Recovery and regeneration of lithium manganese oxide from spent lithium-ion batteries

Santosh Mathew

University of Nevada, Las Vegas

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RECOVERY AND REGENERATION OF
LITHIUM MANGANESE OXIDE
FROM SPENT LITHIUM-ION
BATTERIES

by

Santosh Mathew
Bachelor of Science
Calicut University, India
1990

A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science

in

Civil and Environmental Engineering

Department of Civil and Environmental Engineering
University of Nevada, Las Vegas
May 1998

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The Thesis prepared by

SANTOSH MATHEW

Entitled

RECOVERY AND REGENERATION OF LITHIUM MANGANESE OXIDE FROM SPENT LITHIUM BATTERIES

is approved in partial fulfillment of the requirements for the degree of

Master of Science in Civil and Environmental Engineering

Examination Committee Chair

Examination Committee Member

Examination Committee Member

Graduate College Faculty Representative

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ABSTRACT

Recovery And Regeneration of Lithium Manganese Oxide From Spent Lithium-Ion Batteries

by

Santosh Mathew

Dr. David James. Examination Committee Chair
Professor of Civil and Environmental Engineering
University of Nevada, Las Vegas

This study presents a method for recovering and regenerating Lithium Manganese Oxide (LMO) from spent Lithium-polymer batteries in order to recycle it in an environmentally friendly way. Two different processes for separating LMO were developed and the environmental impact of the two processes was analyzed. A process for relithiating the lithium-deficient LMO after recovery was also developed. Experiments were carried out to determine the regeneration chemical process parameters, and process conditions were optimized for the best spinel LMO formation. Various physical and chemical analysis of the regenerated LMO showed that its all major characteristics, such as crystal structure and manganese oxidation state, are in agreement with the LMO used in the original process of battery making. The electrochemical behavior of the regenerated LMO was studied and the results reinforced the feasibility of the recovery and regeneration processes.
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CHAPTER 1

INTRODUCTION

Energy consumption, like population, is not distributed evenly. While the energy usage of developed countries is already high and is expected to rise further, developing countries will require enormous energy sources to raise their economies to levels of the developed countries, and hence the global energy consumption is expected to double at least by the middle of the next century. Current energy needs are nearly totally dependent on fossil fuels and this excessive use of fossil fuels raises two major concerns to the future of mankind: the limit of the energy sources and the negative impact on the global environment. Therefore, what is needed for the future is an efficient and uninterrupted power source.

A battery, by definition, is an electrochemical device that generates electric current by converting chemical energy to electrical energy. A wide range of batteries have been used since the invention of the first electrochemical device because of their convenience as portable power source. However, the constraints imposed by growing environmental concerns in large urban areas, the wide use of consumer electronic products, and the need for a more rational utilization of our energy resources urgently call for new and efficient electrochemical power sources. Increasing use of portable devices such as cellular phones, camcorders and computers, where the high degree of sophistication of the electronic circuitry is contrasted by a still inadequate battery package, has lead to the development of high-energy density rechargeable batteries. High-energy density batteries are also needed for the development of long range electric vehicles in order to improve air quality in congested cities. Starting from the first generation batteries,
the electrochemical cell has now advanced to the lithium-ion (Li-ion) rechargeable cell where the theoretical energy density of a lithium battery expressed as milli-amp hours per gram (mAhr/g) significantly exceeds that of more conventional electrochemical systems, such as lead-acid, nickel cadmium, or the most recently developed nickel-metal hydride (Journal of Power Sources. 1997).

Concerns about environmental problems created by spent batteries have forced scientists, engineers and environmentalists to think of suitable disposal methods for spent batteries. These environmental concerns, coupled with the profitability of the industry, have led to the invention of recycling processes of battery components and battery chemicals from most of the widely used batteries. The new generation, high power Li-ion battery may claim a large market share in the future because of its many advantages such as high capacity and energy intensity over its predecessors. Therefore, there are going to be some environmental problems associated with the lithium batteries if no proper disposal or recovery methods are developed. This study was aimed at addressing these environmental problems by suggesting suitable methods to recycle the lithium-ion battery components.

**Thesis Outline and Objectives**

In this thesis, two different methods of recovering and regenerating the active cell chemicals of spent lithium-ion batteries are studied in order to recycle them effectively. The methods address the following issues:

1. **Develop a method for recovering Lithium Manganese Oxide (LMO) from the positive electrode of a lithium-ion spent battery.**

2. **Develop a process to regenerate the recovered lithium-deficient LMO to the standard spinel LMO used as raw material.**
3. Analyze the chemical and physical characteristics of the recovered and regenerated LMO and compare them with the standard LMO.

4. Demonstrate experimentally the recyclability of the recovered LMO by making a cell with recovered material, carrying a charge-discharge cycle analysis, and comparing results to charge-discharge cycle performance of standard LMO.

From this study, the development of a technically and economically feasible technology for the recycling of lithium manganese oxide from spent Li-ion battery is expected.
Concerns about the environmental impacts of batteries are higher now compared to the recent past. This is good news from the environmental standpoint, but there has not been much work done on the recycling of new generation batteries. Although ninety-eight percent of lead-acid batteries from automotive electrical systems are now commercially recycled after use (Gains and Singh, 1996), there have been few attempts to concentrate sufficient amounts of small batteries in a single location for economic recycling. Except for automotive lead-acid batteries, the technology to recycle battery components and chemicals for other battery types such as sodium/sulfur, nickel/cadmium and nickel metal hydride has not been developed commercially. This is because the primary focus of interest has been to design and develop new batteries and little importance given to the recycling of them. Also, most of the information is proprietary.

It is the purpose of this study to explore the feasibility of recycling the spent Li-ion batteries. US patent Nos. 5,352,270 (Shackle, 1994) and 5,491,037 (Kawakami, 1996) explain the approaches for recovering metallic lithium by opening the lithium cell in an ignition free environment, washing the cell by submersion in water and maintaining the cell submerged in water until the metallic lithium is converted to lithium hydroxide. Therefore, recycling of lithium cells to date has focused on crushing and pulverizing the cell submerged under water and encouraging formation of lithium hydroxide as safely as possible. In the prior art, the objective has been to separate and recover lithium, with no treatment specified for other components. Therefore, what is needed is a method to recover the Li in its metallic oxide form, and other materials from the spent lithium-ion cell.
to foster the objective of recycling. A recent article (Tedjar, 1997) mentioned that electroactive manganese dioxide could be recovered from battery scrap by a hydrometallurgical process followed by purification treatments.

A lithium-ion cell has a lithium metal oxide (LiMO₂, where M = Mn, Ni, Co) positive electrode that has a special lattice (crystalline structure) enabling the Li-ion to migrate between anode and cathode during charge-discharge cycles, and a graphite or carbon anode. A 1 molar solution of lithium hexafluorophosphate (LiPF₆) in EC-PC or EC-DMC solvent mixtures (EC = ethylene carbonate, PC = propylene carbonate, DMC = dimethyl carbonate) is used as electrolyte. Because of the economical and environmental advantages, lithium manganese oxide (LMO) cathode has attracted great deal of research.

For the last two decades there has been an increasing interest in lithium batteries due to their high specific capacity (3800 Ahr/kg of lithium compared to only 260 Ahr/kg for lead) and highly electropositive nature of the lithium metal, leading to high voltage cells (Tarascon, J. M. 1993). Li has a standard reduction potential of -3.01 V at 25 °C which is highest among other anode materials. Li is the first in the alkali metal group in the periodic table of elements. The ease of involving the outermost (2s¹) electron in bonding, coupled with the very high second stage ionization energy, immediately explains both the great chemical reactivity of the metal and the fact that its oxidation state in compounds never exceeds +1. Metallic lithium is highly reactive and acts as a powerful reducing agent.

The lithium metal is not abundant on earth. Lithium tends to occur in ferromagnesian minerals where it partly replaces magnesium. It occurs to the extent of about 18 ppm by weight in crustal rocks, and this reflects its relatively low abundance in the cosmos (Greenwood, 1984). The most important mineral is spodumene, LiAlSi₂O₆, and large deposits occur in the USA, Canada, Brazil, Argentina, Russia, Spain and the Congo. The complex metallurgical operations involved in the separation of Li metal from its ore make lithium costly, and the increasing usage of Li in the battery industry increases its scarcity. Therefore, any technology that is intended to recycle lithium metal or lithium compounds is very important from the economic and environmental point of view.
Among the problems associated with the recycling of LMO from used battery cells, the most important is the structural distortions happened to the LMO spinel as the effect of continued cycling. It has been demonstrated (Wen et al. 1996) that in the 3V region, the electroactive material becomes electronically disconnected from the rest of the cathode due to the fracture of oxide particles and/or expansion and contraction of the active material (LMO) during cubic-to-tetragonal phase transformation. In the upper voltage region, the active material is gradually converted to a lower voltage defect spinel phase via dissolution of manganese in the electrolyte. This will also cause the formation of other forms of lithium and manganese oxides. Therefore, the recovered LMO from used battery needs a regeneration process to retain the spinel in order to recycle it.

**Electrochemical Cell**

A battery is a device that converts chemical energy contained in its active materials directly into electrical energy by means of an electrochemical oxidation-reduction reaction involving the transfer of electrons from one material to another through an electric circuit. A battery consists of one or more electrochemical cells connected in series or parallel depending on the desired output voltage and capacity. Figure 2.1 shows a schematic representation of three major components of a cell: Anode, Cathode and Electrolyte. These three components are selected according the power and voltage requirements to a specific use. Also, it depends on the design criteria appropriate for the intended use of the cell.

**Operation of a cell**

As shown in Figure 2.1, due to the electrochemical reaction between the anode and cathode electrodes, energy is produced as electric current. When the cell is connected to an external load, electrons flow from the anode, which is oxidized, through the external load to the cathode, where the electrons are accepted and cathode material is reduced.
Operation of a Cell

Figure 2.1: Electrochemical discharge of a cell (Linden, 1995). Electrons flow from the anode to cathode through the external load and the ions travel through the electrolyte to the respective electrodes.

