plots of 1-(1- $\alpha$ )<sup>1/3</sup> vs. time. By calculating back to Equation (5.13), k can be obtained. For k in shrinking sphere model, the Arrhenius formula can

be applied as well.

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$
(5.13)

Lastly, it is known that kinetics is diffusion controlled when  $E_a$  is less than 20 kJ/mol and chemical reaction controlled when more than 40 kJ/mol.

## 5.7.2. Thiosulfate Reduction

**Figure 5.40** shows x in  $Li_xFePO_4$  vs. time at 25 °C, 45 °C and 65 °C in the case of thiosulfate reduction in B2 brine. At 65 °C, the reaction was completed in 2 hours or so.





**Figure 5.41** shows graphs for the calculation of Pseudo first-order model. Rate constant k and activation energy  $E_a$  are obtained as a slope of those graphs. While the correlation coefficient is low at 25 °C, the other three graphs have good correlation.



Figure 5.41 Calculation of Pseudo first-order model: "ln (1-α) vs. time at 25 °C, 45 °C and 65 °C" and "ln k vs. -1000/RT" in the case of thiosulfate (TS) reduction (B2 brine solution). α: fraction of reacted, k: reaction rate constant, R: gas constant, T: absolute temperature.

**Figure 5.42** shows graphs for the calculation of the shrinking sphere model. Again, the graph at 25 °C has a worse correlation but the others have a better one.



Figure 5.42 Calculation of shrinking sphere model: "1- $(1-\alpha)^{1/3}$  vs. time at 25 °C, 45 °C and 65 °C" and "ln k vs. -1000/RT" in the case of thiosulfate (TS) reduction (B2 brine solution).  $\alpha$ : fraction of reacted, k: reaction rate constant, R: gas constant, T: absolute temperature.

**Table 5.2** is a summary of k values and activation energy of the thiosulfate reduction calculated from the two models. The rate constant of each model gets larger along with temperature. As activation energy is more than 40 kJ/mol in both cases, it is found that the lithium extraction reaction by thiosulfate reduction is chemical reaction controlled.

	reduction.				
Values	Temperature	Pseudo first-order model	Shrinking sphere model		
		[hour <sup>-1</sup> ]	[µm hour <sup>-1</sup> ]		
	25 °C	0.01	0.01		
k	45 °C	0.09	0.04		
	65 °C	1.50	0.47		
Activation energy [kJ/mol]		99.3	90.8		

 Table 5.2 k value and activation energy calculated from kinetics in the case of thiosulfate

roduction

Using the calculated k values, the two models are compared with the experimental results in **Figure 5.43** and **Figure 5.44**, respectively. While the models ignored some complicated reactions and particle size distribution and so on to simplify the discussion, they fit the experimental data well.



Figure 5.43 Comparison of experimental data and calculated values by Pseudo first-order model. x in Li<sub>x</sub>FePO<sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of thiosulfate (TS)

reduction (B2 brine solution).



Figure 5.44 Comparison of experimental data and calculated values by shrinking sphere model. x in Li<sub>x</sub>FePO<sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of thiosulfate (TS)

#### reduction (B2 brine solution).

### 5.7.3. Sulfite Reduction

**Figure 5.45** shows x in  $Li_x$ FePO<sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of sulfite reduction in B2 brine. The reaction was completed in 12 hours and 2 hours at 45 °C and 65 °C respectively.



Figure 5.45 x in Li<sub>x</sub>FePO<sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of sulfite (SF) reduction (B2 brine solution).

Figure 5.46 shows graphs for the calculation of Pseudo first-order model.



Figure 5.46 Calculation of Pseudo first-order model: "ln (1-α) vs. time at 25 °C, 45 °C and 65 °C" and "ln k vs. -1000/RT" in the case of sulfite (SF) reduction (B2 brine solution). α: fraction of reacted, k: reaction rate constant, R: gas constant, T: absolute temperature.

**Figure 5.47** shows graphs for the calculation of the shrinking sphere model. At 45 °C, the correlation coefficient of the graph is a little bit smaller than the others.