The electric circuit is completed in the electrolyte by the flow of anions (negative ions) and cations (positive ions) to the anode and cathode respectively. For the battery type that is the subject of this investigation, the discharge reactions are:

anodic reaction, example: lithium metal
\[ \text{Li} \rightarrow \text{Li}^- + e^- \]  
\[ \text{Equation 2.1} \]

cathodic reaction, example: MnO₂
\[ \text{MnO}_2 + e^- \rightarrow \text{MnO}_2^- \]  
\[ \text{Equation 2.2} \]

The charging cycle of a rechargeable battery is just the reverse operation of discharge. During charging, the current flow is reversed and reduction takes place at the new positive electrode and oxidation at the new negative electrode. The new positive electrode is now the battery's anode and the new negative electrode is the battery's cathode.
Whenever a chemical reaction occurs, there is a decrease in the free energy of the system, which is a function of temperature and concentration of the system, and is expressed as:

\[ \Delta G = \Delta G'' - RT \ln \left( \frac{C_{\text{product}}}{C_{\text{reactant}}} \right) \]  

where \( \Delta G'' \) = change in free energy at 25 °C and 1 atm

\( R \) = the ideal gas constant (1.99 Cal/mole °K)

\( T \) = absolute temperature (°K)

\( C \) = the active concentration

When no net current is flowing, the equilibrium potential of the cell is given by the Nernst equation (Perry and Green, 1997):

\[ E'' = -\frac{\Delta G_t}{nF} \]  

where \( F \) = Faraday’s constant (268 Ahr)

\( \Delta G_t \) = change in free energy at the cell’s operating temperature

\( n \) = number of electrons involved in stoichiometric reaction

\( E'' \) = electrochemical equilibrium potential (V)

When current is flowing, the actual cell operating potential is given by:

\[ E = E'' - \left( a_m - a_{ca} \right) - \left( b_m + b_{ca} \right) \left( \frac{RT}{nF} \right) \ln i - A_i \]  

where \( a, b \) = characteristic constants for the electrochemical reactions at the electrode materials

\( i \) = current density (A/cm²)

\( A \) = area-specific resistance of the cell (Ω-cm)

The standard potential or the cell voltage of a cell can be calculated from the standard electrode potentials as follows:
Anode (oxidation potential) - cathode (reduction potential) = standard cell potential \[ 2.6 \]

The capacity of a cell is expressed as the total quantity of electricity involved in the electrochemical reaction and is defined in terms of coulombs or ampere-hours. The theoretical capacity of a battery system, based only on the active materials participating in the electrochemical reaction, is calculated from the equivalent weight (Ah/g or g/Ah) of the reactants.

Batteries are classified mainly into two types:
- Primary or nonrechargeable cells
- Secondary or rechargeable cells.

Primary cells are not capable of being recharged electrically and, hence, are used (discharged) once and discarded. The primary battery is convenient, usually relatively inexpensive, light weight source of packaged power for portable electronic and electric devices. The general advantages are good shelf life, high energy density at low to moderate discharge rates, and ease of use. The vast majority of primary cells are small cylindrical or button cells.

Secondary cells can be recharged electrically after discharge, to their original condition. Therefore they are reusable storage devices for electrical energy. Two main categories of application of the secondary batteries are:

1. being electrically connected and charged by a prime energy source and delivering its energy to a load on demand. Examples are, aircraft and automotive systems, emergency no-fail and standby power sources, and stationary energy storage (SES) systems for electric utility load leveling.

2. being used and discharged like a primary battery, but recharged after use rather than being discarded. Examples are, batteries in portable consumer electronics, electric vehicles, and in applications requiring power drains beyond the capability of primary cells.

Li is used in both primary and secondary cells and several lithium systems (CuO/Li, MnO₂/Li and FeS₂/Li) have been commercialized. In all these systems, metallic Li is used as anode (negative) electrode and several safety problems are associated with use of metallic Li, including high reactivity with water with evolution of hydrogen gas.
The advantages and disadvantages of the lithium rechargeable cell are listed below:

**Advantages**
1. High energy density
2. High voltage
3. Good charge retention, low self-discharge rate

**Disadvantages**
1. Low cycle life with metallic lithium system
2. Relatively poor high-rate performance
3. Capacity fading
4. Potential safety problems with metallic Li systems

**Li-Ion Battery**

More recently the Li-ion system, which has a potential safety advantage over other lithium secondary cells as it does not contain lithium in a metallic form, has been marketed as a power source for consumer electronics and a potential power source for emission-free vehicles. In place of Li-metal, a material able to reversibly intercalate Li-ions is used in the Li-ion cells. An intercalation compound is comprised of a crystalline lattice that acts as an electron donor and "foreign" electron acceptor atoms interspersed or diffused between the planes of the lattice. A battery with intercalation compounds has been called the "rocking chair" (Tarascon. J. M. 1993) battery because Li-ions rock back and forth between the intercalation compounds during charge-discharge cycles (Figure 2.2).

Both the cathode and anode materials are intercalation compounds. The output voltage of the Li-ion cell is determined by the difference between the electrochemical potential of lithium with the two lithium intercalating electrodes. It is important to have, as the positive and negative electrodes, cheap compounds that can reversibly intercalate Li at high and low voltages, respectively. The Li intercalation voltage for some interaction compounds is shown in Figure 2.3 (Tarascon. J. M. 1993; Linden. 1995). As indicated by the figure, there are only three Li-based compounds, LiNiO₂, LiCoO₂, and LiMn₂O₄, that satisfy the requirement of reverse intercalation of Li above 4V. LiNiO₂ and LiCoO₂ have
layered structures, where the lithium and transition metal cations occupy alternate layers of octahedral sites in a distorted cubic close-packed oxygen-ion lattice. The layered metal oxide framework provides a two-dimensional interstitial space which allows for the easy removal of the lithium ions. The LiMn$_2$O$_4$ spinel framework possesses a three-dimensional space via face-sharing octahedral and tetrahedral structures provide the shared faces conducting pathways for the insertion and extraction of Li-ions.

**Li-Ion Battery**

![Diagram of Li-Ion Battery](image)

Figure 2.2: The charge-discharge mechanism of a lithium-ion battery. Both the cathode and anode materials are intercalation compounds (Tarascon, 1993).
The reversible capacity of the above three cathode materials is about the same (135mAh/g), but among them the LiMn$_2$O$_4$ spinel has attracted a great deal of research because of its environmental and economic advantages. It is more abundant, less expensive than the other compounds and nontoxic too.

The removal and insertion of the Li-ion for the lithium manganese oxide is:

$$\text{LiMn}_2\text{O}_4 \leftrightarrow \text{Li}_{1-x}\text{Mn}_2\text{O}_4 + x\text{Li}^- + xe^-$$

Use of spinel manganese oxide material instead of layered cobalt oxide or nickel oxide has an additional advantage that LiMn$_2$O$_4$ can intercalate a second lithium atom at an average voltage of 3V. Further studies by Bellcore (Tarascon, 1993) show this second plateau is used as a Li reservoir to improve the specific capacity of these batteries. They have also developed a new electrolyte composition that has good range (0-5V) of stability against electrolyte oxidation. Research and development by the Valence Technology on the original Bellcore method of making Li-ion battery has further advanced the

Electrochemical Potential Range of Li-Intercalation Compounds

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Li$_x$CoO$_2$</th>
<th>Li$_x$NiO$_2$</th>
<th>Li$_x$MnO$_2$</th>
<th>Li$_x$MoO$_2$</th>
<th>Li$_x$V$_2$O$_5$</th>
<th>Li$_x$TiS$_2$</th>
<th>Li$_x$WO$_2$</th>
<th>Li$_x$Al</th>
<th>Li$_x$Graphite</th>
<th>Li$_x$Coke</th>
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<tr>
<td>5</td>
<td></td>
<td></td>
<td>Spinel</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Li$_x$V$_2$O$_5$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Li$_x$CoO$_2$</td>
<td>Li$_x$NiO$_2$</td>
<td>Li$_x$MnO$_2$</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>Li$_x$MoO$_2$</td>
<td></td>
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</tr>
<tr>
<td>1</td>
<td>Li$_x$WO$_2$</td>
<td>Li$_x$Al</td>
<td>Li$_x$Graphite</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Li metal</td>
<td></td>
<td></td>
<td>Li$_x$Coke</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>

Fig. 2.3: Electrochemical potential range of Li-intercalation compounds as measured with respect to Li metal for a wide variety of compounds (Linden, 1995).
technology. In these batteries (Levy, 1997), soft carbon (e.g., natural and synthetic graphite and petroleum coke) is used as the anode, where the intercalation mechanism of lithium occurs between the graphite layers via a staging mechanism:

$$\text{LiC}_{12} \rightarrow \text{LiC}_{12} \rightarrow \text{LiC}_6$$

The maximum reversible capacity is 372 mAh/g from stage 1, LiC₆, when cycled against Li. The main intercalation process occurs between 0.5V and 0.05V.

The polymeric electrolytic cell used for this study is comprised of polymeric film composite electrodes, separator membranes and electrolyte. The cathodic electrode is a compound of LMO with binder and a small percent of conductive carbon coated on both sides of a current collector grid, usually made of aluminum. The anodic electrode is a mixture of graphite and binder coated on a copper current collector. An electrode

Assembly of a Cell

![Diagram of Li-ion cell structure](http://example.com/diagram.png)

Figure 2.4: Typical Li-ion cell structure. Thickness and weight of electrodes are determined by the power requirements of the specific application.

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separator membrane composed of a polymeric matrix made ionically conductive by the incorporation of an organic solution of a lithium salt (electrolyte) which provides ionic mobility.

The thickness of each electrode varies from 300 microns to 900 microns depending on the mass ratio needed for the active ingredients in the anode and cathode electrodes. Therefore, the total thickness of a bicell, comprised of two anode electrodes and a cathode electrode, ranges from 500 microns to 2000 microns. A typical Li-ion bicell is shown in Figure 2.4. Any number of bicells can be connected in parallel or series to get the power and voltage for the intended use.

Since liquid electrolyte is used in the cell, the electrodes are soaked in the electrolyte. That is, the electrolyte impregnates through all the bicell layers and is present everywhere including the positive electrode.

**Lithium Manganese Oxide Cathode**

Lithium manganese oxide (LiMn$_2$O$_4$) has a normal spinel structure, but the Li-Mn-O system with spinel structure seems to be a complicated system. The stoichiometry can shift to any direction (Figure 2.5) and a defect structure occurs in valency disordered spinels because all crystallographically identical sites within the unit cell are not occupied by the same cation (Greenwood and Earnshaw, 1984). It has been reported that the electrochemical properties of the LMO spinel are very sensitive to the synthesis conditions and Li/Mn stoichiometry. Also, the crystal structure, Li reversible and irreversible capacity and electrochemical behavior are related to the chemical composition of the synthesized spinel. A stoichiometric LiMn$_2$O$_4$ can be written in terms of its valence as (Saidi, 1996)

\[
\text{Li}_z\text{Mn}^{3+}\text{Mn}^{4+}\text{O}_4
\]

where

\[
z + 3x + 4y = 8
\]
The structure of the spinel consisting of cubic close-packed oxide ions with manganese ions in half of the octahedral sites and lithium ion in an eighth of the tetrahedral sites. The Mn$_2$O$_4$ framework occupies a three-dimensional region via face-sharing octahedra and tetrahedra which provides pathways for the insertion and the extraction of Li ions. Thus, a lithium-rich spinel (Saidi. 1996) can be written as (Li)$_{x_a}$[Mn$_{2-x}$Li$_x$]$_{16d}$O$_4$. The 8a and 16d designate the sites where the lithium and manganese ions would be located in the standard spinel. Figure 2.5 (Berg, H. 1997) represents a lithium manganese oxide phase diagram.

Lithium manganese oxide compounds are available in two forms:

1. rock-salt-related, low voltage (above 3V vs. Li) Li$_{1-x}$Mn$_{2-x}$O$_4$ form capable of accepting Li

2. spinel-related, high voltage (above 4V vs. Li) Li$_{1-x}$Mn$_{2-x}$O$_4$ form capable of releasing Li

In the $0 \leq x \leq 1$ range, the electrode cycles around 4V vs. Li. The cubic symmetry of the spinel structure is maintained and the electrode compound may expand and contract isotropically during Li extraction-insertion process at this range. This, in turn, allows

LMO Phase Diagram

![LMO Phase Diagram](image)

Figure 2.5: Region of the phase diagram around Li$_{1-x}$Mn$_{2-x}$O$_4$ (Berg, H. 1997).
cyclic charging and discharging of the battery. The high voltage form of the lithium manganese oxide spinel is widely used because of its high voltage application.

In the $1 \leq x \leq 2$ range, the electrode cycles around $3\text{V vs Li}$. Following Li insertion, the average Mn ion valency falls below 3.5 and a Jahn-Teller distortion (distortion imposed by the higher concentration of $\text{Mn}^{3+}$) is induced in the compound structure, varying the crystal symmetry from cubic to tetragonal with a very large increase of the cathode/anode ratio of the unit cell. This affects the structural integrity and thus the electrode cyclability.

Lithium manganese oxide is traditionally manufactured by mixing appropriate amounts of $\text{Li}_2\text{CO}_3$ with a manganese oxide and heating at 850 °C in air (Hunter, 1981). Manganese oxides used include $\text{Mn}_3\text{O}_4$, $\text{Mn}_2\text{O}_4$ and $\text{MnO}$. Another method to prepare micron-sized spinel lithium manganese oxide is explained by Zhiping Jiang and K. M. Abraham (Jiang et al., 1996). A mixture of 1 to 4 molar ratio of $\text{Li}_2\text{CO}_3$ and $\text{MnCO}_3$ is dispersed in hexane and stirred for 3 hours. After removing the solvent by distillation, the mixture is heated at 850 °C in an atmosphere of flowing oxygen for several hours to obtain the spinel LMO.

A cathode electrode is fabricated by blending the $\text{LiMn}_2\text{O}_4$ powder with conductive carbon and binder coated on an aluminum current collector. The major disadvantage of the $\text{LiMn}_2\text{O}_4$ cathode electrode is that its capacity fades upon cycling. This may be due to electrolyte oxidation at high potential during charge, onset of Jahn-Teller distortion in deeply discharged $\text{Li}_x\text{Mn}_2\text{O}_4$, or to dissolution of Mn into electrolyte as $\text{Mn}^{2+} (2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} - \text{Mn}^{2+})$ with subsequent anodic Mn deposition leading to increasing cell resistance and polarization, or to loss of contact and morphological disuniformities in the cathodic blend. Several approaches have been used to overcome the above capacity fading problems and to improve battery cycling capabilities. They are:

a) incorporate excess lithium (Levy, 1997; Berg, H. 1997) into the spinel and thus create defects in the Mn-O lattice. By increasing the Li/Mn ratio, the 'extra' Li substitutes into the structure at the octahedral Mn vacancies which are created. This will increase the average Mn ion valency marginally above 3.5 in order to prevent Jahn-Teller effects. Also, increase in $\text{Mn}^{4+}$ content will suppress the disproportionation reaction and thus $\text{Mn}^{2+}$

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dissolution into the electrolyte. By the presence of the residual Li, the lattice contraction upon total extraction is restricted and thus reduces the volume changes and increases the structural stability. A study (Levy, Samuel C. 1997) of capacity vs. cycling number for Li$_{1-x}$Mn$_{2-x/3}$O$_4$ at various values of ‘x’ (Figure 2.6) shows that a better cycling stability can be achieved at the expense of initial capacity.

Cell Capacity at Various Li Contents

![Graph showing cell capacity at various Li contents](image)

Figure 2.6: Experimental result of cell cycling performance (discharge capacity) at various x of Li$_{1-x}$Mn$_{2-x/3}$O$_4$. With the presence of excess Li, better cycling stability is achieved at the expense of initial capacity (Levy, 1997).

The chemistry and behavior of excess Li in LiMn$_2$O$_4$ spinel is well explained (Saidi, Yazid 1996) in Table 2.1 where, the calculated theoretical capacity at various stoichiometries of lithium manganese oxide is listed. Therefore, there is a compromise between capacity retention and cycle life of the cell and it is recommended that x = 0.05 (or, a specification of x = 0.03 - 0.08) is optimum for the best performance.

b) Improvements of synthesis conditions approach.

Addition of Mn(CH$_3$COO)$_2$·4H$_2$O to a solution of Li$_2$CO$_3$ in a 4:1 mole ratio (Levy, 1997). The solids are precipitated out from the solution and fired at 600 °C. Final product obtained is expected to have improved cycle life.
c) The doping approach

The partial substitution of Mn(III) in spinel by M(III), where M = Cr, Co, Ni,..., enhances the stability of the octahedral sites in the spinel skeleton structure (Levy, 1997). This reduces the extent of phase transformation during cycling, enhancing electrode cyclability.

### Theoretical Capacity of LMO at Various Stoichiometries

<table>
<thead>
<tr>
<th>Stoichiometry</th>
<th>x in Li$_{1-x}$Mn$_x$O$_4$</th>
<th>Oxidation State (Mn)</th>
<th>Oxidized compound</th>
<th>Theoretical capacity, mAh/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>0.00</td>
<td>3.50</td>
<td>Mn$_2$O$_4$</td>
<td>154</td>
</tr>
<tr>
<td>Li$<em>{1.01}$Mn$</em>{0.99}$O$_4$</td>
<td>0.01</td>
<td>3.51</td>
<td>Li$<em>{0.04}$Mn$</em>{1.09}$O$_4$</td>
<td>153</td>
</tr>
<tr>
<td>Li$<em>{1.02}$Mn$</em>{0.98}$O$_4$</td>
<td>0.02</td>
<td>3.52</td>
<td>Li$<em>{0.06}$Mn$</em>{1.08}$O$_4$</td>
<td>144</td>
</tr>
<tr>
<td>Li$<em>{1.04}$Mn$</em>{0.96}$O$_4$</td>
<td>0.04</td>
<td>3.55</td>
<td>Li$<em>{0.10}$Mn$</em>{0.96}$O$_4$</td>
<td>135</td>
</tr>
<tr>
<td>Li$<em>{1.06}$Mn$</em>{0.92}$O$_4$</td>
<td>0.06</td>
<td>3.58</td>
<td>Li$<em>{0.24}$Mn$</em>{0.76}$O$_4$</td>
<td>126</td>
</tr>
<tr>
<td>Li$<em>{1.10}$Mn$</em>{0.90}$O$_4$</td>
<td>0.10</td>
<td>3.63</td>
<td>Li$<em>{0.40}$Mn$</em>{0.60}$O$_4$</td>
<td>108</td>
</tr>
<tr>
<td>Li$<em>{1.33}$Mn$</em>{0.67}$O$_4$</td>
<td>0.33</td>
<td>4.00</td>
<td>Li$<em>{1.33}$Mn$</em>{0.67}$O$_4$</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2.1: Theoretical capacity and oxidation state of Mn at various stoichiometries of lithium manganese oxide (Saidi, 1996).

### Reactivity of Battery Components

A study on the reactivity, toxicity and other hazardous characteristics of the various components of a lithium-ion cell with lithium manganese oxide cathode is included because safety precautions are required for the handling of these chemicals before doing experiments on the recyclability of the battery components.

Among the battery components, the lithium hexafluorophosphate used in the polymer electrolyte is the most hazardous chemical since it is a strong oxidizing agent and acute and chronic exposure causes health problems. Titration with calcium chloride solution is recommended as the disposal method. According to Occupational Safety and Health Administration (OSHA), its permissible exposure limit (PEL) is 2.5 mg/m$^3$ (ACROS, 1994; Advance Chemicals, 1995).
Binder (polyvinylidene) used in the electrodes is not hazardous at normal conditions but its combustion generates irritating and toxic fluorinated by-products (ELF Atochem. 1994). Treatment of this product mentioned later in this chapter. The copolymer does not contain any chemicals currently on the Superfund Amendments and Reauthorization Act (SARA) or Hazard Substance lists.