Figure 5.47 Calculation of shrinking sphere model: "1- $(1-\alpha)^{1/3}$  vs. time at 25 °C, 45 °C and 65 °C" and "ln k vs. -1000/RT" in the case of sulfite (SF) reduction (B2 brine solution).  $\alpha$ : fraction of reacted, k: reaction rate constant, R: gas constant, T: absolute temperature.

**Table 5.3** is a summary of k values and activation energy of the sulfite reduction calculated from the two models. Like the thiosulfate case, the rate constant is more significant at a higher temperature. The extraction reaction of lithium by sulfite reduction is also chemical

reaction controlled since activation energy is more than 40 kJ/mol.

reduction.				
Values	Temperature	Pseudo first-order model	Shrinking sphere model	
		[hour <sup>-1</sup> ]	[µm hour <sup>-1</sup> ]	
k	25 °C	0.04	0.02	
	45 °C	0.24	0.19	
	65 °C	2.57	0.61	
Activation energy [kJ/mol]		88.3	76.7	

Table 5.3 k value and activation energy calculated from kinetics in the case of sulfite

Using the calculated k values, the two models are compared with the experimental results in **Figure 5.48** and **Figure 5.49**, respectively. While the models ignored some complicated reactions and particle size distribution and so on to simplify the discussion, they fit the experimental data well.



Figure 5.48 Comparison of experimental data and calculated values by Pseudo first-order model. x in Li<sub>x</sub>FePO<sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of sulfite (SF) reduction

(B2 brine solution).



Figure 5.49 Comparison of experimental data and calculated values by shrinking sphere model. x in Li<sub>x</sub>FePO<sub>4</sub> vs. time at 25 °C, 45 °C and 65 °C in the case of sulfite (SF) reduction (B2 brine solution).

## 5.8. Summary

The preparation of FP as an adsorbent was studied. It was challenging to prepare ferric phosphate from FPD and reagent-grade LFP, but persulfate oxidation of battery-grade LFP successfully made heterosite FP, which can be used for lithium extraction. Next, a variety of reducing agents was studied. Out of Cu<sup>+</sup>, TS and SF, TS and SF seemed appropriate for the lithium recovery reaction. The cuprous reduction experiments were not successful. With the adsorbent and reducing agents, all the experiments were carried out. By checking XRD patterns, it was found that FP was successfully reduced to LFP in most cases with a significant dependence on temperature. When sulfite is used for brine solution containing calcium ions, calcium sulfite salts were produced. At 65 °C, sodium iron phosphate was formed in the absence of lithium. Experimental results showed the lithium adsorption density could be the same as the theoretical value of 46.0 mg/g. For example, the value was 45.9 mg/g in the case of sulfite reduction at 65 °C. Lithium selectivity was also high. The selectivity over sodium, for instance, 2541 in the case of sulfite reduction at 45 °C. There were pH changes during experiments, but they didn't have much impact on adsorption density and iron dissolution. However, 40% of iron was extracted when thiosulfate was used at 65 °C. The dissolution of iron can be prevented by pH control to  $\sim$  7. When it comes to practical operation, FP and LFP should be recycled. The cycle of the loading and stripping test was repeated, and it was confirmed that FP and LFP could be recycled without degradation. In the last, kinetics was studied by using Pseudo first-order model and shrinking sphere model. These models were well fitted to experimental results and found that the lithium extraction reaction was chemical reaction controlled in both thiosulfate and sulfite cases.

# **Chapter 6.** Conclusion

Lithium is now getting more and more attention from around the world as an essential material for various energy storage systems, especially for electric vehicles, and demand for lithium has been increasing rapidly. To meet the demand, lithium has been mined from ore minerals and brines. Since it is known that brines have more lithium reserves than ore minerals in the world, many researchers are now studying how to recovery lithium effectively from brine. The difficulty is that brine contains a high concentration of sodium, potassium, magnesium and calcium, which limit selective extraction of lithium. Conventionally, solar evaporation has been used to reject those cations into a solid phase and concentrate lithium in brine. However, as the evaporation process takes more than one year and is highly dependent on climatological conditions, a more rapid process is strongly desired for the accelerating demand. Therefore, many studies have investigated new rapid lithium recovery methods using ion exchange resin, solvent extraction, inorganic absorbents such as manganese oxide, titanium oxide and ferric phosphate, phosphate precipitation, nanofiltration, membrane electrolysis and so forth. This thesis focuses on two types of adsorbents: ion exchange (IX) resin and heterosite-type ferric phosphate (FP).