Another component of the cathode and anode electrodes is the conductive carbon which is not reactive under normal conditions. It ignites at above 500 °C and releases CO₂. Minor amounts of carbon monoxide (CO) may evolve based on the combustion conditions. Use general chemical handling measures. Burial or incineration is recommended for disposal.

Aluminum and copper are electrode current collector grids used in the battery and are not reactive to any chemicals explained in the process of recovery and regeneration. The process conditions encountered during cell fabrication or LMO recovery also do not affect their stability. Therefore, no special handling measures need to be taken other than the general work safety measures.

Lithium manganese oxide, the active ingredient of the cathode electrode of the Li-ion battery, has a National Fire Protection Association (NFPA) 704M rating of 1 for health, and zero for both fire and reactivity (Chemicals. 1995). The Hazard Material Identification System (HMIS) also has a similar rating. Manufacturer's hazard evaluation has identified LMO (with LiMn₂O₄ > 98%) as hazardous under OSHA's hazard communication rule, 29 CFR 1910.1200 (Chemical Abstract Services (CAS) # 12057-17-9). Threshold Limit Values (TLV) and PEL's for LMO have not been established. However, data shown in Table 2.2 are for manganese compounds in mass per unit volume of air according to OSHA and National Institute for Occupational Safety and Health (NIOSH).

Inhalation of manganese can cause central nervous system disorders. Specific toxicological information for lithium manganese oxide is not available. Manganese and lithium are not listed as carcinogens. Lithium manganate could be considered as a weak oxidizer. Mixing with strong reducing agents may enhance chemical reaction. It reacts
Exposure Limits for Manganese Compounds
(OSHA and NIOSH)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust Ceiling</td>
<td>5 mg/M³ (OSHA)</td>
</tr>
<tr>
<td>Dust short term exposure limit (STEL)</td>
<td>3 mg/M³ (NIOSH)</td>
</tr>
<tr>
<td>Dust time weighted average (TWA)</td>
<td>1 mg/M³ (NIOSH)</td>
</tr>
<tr>
<td>Fume Ceiling</td>
<td>5 mg/M³ (OSHA)</td>
</tr>
<tr>
<td>Fume STEL</td>
<td>3 mg/M³ (OSHA, NIOSH)</td>
</tr>
<tr>
<td>Fume TWA</td>
<td>1 mg/M³ (OSHA, NIOSH)</td>
</tr>
</tbody>
</table>

Table 2.2: Exposure limits for dust and fumes of manganese compounds set by OSHA and NIOSH (Chemetals, 1995)

with hydrochloric acid evolving chlorine gas. The process conditions described in this thesis, except the regeneration reaction at 800 °C, do not increase the reactivity of LMO and hence, it is chemically stable during the recovery processes.
CHAPTER 3

METHODOLOGY

One objective of this study is to develop a method for recovering particulate material, mainly lithium manganese oxide (LMO), from an electrochemical cell. The other objective is to provide a method for regenerating the recovered lithium-deficient LMO back to its initial nominal condition where it is usable as battery-grade material in an electrochemical cell. Repeated cycling of a lithium-ion cell reduces the capacity of the cell and makes the LMO lithium-deficient compared to the nominal initial condition before cycling in a cell.

Two alternative processes for recovering the active cathode electrode material (LMO) were carefully evaluated. In the first method, an extraction solvent (acetone) was used which does not dissolve the particulate material being recovered but dissolves the binder polymer. This process was designated as the solvent or wet process. In the second method (dry process), the electrode was heated to burn off the polymeric material and thus to separate the LMO from the current collector grid.

Cell Disassembly

The used cell, from which the LMO was to be recovered, was first fully discharged to a relatively safe condition (about 2V) and then the packaging of the cell was removed. The positive electrode of the cell was peeled out from the adjacent portions of the bicell laminate. The separator film was also removed. The peeled out electrode contained two positive electrode films laminated on either side of an aluminum current collector grid.
(Figure 3.1). After all possible physical separation what remained with the peeled out electrode was the assembly containing the Al grid, lithium manganese oxide, conductive carbon, binder and a very small amount of electrolyte.

Cathode Electrode

![Cathode Electrode Diagram]

Figure 3.1: Cathode electrode obtained from a used battery after all possible physical separations. The total weight of a separated cathode electrode varies from 75 g to 750 g.

Analytical Methods

The methods used for analyzing the recovered LMO at various steps of the recovery and regeneration processes are: 1. thermal gravimetric analysis (TGA), 2. inductively coupled plasma analysis (ICP), 3. redox titration and 4. X-ray powder diffraction (XRD).

Thermal Gravimetric Analysis

Thermal gravimetric analysis is conducted to find the weight loss of a sample while it is being heated to a very high temperature. A Perkin Elmer TGA analyzer (TGA7) was used for this study. It has the option of conducting the test either in air or in an atmosphere of helium. During a TGA run for the analysis of the recovered and regenerated LMO, the sample is heated from 25 °C to 900 °C in air at a heating rate of 2 °C/min. Weight loss due to the thermal decomposition of the sample is continuously monitored by the computer attached to it and at the end of the experiment, a plot of
percent weight loss versus temperature is obtained. The derivative of the data is also plotted to determine the onset temperature of the sample.

Inductively Coupled Plasma Analysis

Inductively Coupled Plasma Analysis (ICP) was conducted using a Thermo Jarrell Ash (Atomscan 25) instrument. The ICP analysis of the sample for Li and Mn content was performed using a standard test procedure (Dean, John A. 1995) as follows. About 0.1 g of sample was heated with 1 ml of concentrated HCl. When the sample was completely dissolved in HCl, the solution was diluted to 100 ml in a volumetric flask using 1% HCl solution in deionized water. One ml of this solution was then taken and diluted to 50 ml with 1% HCl solution in a volumetric flask. Plasma analysis for Li at a wavelength of 670.78 nm was performed on this sample solution after calibration of the ICP. The test result obtained was converted to weight percent with respect to the original sample. For the analysis of percentage Mn present in the sample, 1 ml of solution from the 50 ml flask was further diluted to 25 ml with 1% HCl solution and analyzed in the plasma analyzer after calibrating the ICP for Mn. Calibration was done for three different wavelengths (260.569 nm, 294.920 nm and 257.610 nm) of Mn and the appropriate wavelength was chosen from the correlation curve obtained from the calibration run.

X-Ray Powder Diffraction

The spinel structure of a sample is determined by X-ray diffraction using a Siemens diffractometer (Diffraktometer D5000) with Cu Kα1 radiation. X-ray powder diffraction is used to observe the crystal lattice of a crystalline material. The relation between the wavelength of the X-radiation, the angle of diffraction and the distance between each set of atomic planes of the crystal lattice (Dean, John A. 1995; Wormald, 1973) is explained in the Bragg equation. From the rearranged Bragg equation,

\[ \theta = \sin^{-1}(\lambda / 2d) \]  

3.1
where $\theta =$ angle of diffraction.

$\lambda =$ wavelength of the X-ray radiation.

$d =$ distance between the atomic planes.

The interplanar spacings depend solely on the geometry of the crystal's unit cell, while the intensities of the diffracted X-rays depend on the type of atoms in the crystal and the location of the atoms in the fundamental repetitive unit, the unit cell. The X-ray pattern of a pure crystalline substance can be considered as a "fingerprint" with each crystalline material having, within limits, a unique diffraction pattern. The diffraction pattern is a series of nonuniformly spaced cones (maxima) whose spacings are determined by the prominent planes of the crystallites.

For the XRD analysis of the sample, a small amount of sample is placed on the sample holder. The radiation emanating from the line focus of the X-ray tube is diffracted at the sample and recorded by the detector. The sample rotates at a constant angular velocity such that the angle of incidence of the primary beam changes whilst the detector rotates at the twice the angular velocity around the sample. The diffraction angle ($2\theta$) is thus always equal to twice the incident angle ($\theta$). Each time the Bragg condition is satisfied, the primary beam is reflected from the sample to the detector. The detector and the connected measuring electronics measure the intensity of the reflected radiation and thus the pulse counts or diffraction patterns are obtained.

Redox Titration

The redox titration of the recovered LMO material was done using a standard titration procedure used in the laboratory (Dean, John A 1995; Glover, D. 1989). An Orion model 950 titrator was used to obtain the data and an Orion redox electrode was used for the titration. First the KMnO$_4$ solution is standardized using a standard solution of Mn and the manganese factor ($F_{\text{Mn}}$ quantity of Mn expressed in mg reacting with exactly 1 ml of the KMnO$_4$) of the KMnO$_4$ solution is determined.
The available oxygen in manganese dioxide (i.e., oxygen in LMO) is first calculated by the reduction of MnO₂ by an acidic solution of ammonium ferrous sulfate followed by a back titration of excess ferrous ions with KMnO₄.