First, IX resin was studied. More than twenty cation exchange resins were tested in both lithium chloride solution without any other metal cations and a mixed saline solution containing lithium, sodium, potassium, magnesium and calcium chloride. Sulfonate, iminodiacetate and aminomethylphosphonate resins successfully extracted lithium from the lithium chloride solution. The resins recovered 16.3–32.9 mg of lithium per one gram of dried resins. However, no resins could adsorb lithium strongly or selectively from the saline solution with less than 1 mg of lithium per one gram of dried resins in loading. This behavior was due to the lack of selectivity for lithium

extraction. Sodium, potassium, magnesium and calcium ions compete with the lithium adsorption. Therefore, aluminum loaded resin, which some past studies reported that had relatively good selectivity for lithium, was also tested. This resin extracts lithium on the surface in the form of LiCl·2Al(OH)<sub>3</sub>·nH<sub>2</sub>O. It showed higher capacity and selectivity than any other resins tested in this study in the saline solution with the value of 6.6 mg/g. Nevertheless, overall, it was found that IX resins poorly suited for lithium recovery.

A second study focused on FP as an adsorbent. FP can adsorb lithium ion from solution by a reduction reaction and turns to lithium iron phosphate (LFP). As a second step, an oxidizing agent can strip lithium and regenerate FP. In this project, sodium thiosulfate (TS) or sodium sulfite (SF) was used as a reducing agent. By analyzing X-ray diffraction patterns of the products after the reduction, it was found that FP was successfully reduced to LFP in most cases with faster reaction at a higher temperature. However, when SF was used as a reducing agent for lithium loading from a brine solution containing calcium ions, calcium sulfite salts were produced. In addition, at 65 °C, sodium iron phosphate was formed in addition to LFP. The maximum of lithium adsorption capacity was almost the same value as the theoretical value of 46.0 mg-Li/g-FP. For example, the value was 45.9 mg/g in the case of SF reduction at 65 °C. Lithium selectivity was also high. The selectivity over sodium, for instance, 2541 in the case of SF reduction at 45 °C. When TS and SF are compared as a reducing agent, TS is better when a brine solution contains calcium because SF produces calcium sulfite. On the other hand, SF needs an only half dosage of TS since SF reacts with FP with the ratio of one to two while TS does with the ratio of one to one. There was a pH decrease from around 7 to 4 during experiments, but pH did not have much impact on adsorption capacity. However, 40% of iron was dissolved when TS was used for reduction at 65 °C. This problem of iron dissolution can be prevented by pH control in the neutral region of – 7. When it comes to practical operation, FP should be recycled. The cycle of the loading and

stripping test was repeated, and it was confirmed that FP could be recycled without degradation. In the last part of the study, the kinetics of lithium extraction was also studied and fit using both Pseudo first-order model and shrinking sphere model. These models fit the experimental results and indicated that the lithium extraction reaction was chemical reaction controlled in both the TS and SF cases.

In conclusion, as this study found out that the ferric phosphate method is a promising technology, it is recommended that this technology be developed further by using natural brine sources.

# References

- Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. J. Appl. Crystallogr. 2011, 44 (6), 1272–1276. https://doi.org/10.1107/S0021889811038970.
- (2) Chagnes, A.; Swiatowska, J. Lithium Process Chemistry: Resources, Extraction, Batteries, and Recycling; Elsevier: Amsterdam, Netherlands, 2015. https://doi.org/10.1016/B978-0-12-801417-2.00007-4.
- (3) United States Geological Survey. *Mineral Commodity Summaries 2018*; 2018.
- (4) Vikström, H.; Davidsson, S.; Höök, M. Lithium Availability and Future Production Outlooks. *Appl. Energy* 2013. https://doi.org/10.1016/j.apenergy.2013.04.005.
- (5) Lee, J. M.; Bauman, W. C. Recovery of Lithium from Brines. Patent US4159311A, 1979.
- (6) Lee, J. M.; Bauman, W. C. Recovery of Lithium from Brines. Patent US4347327A, 1982.
- John L. Burba, I. Method of Making Crystalline 2-Layer Lithium Aluminates in Ion Exchange Resins. Patent US4461714A, 1984.
- Nishihama, S.; Onishi, K.; Yoshizuka, K. Selective Recovery Process of Lithium from Seawater Using Integrated Ion Exchange Methods. *Solvent Extr. Ion Exch.* 2011, 29 (3), 421–431. https://doi.org/10.1080/07366299.2011.573435.
- (9) Tenova. Tenova Lithium Recover Process.
- (10) Tenova. Lithium Processing https://www.tenova.com/product/lithium-processing/
   (accessed Nov 29, 2018).
- Bauman, W. C.; John L. Burba, I. Recovery of Lithium Values from Brines. Patent US5389349A, 1995.

- (12) Bauman, W. C.; John L. Burba, I. Recovery of Lithium Values from Brines. Patent US5599516A, 1997.
- Bauman, W. C.; John L. Burba, I. Composition for the Recovery of Lithium Values from Brine and Process of Making/Using Said Composition. Patent US6280693B1, 2001.
- (14) Harrison, S.; Sharma, C. V. K.; Viani, B. E.; Peykova, D. Lithium Extraction Composition and Method of Preparation Thereof. Patent US8637428B1, 2014.
- (15) John L. Burba, I.; Stewart, R. F.; Viani, B. E.; Harrison, S.; Vogdes, C. E.; Lahlouh, J. G.S. Sorbent for Lithium Extraction. Patent US8753594B1, 2014.
- (16) Boualleg, M.; Lafon, O.; Burdet, F. A. P.; Soulairol, R. C. J. R. Method of Preparing an Adsorbent Material Shaped in the Absence of Binder and Method of Extracting Lithium from Saline Solutions Using Said Material. Patent US20160317998A1, 2016.
- (17) Ooi, K.; Miyai, Y.; Katoh, S. Recovery of Lithium from Seawater by Manganese Oxide Adsorbent. *Sep. Sci. Technol.* **1986**. https://doi.org/10.1080/01496398608056148.
- (18) Miyai, Y.; Ooi, K.; Kato, S. Adsorbent for Lithium and a Method for the Preparation Thereof. Patent US4665049A, 1987.
- (19) Chitrakar, R.; Kanoh, H.; Miyai, Y.; Ooi, K. Recovery of Lithium from Seawater Using Manganese Oxide Adsorbent (H1.6Mn1.6O4) Derived from Li1.6Mn1.6O4. *Ind. Eng. Chem. Res.* 2001, 40 (9), 2054–2058. https://doi.org/10.1021/ie000911h.
- (20) Chitrakar, R.; Makita, Y.; Ooi, K.; Sonoda, A. Magnesium-Doped Manganese Oxide with Lithium Ion-Sieve Property: Lithium Adsorption from Salt Lake Brine. *Bull. Chem. Soc. Jpn.* 2013, 86 (7), 850–855. https://doi.org/10.1246/bcsj.20130019.
- (21) Chitrakar, R.; Makita, Y.; Ooi, K.; Sonoda, A. Lithium Recovery from Salt Lake Brine by H2TiO3. *Dalt. Trans.* 2014. https://doi.org/10.1039/c4dt00467a.
- (22) Neometals. Successful 'Proof of Concept' testing of Direct Lithium and Potassium

Extraction from Brines https://www.neometals.com.au/reports/749-DX01062017.pdf (accessed Nov 29, 2018).