First phase: Reduction of MnO₂

\[ \text{MnO}_2 + 2\text{Fe}^{2+} + 4\text{H}^+ \rightarrow \text{Mn}^{2+} + 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \]  \hspace{1cm} (3.2)

Second phase: Oxidation of excess ferrous ions with KMnO₄

\[ \text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \]  \hspace{1cm} (3.3)

A known weight of the test material is treated with 20 ml of ferrous ammonium sulfate. A blank is also made with 20 ml of ferrous ammonium sulfate and both the sample and the blank are titrated against standardized KMnO₄ solution to the end point. The available oxygen, expressed in percentage, is given by the expression:

Available O₂ (as MnO₂) = \( \frac{(X-Y)}{P} \times F_{\text{Mn}} \times 0.9891 \times 100 \)  \hspace{1cm} (3.4)

Where,

- \( X \) = volume of KMnO₄ used for the blank in ml.
- \( Y \) = volume of KMnO₄ used for the sample solution in ml.
- \( P \) = weight of the sample in gram.
- 0.9891 = conversion factor

Manganese in manganese dioxide (i.e., Mn in LMO) is then calculated by measuring the manganous ion, obtained by the reduction of MnO₂ with HCl by potentiometric titration with KMnO₄ in the presence of an excess sodium pyrophosphate at a pH maintained between 6.5 and 7.0.

\[ \text{Mn}^{7+} - 4\text{Mn}^{2+} \rightleftharpoons 5\text{Mn}^{2+} \]  \hspace{1cm} (3.5)

a) Taking the MnO₂ into solution:

\[ \text{MnO}_2 + 4\text{HCl} \rightarrow \text{Mn}^{2+} + \text{Cl}_2 + 2\text{Cl}^- + 2\text{H}_2\text{O} \]  \hspace{1cm} (3.6)
b) Titration:

\[
\text{MnO}_4^- \rightarrow 4\text{Mn}^{2+} + 8\text{H}^+ + 15\text{H}_2\text{P}_2\text{O}_7^{2-} \rightarrow 5\text{Mn(H}_2\text{P}_2\text{O}_7)^{3-} + 4\text{H}_2\text{O}
\]

The manganese content is expressed in percentage and is given by the expression:

\[
\text{Manganese content (\%)} = \frac{Y \times F_{\text{Mn}}}{P} \times 100
\]

Where,

- \( Y \) = volume of KMnO\(_4\) used in the titration in ml.
- \( P \) = weight of the sample in gram.
- \( F_{\text{Mn}} = F_{\text{Mn}}/1000 \)

From the results of available \( O_2 \) and manganese content, the manganese oxidation state is calculated using the following equation:

\[
\text{Mn oxidation} = 2 \downarrow 1 + (54.94/86.94) \times (\text{available } O_2 \text{ as MnO}_2 / \text{Mn content}) \uparrow
\]

**Solvent Process: Solvent Extraction, Separation and Regeneration**

**Solvent Extraction**

Selection of the appropriate solvent to dissolve the binder used in the Li-ion cells is based on many factors. There are several solvents capable of dissolving the polymeric binder, but their availability, toxicity and cost are also to be compared before choosing a solvent. Table 3.1 lists some of the solvents that can be used for the extraction of cathode electrode to separate LMO. The polarity, hydrogen bonding and the total polymer solubility are given in the table (Bottino et al., 1988). It is observed that, acetone is compatible with any other solvents for its total solubility and at the same time it is the most cost effective and least toxic solvent. Therefore, acetone is recommended as the solvent for the extraction process for the separation of LMO from cathode electrode.
### Solubility Parameters of Binder

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Polarity (MPa$^{1/2}$)</th>
<th>H-Bonding (MPa$^{1/2}$)</th>
<th>Total Polymer Solubility (MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>10.4</td>
<td>7.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Dimethylacetamide (DMAC)</td>
<td>11.5</td>
<td>10.2</td>
<td>22.7</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>13.7</td>
<td>11.3</td>
<td>24.8</td>
</tr>
<tr>
<td>Dimethylsulfoxide (DMSO)</td>
<td>16.4</td>
<td>10.2</td>
<td>26.7</td>
</tr>
<tr>
<td>Ethyl acetate (EtAc)</td>
<td>5.3</td>
<td>7.2</td>
<td>18.1</td>
</tr>
<tr>
<td>Methyl ethylketone (MEK)</td>
<td>9</td>
<td>5.1</td>
<td>19.0</td>
</tr>
<tr>
<td>N-methyl pyrrolidone (NMP)</td>
<td>12.3</td>
<td>7.2</td>
<td>22.9</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>5.7</td>
<td>8.0</td>
<td>19.4</td>
</tr>
<tr>
<td>Triethyl phosphate (TEP)</td>
<td>11.5</td>
<td>9.2</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Table 3.1: Solubility parameters of the binder with some common solvents (Bottino et al., 1988)

A separated cathode electrode, which will be used for the LMO recovery, is shown in Figure 3.1. The thickness of the electrode varies from 300 microns to 900 microns and the area of the electrode varies from 50 cm$^2$ to 250 cm$^2$ depending on the type of the battery. A typical separated electrode contains 6-12% by weight binder, 3-8% conductive carbon and up to 80% LMO. The current collector grid and electrolyte together will constitute about 6% by weight of the separated electrode.

The peeled out cathode electrode was first soaked in acetone and placed on a shaker set at 50 rpm for about 6 hours. The polymer dissolved in acetone leaving LMO particles and the Al grid suspended in the solvent. The Al grid was separated by filtering through a large mesh, and the suspended particulates were removed by a fine filter and dried. The separated cathode material contained mainly LMO and a small portion of conductive carbon. Binder and electrolyte present in the original electrode were carried away by acetone.

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Few other tests were done to optimize the electrode extraction period, the extraction temperature, and the amount of acetone used for the solvent separation process. Increasing the extraction period and warming the solvent up to 50 °C could enhance the extraction process. It can be theoretically calculated the amount of acetone needed for the extraction of electrode based on the amount of binder in it. but experiments showed that up to 80% excess acetone is needed for the complete dissolution of the binder from the electrode. It was estimated, based on the theoretical calculations, that 1 gram of binder needs approximately 5 grams of acetone.

Thermal gravimetric analysis were conducted on samples of the recovered material to find the weight percent of the combustible materials in the recovered cathode powder. It was observed that a major weight loss occurred before 600 °C for every TGA samples.

The main portion of the recovered material was then heated to 600 °C for 1 hr in the presence of air, to burn off the carbon and remaining binder, if any. With this step a pure form of lithium deficient LMO was assumed to obtain.

The separated LMO was then chemically analyzed using a inductively coupled plasma analyzer and thermal gravimetric analyzer and the spinel structure of the sample was determined using X-ray diffraction. The results of X-ray diffraction, ICP analysis, TGA, and the redox titration are discussed in the following chapter.

**LMO Regeneration**

The next step and the main objective of this study is to find out a suitable method to regenerate the separated LMO to the required Li :Mn ratio and to restore the spinel structure that is important in the performance of Li-ion battery. Six samples were made with different ratios of laboratory grade lithium carbonate and the separated LMO. These samples were heated to 850 °C in air at a heating rate of 2 °C/min and held at that temperature for 12 hr. The samples were then slowly cooled at 2 °C/min to room temperature. Three more samples were made with recovered LMO and lithium carbonate taken in a stoichiometric ratio that will make the lithium content (Li atoms) in the regenerated sample just above 1. These samples were then heated at 750 °C, 800 °C and
900 °C respectively, but maintained all other previously explained reaction conditions. All the calcined samples were then analyzed for chemical composition, structure and oxidation state. The Li:Mn ratio of each sample was compared with the theoretical value calculated based on the Li₂CO₃: LMO ratio initially present at the start of calcination. Few other samples were also prepared with Li₂CO₃ and recovered LMO to study the effects of varying the heating and cooling rates, and duration of the calcination period.

**Electrochemical Analysis of LMO**

Cells were made with regenerated LMO in order to perform a comparative charge-discharge cycling study of the regenerated LMO with standard LMO. For this, a film was made with a mixture of regenerated LMO, plasticizer, conductive carbon and binder at a certain composition (proprietary for Valence Technology Inc.). A well-mixed cathode mixture was made into film by pressing the mixture in a heated (150 °C) hydraulic press. Pressure was slowly applied to the sample for effective and evenly distributed heat transfer within the sample. The film thus made was cut into small discs using a 2.4 cm² die. The plasticizer was then extracted out from these discs by immersing in methanol for 20 minutes. The increased pore volume (due to the extraction of plasticizer) of the discs was intended to enhance the ionic mobility of Li-ions in the cathode electrode. Using the extracted film discs as cathode, fiber glass thin layer as separator and metallic lithium as anode, battery cells were made and the electrochemical measurements were carried out.

For the electrochemical measurements of the cell, thermostatic conditions at 23 °C was used. The Electrochemical Voltage Spectroscopy (EVS) as explained by Jerry Barker (Barker, J. 1995) was used to perform the charge-discharge cycling of the cell. The EVS instrumentation used was an Advantest R6142 Precision Voltage source/sink coupled to a Hewlett Packard Model HP34401A Digital Multimeter (DMM) for current monitoring. The experimental instrument control was performed using a custom software written in HP Instrument BASIC. The charge-discharge cycles were set at a constant voltage step change of 10 mV and the current was continuously monitored until decayed to a preset minimum value of 0.5 mA. The cell was cycled from 3V to 4.2V. Cumulative capacity
and the differential capacity (dQ/dV) were monitored and recorded continuously by the computer.

A second cell was made from the same solvent process regenerated LMO and cycled under constant current (0.2 mA/cm²) condition to study the cycle life and the capacity fading of the cell. In a similar way, cells were made from standard LMO and set for cycling with the same conditions used for the regenerated LMO cells. The standard LMO was supplied by a commercial manufacturer and was used as received.

**Dry Process: Separation by Combustion and Regeneration**

Separation by Combustion

A simpler and more economical method for separating the LMO was considered. The peeled-out cathode electrode (Figure 3.1) was placed in a wide crucible and heated in a furnace at 600 °C for about an hour. The temperature at which the electrode to be heated to burn off the carbon was estimated based on a TGA analysis of the electrode. It was expected that the binder and conductive carbon would burn off at that temperature leaving the aluminum grid and LMO powder in the crucible. As the binder burned, the bond between the LMO particles as well as the particles to the grid was destroyed causing separation of LMO particles from the Al grid. This method of separation of LMO from electrode of spent battery without using any solvent was named the "dry process". About 200 grams of electrode was taken in the crucible and about 130 grams of LMO was recovered from this process.

The LMO thus separated was then analyzed for its chemical composition using ICP analysis and redox titration using the methods explained earlier. The spinel structure of the sample was determined using X-ray diffraction.

Regeneration of LMO

The regeneration of recovered LMO from the dry process was done using the same process used for the regeneration of solvent recovered LMO. Since the reaction
conditions were already established from the regeneration reaction experiments conducted for solvent recovered LMO. only two regeneration reactions were conducted with the recovered LMO from dry process to assess the repeatability of the reaction.