- (23) Intaranont, N.; Garcia-Araez, N.; Hector, A. L.; Milton, J. A.; Owen, J. R. Selective Lithium Extraction from Brines by Chemical Reaction with Battery Materials. *J. Mater. Chem. A* 2014. https://doi.org/10.1039/c4ta01101e.
- (24) Intaranont, N. Selective Lithium Extraction from Salt Solutions by Chemical Reaction with FePO4, PhD Thesis, University of Southampton, 2015.
- (25) Owen, J. R.; Garcia-Araez, N.; Intaranont, N. Sequestration of Lithium.WO2015121684A1, 2015.
- (26) POSCO. POSCO Begins Lithium Production First Time in Korea http://www.posco.com/homepage/docs/eng5/jsp/prcenter/news/s91c1010025v.jsp?idx=27 01&onPage=1 (accessed Nov 29, 2018).
- (27) Jamasmie, C. POSCO to Buy Lithium Mining Rights in Argentina from Galaxy http://www.mining.com/posco-buy-lithium-mining-rights-argentina-galaxy/ (accessed Nov 29, 2018).
- (28) Somrani, A.; Hamzaoui, A. H.; Pontie, M. Study on Lithium Separation from Salt Lake Brines by Nanofiltration (NF) and Low Pressure Reverse Osmosis (LPRO). *Desalination* 2013, *317*, 184–192. https://doi.org/10.1016/J.DESAL.2013.03.009.
- (29) Bogner, S. Successful Independent Verification of the MGX Lithium Extraction Technology https://www.rockstone-research.com/images/PDF/MGX20en.pdf (accessed Nov 29, 2018).
- (30) McEachern, P. Lithium Recovery from Oilfield Produced Water Brine & Wastewater Treatment https://rockstoneresearch.com/images/pdfs/MGX\_TechnicalReportRapidLithiumExtractionProcess.pdf

(accessed Nov 29, 2018).

- Liu, X.; Chen, X.; Zhao, Z.; Liang, X. Effect of Na+ on Li Extraction from Brine Using LiFePO4/FePO4 Electrodes. *Hydrometallurgy* 2014, *146*, 24–28. https://doi.org/10.1016/J.HYDROMET.2014.03.010.
- (32) Liu, X.; Chen, X.; He, L.; Zhao, Z. Study on Extraction of Lithium from Salt Lake Brine by Membrane Electrolysis. *Desalination* 2015. https://doi.org/10.1016/j.desal.2015.08.013.
- (33) Romero, V. C. E.; Tagliazucchi, M.; Flexer, V.; Calvo, E. J. Sustainable Electrochemical Extraction of Lithium from Natural Brine for Renewable Energy Storage. *J. Electrochem. Soc.* 2019, *165* (10), A2294–A2302.
- (34) Díaz Nieto, C. H.; Palacios, N. A.; Verbeeck, K.; Prévoteau, A.; Rabaey, K.; Flexer, V.
   Membrane Electrolysis for the Removal of Mg2+ and Ca2+ from Lithium Rich Brines.
   *Water Res.* 2019, 154, 117–124. https://doi.org/10.1016/J.WATRES.2019.01.050.
- (35) Sawada, A. Current Situation of Lithium Resource Development in the World. *Bull. Soc. Sea Water Sci. Japan* 2012, 66, 2–7.
- (36) Manthiram, A.; Fu, Y.; Chung, S.-H.; Zu, C.; Su, Y.-S. Rechargeable Lithium–Sulfur Batteries. *Chem. Rev.* 2014. https://doi.org/10.1021/cr500062v.
- Martin, G.; Rentsch, L.; Höck, M.; Bertau, M. Lithium Market Research Global Supply, Future Demand and Price Development. *Energy Storage Mater.* 2017. https://doi.org/10.1016/j.ensm.2016.11.004.
- (38) Jamasmie, C. Lithium demand from battery makers to almost double by 2027
   http://www.mining.com/lithium-demand-battery-makers-almost-double-2027/ (accessed Sep 12, 2019).
- (39) Kavanagh, L.; Keohane, J.; Garcia Cabellos, G.; Lloyd, A.; Cleary, J. Global Lithium

Sources—Industrial Use and Future in the Electric Vehicle Industry: A Review. *Resources* **2018**. https://doi.org/10.3390/resources7030057.