A cell was made from the regenerated LMO and subjected to charge-discharge cycling using the EVS technique explained earlier. A second cell was made from the same dry process LMO and cycled under constant current condition to study the cycle life and cycle loss. To compare the performance of the regenerated LMO from both the solvent process and dry process with the standard LMO, cells were made with standard LMO in exactly the same way as cells made with regenerated LMO. All cells were cycled under identical conditions of voltage and charge-discharge rates.
CHAPTER 4

RESULTS AND DISCUSSIONS

Solvent Process

A fully discharged cell has all its Li ions back to the LMO in the cathode electrode and thus it is very important to discharge a cell completely before it is cut open for separating the electrodes. Also it is very important from safety point that a charged cell may cause fire when it is opened if short circuit occurs. Theoretically, a cell can be discharged to zero volts, but it is sufficient if the battery can be discharged to 2V or less. Ninety-nine percent of Li ions will return to cathode electrode at 3 volts and the largest power drain occurs when discharged from 4.2V to 3.8V. Therefore, a spent cell at 2V is safe enough to cut open to use for recycling. Once the packaging of the cell is cut open, it is easy to separate the cathode electrode from the anode electrode and the separator film.

LMO Separation

A complete process flow diagram of the solvent process of LMO recovery and regeneration is shown in Figure 4.1.

There are several solvents that can be used for the dissolution of the binder in cathode electrode but acetone is the most common and economical solvent that can be used for the separation process. Experiments showed that vigorous shaking of sample with acetone is required for the effective dissolution of binder in the solvent. From the various experiments conducted for the dissolution of binder from the electrode, it is concluded
Flow Diagram of the Solvent Process

Figure 4.1: Process flow diagram of the solvent extraction method for the recovery and regeneration of LMO from spent battery.
that an extraction with acetone, eight to ten times more the amount of binder by weight, for approximately 8 hours at 50 °C with constant agitation of the sample will effectively separate the LMO from the current collector grid by the dissolution of binder. This operation makes a slurry of LMO, carbon and the binder dissolved in the solvent acetone. The current collector grid from the slurry can be separated by a sieve with mesh number 10. The LMO and carbon particles can be separated by centrifuging the slurry at 2000 rpm for 20 minutes. Repeated washing and centrifuging make the separated LMO-carbon mixture binder free. The thick slurry, containing LMO and carbon, from the centrifuge is air dried before heating at 600 °C to burn off the carbon.

TGA Curve of a Solvent Recovered LMO

![TGA Curve of a Solvent Recovered LMO](image)

Figure 4.2: TGA curve of a solvent recovered LMO before burning of the carbon. About nineteen percent by weight of the recovered material were combustible under temperatures below 600 °C.

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The TGA run (Figure 4.2) of a sample before burning of the carbon showed that about 19 percent of the initial sample weight was lost before temperature reached 600 °C. Similar results were obtained with all TGA runs with recovered LMO from other experiments. This is an indication of the amount of combustible impurities present in solvent-recovered LMO and the TGA curve gives an idea of the temperature at which the LMO must be heated to get rid of all combustible impurities present in it. Therefore, in order to get a carbon-free LMO, the solvent-extracted LMO was heated to 600 °C in air for an hour.

The ICP analysis on one of the separated LMO samples after burning of the carbon gave the composition of material obtained. The Li was 2.94% by mass and Mn 59.56% (Li/Mn = 0.049) while in a standard LMO (LiMn$_2$O$_4$) it is 3.84% and 60.77% respectively (the Li:Mn ratio in a standard LMO is 0.063). This shows that the recovered LMO is deficient in Li ion, resulting in a suggested molecular formula of Li$_{1.74}$Mn$_{1.96}$O$_4$. But from the redox titration, the number of oxygen atoms in the molecule was estimated as 3.74. Therefore, the molecular formula of the recovered sample can be modified as Li$_{1.74}$Mn$_{1.96}$O$_{4.74}$. This form of molecular formula for a LMO spinel is very difficult to explain and hence we may assume that there are some different forms of lithium oxides, such as Li$_2$Mn$_2$O$_4$ and Li$_2$MnO$_3$, associated with it. The average Mn oxidation (Mn valency) calculated from the redox titration was 3.12. This is far below the average valency of 3.5 of a base spinel LiMn$_2$O$_4$. This is the indication of the presence of more Mn$^{3+}$ than Mn$^{4+}$ in the recovered sample. Heating of Li-deficient recovered material to burn off the carbon would have resulted in the evolution of oxygen (Dahn, 1994). Therefore, it is very difficult to predict the exact molecular formula of the recovered material without further analysis. The lithium deficiency may be due to the effect of long cycle life and the inadequate discharge of the cell before the electrodes were separated. Perhaps the Mn remained in its original oxidation state. According to Table 2.1, a stoichiometry with 1.96 Mn means the standard LMO used for the making of this battery had a lithium content of 1.04 (Li$_{1.04}$Mn$_{1.96}$O$_4$).

ICP analysis and redox titration on two other separated LMO gave different Li:Mn ratios. Therefore it is assumed that the Li:Mn ratio is depending on the number of cycles.
the battery had undergone before separating the LMO by solvent process. Higher the number of cycles, greater the deficiency in Li and also greater the distortion happened to the LMO spinel. Therefore, test results of a single batch of recovered LMO are discussed in this section.

The X-ray diffraction pattern of the recovered LMO (Figure 4.3) after heating to burn off the carbon shows deviations from the spinel structure. Figure 4.6 is the XRD pattern of a standard LMO for comparison. There were some additional peaks (asterisk marks) which are not due to the spinel structure in the X-ray diffraction pattern. It was proved that a Li-deficient LMO releases oxygen when it is heated and that the temperature at which oxygen evolution occurs depends on the lithium content in the LMO (Dahn, 1994). This process could have resulted in the contraction of the lattice of the recovered LMO. To remove the carbon and other impurities present in the recovered LMO, heating at 600 °C is suggested. The additional peaks show the presence of some impurity phase, Mn$_2$O$_3$ for example, in the sample.

**Regeneration of LMO**

The next step of experiment was to find a process to restore the spinel configuration and to compensate for the lost lithium in the recovered LMO. The decision to react recovered LMO with lithium carbonate salt at a temperature range of 750 °C to 900 °C was backed by several literature citations of lithium manganese oxide synthesis from manganese oxide and a lithium salt (Dahn, 1994; Hunter, 1981). Several experiments conducted (as explained in the methodology) proved that the optimum regeneration temperature is 800 °C. Experiments with a mixture of recovered LMO and lithium carbonate taken in Li: Mn ratios less than that of the stoichiometric spinel did not give the expected result as the XRD patterns were different from a standard LMO. However, the samples taken in the exact stoichiometry of LMO and those taken in excess Li content (x ~ 0.05), as in the case of a standard LMO, were regenerated as expected. Therefore, it is concluded that if the ratio of lithium carbonate and the recovered LMO was chosen to
Figure 4.3: X-ray diffraction pattern of recovered LMO by solvent process after heated to 600 °C to burn off the carbon. Asterisk mark (*) indicates the impurities (possibly by Mn$_2$O$_3$) in the lattice.
give a Li$_{1-x}$Mn$_2$O$_4$ spinel (where x = 0 to 0.1), the reaction will be nearly complete provided the other process conditions are favoring the reaction. From the various experiments, it can be concluded that a regeneration reaction at 800 °C in air or oxygen for 12 hr. with a slow heating and cooling rate of 2 °C per min and 1 °C per min respectively, gives better results for all analysis.

Since all other experiment results are used to find the optimum reaction conditions and those results do not demonstrate the regeneration capability of the process, only the test results of the regenerated LMO obtained from the optimum conditions are analyzed in this section. A second regeneration experiment was also performed using the same conditions to study the repeatability of the process.

As explained in the experimental section of this report, a calculated amount of Li$_2$CO$_3$ that was needed to make a standard LMO was mixed with recovered LMO and reacted at 800 °C. This step, by the concept of this thesis, should give a LMO that will be very similar to the standard LMO by its spinel structure, Li:Mn ratio, particle size and surface area. As explained elsewhere in this study, the amount of lithium carbonate added to the LMO for regeneration was based on the optimum range of x (x = 0.03 to 0.08, Li$_{1-x}$Mn$_{2-x}$O$_4$) in the regenerated LMO. Theoretically a regenerated cathode should perform well in cells made from this material.

The ICP analysis on the regenerated LMO gave the composition of material obtained. The Li was 3.93% and Mn was 61.00% (Li: Mn = 0.065) while in a standard LMO (LiMn$_2$O$_4$) it is 3.84% and 60.77% respectively. This shows that the regenerated LMO is Li-rich compared to the stoichiometric LiMn$_2$O$_4$. Based on the amount of Li$_2$CO$_3$ added, the calculated (Table 4.1) molecular formula of the regenerated LMO is Li$_{1.06}$Mn$_2$O$_4$.

Figure 4.4 and Figure 4.5 are the TGA curves of a standard LMO and the regenerated LMO from solvent process, respectively. The calculated value of "x" for the regenerated LMO from a TGA analysis was 0.06. The x value was calculated from a relationship of onset temperature (T$_c$) with x, obtained from the calibration curve of TGA with LMO samples of known stoichiometry.

\[
x = \frac{(2285.78 - T_c)}{1442.85}
\]
Li: Mn Ratio of the Regenerated LMO

<table>
<thead>
<tr>
<th></th>
<th>Calculated for Regeneration</th>
<th>Actual from ICP analysis after Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium (%)</td>
<td>4.08</td>
<td>3.93</td>
</tr>
<tr>
<td>Manganese(%)</td>
<td>60.77</td>
<td>61.00</td>
</tr>
<tr>
<td>Li/Mn</td>
<td>0.067</td>
<td>0.065</td>
</tr>
<tr>
<td>$x$ in $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$</td>
<td>0.06</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 4.1: Chemical composition of regenerated LMO from solvent process based on: (a) ratio of Li and Mn present in the mixture of recovered LMO and $\text{Li}_2\text{CO}_3$ before the regeneration reaction. (b) ICP analysis.

These slight variations in the value of $x$ from various methods may be due to the experimental error and the tolerance of the instruments. All the above comparisons of the composition of recovered material leads to the assumption that the reaction equation during the regeneration process will be:

$$\text{Li}_{1-x}\text{Mn}_2\text{O}_4 - x/2\text{Li}_2\text{CO}_3 \rightarrow \text{LiMn}_2\text{O}_4 + x/2 \text{CO}_2 - x/4 \text{O}_2$$

During the regeneration process, at temperatures below about 400 °C, all polymeric impurities, if any, will burn off. and at about 600 °C, carbon burns. At about 735 °C, $\text{Li}_2\text{CO}_3$ melts and reaction with LMO begins. LMO melts above 1000 °C, and hence, temperatures above 950 °C are not desired. The above reaction between LMO and $\text{Li}_2\text{CO}_3$ is considered as a solid-phase reaction. Figure 4.6 and Figure 4.7 are the X-ray diffraction (XRD) patterns of a standard LMO and the regenerated LMO. The calculated value of Miller indices of different planes (h,k,l) of a standard LMO is marked on the XRD pattern. The Miller indices of the plane completely specify the orientation and the separation of the planes in that particular family. A comparative study of these figures shows that each peak in the XRD of regenerated LMO is in exact match with the
Figure 4.4: TGA curve of a standard LMO. The calculated value of Li is 1.04 ($x = 0.04$) and the onset temperature ($T_{c1}$) is 790 °C.
Figure 4.5: TGA curve of the regenerated LMO by solvent process. The calculated value of Li is 1.06 ($x = 0.06$) and the onset temperature ($Tc_1$) is 757.4 °C.
corresponding peak in the XRD of standard LMO. The pattern of the regenerated LMO represents a pure form of LMO.

**Electrochemical Analysis**

Charge-discharge cycle (EVS) diagrams of cells made from the standard LMO and reclaimed LMO using the solvent process are shown in Figure 4.8 and Figure 4.9 respectively. Cells were cycled between 3V and 4.2V. The first few cycles are shown. The charge capacity of the cell from standard LMO was 123 mAh/g and the discharge capacity was 118 mAh/g for the first cycle. The first cycle loss was 4.01%. Cell from regenerated LMO had the same amount of charge capacity but a first cycle loss of 10 mAh/g (8.13%) was observed. The first cycle loss for experimental cells with standard LMO usually varies from 5 to 15 percent, and hence the performance of the regenerated LMO cell can be considered normal.
Figure 4.6: X-ray diffraction pattern of a standard LMO. The diffraction angle ($2\theta$) ranges from 10 to 80 degrees. The Miller indices marked on the pattern specify the orientation of the planes in the LMO spinel.
Figure 4.7: X-ray diffraction pattern of regenerated LMO by solvent process. All intensity peaks are in match with the XRD pattern of standard LMO. The Miller indices marked on the pattern specify the orientation of the planes in the LMO spinel.
Figure 4.8: Charge-discharge cycle (EVS) diagram of a cell with standard LMO. Cell was cycled between 3V and 4.2V with a voltage step size of 10 mV for a current limit of 0.5 mA.
Figure 4.9: Charge-discharge cycle (EVS) diagram of a cell with regenerated LMO by solvent process. Cell was cycled between 3V and 4.2V with a voltage step size of 10 mV for a current limit of 0.5 mA.
Dry Process

LMO Separation

In the dry process, separation of LMO from other cathode materials was accomplished by heating the cathode electrode to a temperature high enough to burn polymer, carbon and other combustible impurities. Figure 4.10 is a complete flow diagram of LMO recovery and regeneration by dry process. By this method, the formation of liquid waste was avoided. However, the heating of electrode generates toxic gases such as HF, and these must be scrubbed out with a base bath before venting to atmospheric air.

LMO obtained by this method from the first experiment was analyzed as in the case of solvent-recovered LMO to calculate the amount of lithium carbonate to be added for regeneration. ICP analysis on the separated LMO gave a composition of Li = 3.21%, Mn = 63.48% by mass and the Li:Mn ratio = 0.051. In a stoichiometric LMO (LiMn₂O₄) it is 3.84%, 60.77% and 0.063 respectively. Based on the Mn and MnO₂ readings from the redox titration, the estimated chemical formula of this recovered LMO powder is LiₓMn₁₊ₓO₁−ₙ₋₂ₓ. The Mn oxidation state (average valency) is 3.4. An average valency less than 3.5 indicates that there are more Mn²⁺ ions than Mn³⁺ ions. These two analyses show that the dry process LMO is deficient in Li ion. Also, when the lithium-deficient LMO was heated it lost a small amount of oxygen. It could also be possible that two or more phases of lithium manganese oxide (LiₓMn₂O₄, Li₂MnO₃ etc.) are present in the recovered powder.

The XRD pattern of this non-regenerated sample (Figure 4.11) has a number of unexplainable peaks that confirms the presence of other forms of manganese oxides. It was observed that there are more unmatched peaks in the XRD pattern of the dry process recovered LMO than the solvent recovered LMO. This may be due to the reactions taking place between the chemicals while heated at 600 °C. Therefore, more deviation from the spinel was observed for the dry process LMO.
Figure 4.10: Process flow diagram of the dry process for the recovery and regeneration of LMO from spent battery.
Figure 4.11: The XRD pattern of non-regenerated LMO obtained from Dry Process. Peaks with x and * are from impurities and the peaks with Miller indices marked on them are corresponding to the LMO spinel.
Analysis on the recovered LMO by dry process from the second experiment also gave similar results from ICP, redox titration and XRD. However, the Li:Mn ratio of the sample was less compared to the Li:Mn ratio of the sample obtained from the first experiment. This indicates that the composition of the recovered LMO from different cells will vary irrespective of the process and the variation basically depends on the number of cycles the cell had undergone before opened to separate LMO. Two samples from recovered LMO obtained from each of the above recovery experiments were taken for regeneration and the properties of the regenerated LMOs were studied.

Regeneration of LMO

The regeneration step was carried out in the same manner as that of solvent extracted LMO. The same heating and cooling conditions were followed. Results of various analysis of regenerated LMO by the dry process are listed in Table 4.2. Based on the Mn and MnO₂ readings from the redox titration, the estimated chemical formula of this regenerated LMO powder from the first regeneration experiment is Li₁ₓMn₁₋ₓO₄ₓ₁. The Mn oxidation state (average valency) is 3.58 which means Mn⁴⁺ ≈ Mn²⁺. The TGA curve of the sample is shown in Figure 4.12. The calculated value of “x” in Li₁₋ₓMn₂₋ₓO₄ of the calibrated TGA is 0.06 and is in agreement with the test results given in Table 4.2. The XRD pattern is shown in Figure 4.13. No extra peaks could be found, thus emphasizing the successful performance of the regeneration process.

LMO from the second regeneration experiment on the dry process recovered sample was also analyzed by ICP and XRD. The chemical composition obtained from ICP justified the regeneration reaction. Also, the XRD pattern showed that the regenerated LMO from the second experiment is similar to a standard LMO with respect to its spinel structure. However, LMO from the first experiment was used to make cells for the charge-discharge performance analysis using the EVS and constant current techniques.

The cycling performance of the cell made from regenerated LMO using dry process can be evaluated from the voltage-specific capacity curve (figure 4.14) obtained...
from the EVS technique. The cell had a first cycle charge capacity of 123 mAhr/g at 4.2 V and had a first cycle loss of 17 mAhr/g (13.82%) which is still within the acceptable range.

Li:Mn Ratio of the Regenerated LMO

<table>
<thead>
<tr>
<th></th>
<th>Calculated for Regeneration</th>
<th>Actual from ICP analysis after Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium (%)</td>
<td>3.91</td>
<td>3.99</td>
</tr>
<tr>
<td>Manganese(%)</td>
<td>60.77</td>
<td>58.93</td>
</tr>
<tr>
<td>Li/Mn</td>
<td>0.064</td>
<td>0.068</td>
</tr>
<tr>
<td>x in Li(<em>{1-x})Mn(</em>{2x})O(_4)</td>
<td>0.02</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 4.2: Chemical composition of LMO from dry process based on: a) ratio of Li and Mn present in the mixture of recovered LMO and Li\(_2\)CO\(_3\) before the regeneration reaction, b) ICP analysis.

Figure 4.15 shows the voltage vs. specific capacity curve of the first cycle of cells made from standard LMO, solvent-extracted LMO and dry process LMO. The maximum first cycle loss was observed for the dry process LMO. A differential capacity curve for all three LMO cells are also given (Figure 4.16). It was observed, from the previous experiments, that there could be some variations in cycle performance even with the LMO taken from the same lot. This could be due to the slight variations in the mixing process, amount of other ingredients in the mix and any impurities associated with the chemicals.

Three more cells, one each from standard LMO, solvent extracted LMO, and dry process LMO, were made to study the repeatability of the cycling performance. Cells were cycled between 3.0V and 4.3V at a constant current of 0.2 mA/cm\(^2\). The first cycle charge capacities of these cells were 129 mAhr/g, 131 mAhr/g and 125 mAhr/g for standard
Figure 4.12: TGA curve of the regenerated LMO by dry process. Calculated value of Li from the onset temperature of 756 °C is 1.06 (x = 0.06).
Figure 4.13: X-ray diffraction pattern of the regenerated LMO by dry process. The Miller indices marked on the pattern specify the orientation of the planes in the LMO spinel.

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LMO. solvent extracted LMO, and dry process LMO, respectively, at the maximum voltages and the corresponding discharge capacities were 118 mAh/g, 116 mAh/g and 102 mAh/g. Table 4.3 summarizes the performance of these cells. The capacity data for each cell was recalculated for the voltage range from 3V to 4.2V to match the EVS data obtained from the first experiment. It is to be noted that a higher first cycle capacity loss for both standard LMO cell and dry process LMO cell for the constant current test compared to the EVS test while, the solvent process LMO has a lower first cycle loss in the constant current test. This indicates that even if the same material is used for the making of several cells, there could be capacity difference because there are several other factors controlling the performance of a cell.