- (40) JOGMEC. Metal Resources Report, Current Situation of Lithium Resources; 2010.
- (41) Canada lithium Corp. Objective Capital Rare Earth and Minor Metals Investment Summit: The challenges of developing a lithium project – reopening the Quebec Lithium Project – Peter Secker https://www.slideshare.net/objectivecapital/objective-capital-rare-earth-andminor-metals-investment-summit-the-challenges-of-developing-a-lithium-projectreopening-the-quebec-lithium-project-peter-secker (accessed Dec 29, 2018).
- (42) JOGMEC. Introduction of Cases of Metal Recovery and Refining Technology Development from Seawater and Brines; 2016.
- (43) Rodinia Lithium. Exploring Lithium http://rodinialithium.com/ (accessed Sep 29, 2018).
- (44) Rumble, J. R.; Lide, D. R.; Bruno, T. J.; Martinsen, D. CRC Handbook of Chemistry and Physics, 99th Print.; CRC Press: Boca Raton, U.S., 2018.
- (45) Kim, K. J. Recovery of Lithium Hydroxide from Spent Lithium Carbonate Using Crystallizations. *Sep. Sci. Technol.* 2008. https://doi.org/10.1080/01496390701784088.
- (46) Kumar, A.; Fukuda, H.; Hatton, T. A.; Lienhard, J. H. Lithium Recovery from Oil and Gas Produced Water: A Need for a Growing Energy Industry. *ACS Energy Lett.* 2019, 1471–1474. https://doi.org/10.1021/acsenergylett.9b00779.
- (47) Chon, U.; Lee, I. C.; Kim, K. Y.; Han, G.-C.; Song, C. H.; Jung, S. R. Method for Manufacturing Lithium Hydroxide and Method Using Same for Manufacturing Lithium Carbonate. Patent US9598291B2, 2017.
- (48) Ooi, K.; Miyai, Y.; Katoh, S. Recovery of Lithium from Seawater by Manganese Oxide Adsorbent. *Sep. Sci. Technol.* 1986, *21* (8), 755–766.
  https://doi.org/10.1080/01496398608056148.

- (49) Cohen, L.; McCallum, T.; Tinkler, O.; Szolga, W. Technological Advances, Challenges and Opportunities in Solvent Extraction from Energy Storage Applications. In *Extraction* 2018 Preceedings; 2018; pp 2033–2045.
- (50) Bjorling, C. O.; Westgren, A. Minerals of the Varustrask Pegmatite. IX. X-Ray Studies of Triphylite, Varulite and Their Oxidation Products. *Geol. Föreningens i Stock. Förhandlingar* 1938, 60, 67–72.
- (51) Losey, A.; Rakovan, J.; Hughes, J. M.; Francis, C. A.; Dyar, M. D. Structural Variation in the Lithiophilite-Triphylite Series and Other Olivine-Group Structures. *Can. Mineral.* **2004**, *42* (4), 1105–1115. https://doi.org/10.2113/gscanmin.42.4.1105.
- (52) Okubo, M.; Asakura, D.; Mizuno, Y.; Kim, J.-D.; Mizokawa, T.; Kudo, T.; Honma, I. Switching Redox-Active Sites by Valence Tautomerism in Prussian Blue Analogues AxMny[Fe(CN)6]·nH2O (A: K, Rb): Robust Frameworks for Reversible Li Storage. J. Phys. Chem. Lett. 2010, 1 (14), 2063–2071. https://doi.org/10.1021/jz100708b.
- (53) Islam, M. S.; Daniel J. Driscoll; Fisher, C. A. J.; Slater, P. R. Atomic-Scale Investigation of Defects, Dopants, and Lithium Transport in the LiFePO4 Olivine-Type Battery Material. *Chem. Mater.* 2005, *17* (20), 5085–5092. https://doi.org/10.1021/CM050999V.
- (54) Ellis, B. L.; Lee, K. T.; Nazar, L. F. Positive Electrode Materials for Li-Ion and Li-Batteries. *Chem. Mater.* 2010, 22 (3), 691–714. https://doi.org/10.1021/cm902696j.
- (55) Morgan, D.; Van der Ven, A.; Ceder, G. Li Conductivity in LixMPO4 (M=Mn, Fe, Co, Ni) Olivine Materials. *Electrochem. Solid-State Lett.* 2004, 7 (2), A30–A32. https://doi.org/10.1149/1.1633511.
- (56) Allen, J. L.; Jow, T. R.; Wolfenstine, J. Kinetic Study of the Electrochemical FePO4 to LiFePO4 Phase Transition. *Chem. Mater.* 2007, *19* (8), 2108–2111. https://doi.org/10.1021/CM062963O.

- (57) Wang, J.; Sun, X. Olivine LiFePO4: The Remaining Challenges for Future Energy Storage. *Energy Environ. Sci.* 2015, 8 (4), 1110–1138.
   https://doi.org/10.1039/C4EE04016C.
- (58) Wu, B.; Ren, Y.; Li, N. LiFePO4 Cathode Material. In *Electric Vehicles The Benefits* and Barriers; Soylu, S., Ed.; IntechOpen: London, U.K., 2011; pp 199–216. https://doi.org/10.5772/18995.
- (59) Satyavani, T. V. S. L.; Srinivas Kumar, A.; Subba Rao, P. S. V. Methods of Synthesis and Performance Improvement of Lithium Iron Phosphate for High Rate Li-Ion Batteries: A Review. *Engineering Science and Technology, an International Journal*. 2016. https://doi.org/10.1016/j.jestch.2015.06.002.
- (60) Padhi, A.K.; Nanjundaswamy, K.S.; Masquelier, C.; Okada, S. Goodenough, J. B. Effect of Structure on the Fe3+/Fe2+ Redox Couple in Iron Phosphates. *J. Electrochem. Soc.* 1997. https://doi.org/10.1149/1.1837649.
- (61) Chen, J.; Vacchio, M. J.; Wang, S.; Chernova, N.; Zavalij, P. Y.; Whittingham, M. S. The Hydrothermal Synthesis and Characterization of Olivines and Related Compounds for Electrochemical Applications. *Solid State Ionics* 2008. https://doi.org/10.1016/j.ssi.2007.10.015.
- (62) Ramana, C. V.; Mauger, A.; Gendron, F.; Julien, C. M.; Zaghib, K. Study of the Li-Insertion/Extraction Process in LiFePO4/FePO4. *J. Power Sources* 2009. https://doi.org/10.1016/j.jpowsour.2008.11.042.
- (63) Chitrakar, R.; Kanoh, H.; Miyai, Y.; Ooi, K. Recovery of Lithium from Seawater Using Manganese Oxide Adsorbent (H 1.6 Mn 1.6 O 4) Derived from Li 1.6 Mn 1.6 O 4. Ind. Eng. Chem. Res. 2001. https://doi.org/10.1021/ie000911h.
- (64) Chitrakar, R.; Makita, Y.; Ooi, K.; Sonoda, A. Selective Uptake of Lithium Ion from

Brine by H 1.33 Mn 1.67 O 4 and H 1.6 Mn 1.6 O 4 . *Chem. Lett.* **2012**. https://doi.org/10.1246/cl.2012.1647.

- Yu, Q.; Sasaki, K.; Hirajima, T. Bio-Templated Synthesis of Lithium Manganese Oxide Microtubes and Their Application in Li+ Recovery. *J. Hazard. Mater.* 2013. https://doi.org/10.1016/j.jhazmat.2013.08.027.
- (66) Zhang, Q. H.; Li, S. P.; Sun, S. Y.; Yin, X. S.; Yu, J. G. Lithium Selective Adsorption on 1-D MnO2 Nanostructure Ion-Sieve. *Adv. Powder Technol.* 2009. https://doi.org/10.1016/j.apt.2009.02.008.
- (67) Kuss, C.; Carmant-Dérival, M.; Trinh, N. D.; Liang, G.; Schougaard, S. B. Kinetics of Heterosite Iron Phosphate Lithiation by Chemical Reduction. *J. Phys. Chem. C* 2014. https://doi.org/10.1021/jp502346f.
- (68) Rettig, S. L.; Jones, B. F.; Risacher, F. Geochemical Evolution of Brines in the Salar of Uyuni, Bolivia. *Chem. Geol.* 1980. https://doi.org/10.1016/0009-2541(80)90116-3.
- (69) JOGMEC; Toyota Tsusho. Joint Study of Process Development of Lithium Separation and Refining at Salar Brines in Puna Region, Argentina; 2011.
- (70) Nuibe, Y. Lithium Resources in Argentina and Projects of Exploration Development;2013.
- (71) Dixon, D. G. Chloride-Based Leaching of Sulfides: Principles and Practice.
- (72) Druschel, G. K.; Hamers, R. J.; Banfield, J. F. Kinetics and Mechanism of Polythionate Oxidation to Sulfate at Low PH by O2 and Fe3+. *Geochim. Cosmochim. Acta* 2003. https://doi.org/10.1016/S0016-7037(03)00388-0.
- (73) House, J. E. Inorganic Chemistry; Elsevier Inc., 2008.