<table>
<thead>
<tr>
<th></th>
<th>First cycle charge capacity (mAh/g)</th>
<th>First cycle discharge capacity (mAh/g)</th>
<th>First cycle capacity loss (%)</th>
<th>Discharge capacity after 16 Cycles (mAh/g)</th>
<th>% change discharge capacity (16 cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std LMO</td>
<td>123.39</td>
<td>115.85</td>
<td>6.11</td>
<td>114.0</td>
<td>3.06</td>
</tr>
<tr>
<td>Solvent LMO</td>
<td>123.12</td>
<td>115.56</td>
<td>6.13</td>
<td>82.6</td>
<td>28.96</td>
</tr>
<tr>
<td>Dry LMO</td>
<td>121.43</td>
<td>101.085</td>
<td>16.75</td>
<td>80.0</td>
<td>21.95</td>
</tr>
</tbody>
</table>

Table 4.3: Constant-current cycling performance of cells from standard LMO, solvent process LMO and dry process LMO vs. Li metal anode. Compared to EVS results, the standard LMO and the Dry process LMO cells experienced higher capacity loss for the first cycle.

Figure 4.17 shows the discharge capacity of the cells from the constant current cycle test for several charge-discharge cycles. For the first few cycles, there were increased cycle losses for the regenerated LMO cells from both processes compared to the standard LMO cell. But it is observed that the regenerated LMO cells, especially the dry process LMO cell, achieved cycling stability after the initial few cycles.

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Figure 4.14: Charge-discharge cycle (EVS) diagram of a cell made from the regenerated LMO by dry process. Cell was cycled between 3.0V and 4.2V with a voltage step size of 10 mV for a current limit of 0.5 mA.
Specific Capacity Vs. Voltage

Figure 4.15: Cathode specific capacity-voltage diagram (EVS) for the first cycle of cells from standard LMO, solvent extracted LMO, and dry process LMO. The first cycle losses are 4.0%, 8.1%, and 13.8%, for standard LMO, solvent extracted LMO and dry process LMO, respectively.
Figure 4.16: Differential capacity-voltage diagram (EVS) for the first cycle of cells from standard LMO, solvent extracted LMO, and dry process LMO.
Figure 4.17: Discharge capacity against number of cycles for cells from standard LMO, solvent extracted LMO, and dry process LMO. Cells were cycled between 3.0V and 4.3V at a constant current of 0.2 mA/cm².
The capacity and performance of a cell depends on a number of factors. Among the factors that affect the cathodic reaction, LMO spinel structure, stoichiometry and lithium content are very influential. Other factors that may affect the battery are the particle size of the material, the electrolyte, impurities in the electrode and electrolyte, thickness of the film etc.

From the analysis of the results obtained from ICP, TGA, redox titration and XRD of various regenerated LMOs from different experiments, it was observed that both processes of recovering and regenerating LMO from spent batteries are feasible and able to generate LMO that is compatible with standard LMO produced by any major manufacturer. However, since the performance of the cells from regenerated LMO is not exactly equal to the performance of a standard LMO cell, it may be possible to improve the qualities of the regenerated LMO by overcoming the limitations faced during this study. Some recommendations to improve the engineering of the regeneration process and thus to improve the quality of the recovered LMO are listed below.

1. Optimization of the milling process of reactants before regeneration to improve the distribution of lithium carbonate in the recovered LMO.

2. Continuous mixing of reactants during the regeneration process. A rotary furnace is suggested.

3. Increased air or oxygen flow into the furnace during the regeneration reaction.

4. Optimization of reaction conditions to improve the particle size distribution of the regenerated LMO.

5. Usage of better and improved analyzing techniques for the regenerated LMO for more complete and accurate characterization of its impurities.
CHAPTER 5

ENVIRONMENTAL IMPACTS OF THE PROCESSES

The ever increasing energy demand and the environmental concerns emerging from the burning of fossil fuels are expanding the roll of secondary batteries in our life. By combining the time-varying renewable energy sources with secondary batteries, we can improve the stability of electric power sources. By storing electric power it is possible to achieve a high capacity utilization for generating facilities that have high efficiency and produce little CO₂. The development of practical electric vehicles not only alleviates air pollution but also limits CO₂ emission. The onset of large-capacity lithium batteries with long cycle life, high energy density, high power density, and high energy efficiency in electric vehicles is expected to revolutionize the battery industry and will help the environmental clean-up efforts.

The increasing use of lithium batteries will depend on the cost reduction and the development of recycling processes to protect the environment. As in the case of the lead-acid battery industry where a major portion of the lead demand is met by the secondary (recycled) lead from the spent batteries, environmentally sound technologies, like the one explained in this thesis, will play very significant role in pricing the battery in future.

Safety has been the major issue with lithium batteries ever since their invention about 30 years ago. There have been considerable improvements in material, process, design and concept of lithium batteries for all these years, but a completely safe battery is yet to be invented (Journal of Power Sources, 1997). However, the Li-ion polymer electrolyte battery, such as the one used for this study is considered safer, at its operating conditions, than all its predecessors. It uses manganese oxide, which is safer than other
oxides, as the cathode material, and a polymer electrolyte, which is safer than a liquid electrolyte.

In addition to safety, reliability and cost, environmental considerations must be taken into account. Like every other hazardous material, the disposal of spent Li-ion battery is controlled by the federal, state, and local industrial waste laws. The general method in practice for disposal of Li-ion battery is incineration. What makes a battery an environmental hazard is its final charge level, the hazardous nature of the individual cell components, and the chemical reactivity of the components. The battery is a potential fire hazard if not discharged completely.

Environmental and Safety Concerns of the Processes

Two processes for recycling the lithium manganese oxide from used battery cells were considered in this study. The final charge of the discarded battery, the reactivity of the chemicals inside the battery and the emissions and effluents generated from the recovery and regeneration processes are the major issues to be addressed when considering the engineering and designing of this recycling process. A completely discharged cell eliminates any fire hazard during disassembly of the used cell. The toxicity and reactivity of the battery components are addressed in the literature review (chapter 2) section of this study and safety measures should be taken accordingly. The nature and characteristics of the emissions and wastes from the two recovery processes are different and are briefly discussed below.

Solvent Process

The solvent process is the major source for the liquid waste generation since acetone is used to dissolve the binder to separate LMO from the current collector grid. A minimum of 900 g of acetone is used for each 100 g of binder containing in approximately 1000 g of cathode electrode taken for LMO separation. If 80% recovery efficiency for LMO from cathode electrode is assumed and if electrode with eighty percent by weight
LMO is used for the solvent recovery process. A batch of 1000 g cathode electrode will yield about 640 g LMO and a minimum of 1260 g solvent waste will also be generated. This solvent waste contains the binder and a small amount of electrolyte solution.

The major environmental concern of the solvent process is the treatment of generated waste solvent (acetone) that has binder and electrolyte dissolved in it. The separation of binder is possible by mixing the waste with another solvent that has a very high solubility with acetone compared to the binder. Binder will be separated due to the relative solubility difference and can be removed from the liquid phase. Because of the high volatility of the solvents, the LMO separation process must be performed under a hood to collect the solvent vapor from the process and the collected air must be scrubbed before venting out. All solvents, including EC and DMC from the electrolyte, in the remaining effluent can be separated by fractional distillation. The lithium salt thus will be concentrated in the bottom product. Further studies are needed to establish a systematic process for the recovery and disposal of the solvent-rich effluent from the LMO recovery process.

The regeneration reaction between the recovered lithium-deficient LMO and \( \text{Li}_2\text{CO}_3 \) releases few polluting agents to the atmosphere. While the LMO receives Li from \( \text{Li}_2\text{CO}_3 \), it releases \( \text{CO}_2 \) to the exhaust from the furnace and can be vented through a stack without further treatment.

**Dry Process**

Using the same assumption applied in the case of solvent process, except for the recovery efficiency, (recovery efficiency for LMO from dry process is assumed as 90%) to calculate the amount of the product and waste streams, the amount of LMO obtained from a batch of 1000 g cathode electrode by dry process is about 720 g. The major advantage of the dry process over the solvent process is that there is no liquid waste generation and thus eliminates the solvent treatment problem. But there are some other emissions which are needed equal design considerations because of the toxic nature of the gases.
Since the combustion of associated electrolyte and co-polymer occur during the recovery process of LMO from the cathode electrode in the dry process, stringent safety and environmental measures to be adopted in this step. Both electrolyte and co-polymer generate vapors of hydrogen fluoride (HF) which is corrosive, causes burns on contact with skin and other tissue, and has a TLV of 3 ppm (ELF Atochem. 1994). Also evolved are phosphorus oxides and phosphine. These gases must be collected efficiently and passed through a scrubber that contains basic solutions before venting to the atmosphere. More detailed studies are needed to establish the scrubber design criteria.

As explained earlier, the regeneration step does not cause any environmental hazard as there are few toxic chemicals or vapors generated during the process.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This study addressed an emerging environmental problem caused by the disposal of Li-ion battery by developing two processes for recycling lithium manganese oxide, one of the major components in the Li-ion battery.

Lithium manganese oxide was separated from spent batteries using two separate processes, and the chemical composition and structure were analyzed. The chemical and crystalline properties of the separated material were different from the LMO used for the initial battery making process. It was found that the cycling battery gradually loses its capacity as through a declining ability to intercalate Li ions between anode and cathode electrodes. Therefore, separated LMO from a used battery needs regeneration to bring it back to its original crystal structure and stoichiometry. A regeneration process was developed, and the LMO obtained by this process was analyzed using various methods. The test results were compared with the characteristics of a standard LMO material, and satisfactory results were obtained. Cells made from the regenerated LMO performed well in the EVS cycling.

For the process of separation of LMO from cathodic electrodes of a used battery by the solvent process, acetone is recommended, since it is the most common and economical solvent that can be used for the separation process. It is estimated that, about seventy to eighty percent LMO present in the electrode can be recovered by this process. In the dry process of separation of LMO, heating of electrode at 600 °C is recommended because at that temperature, all combustible components in the electrode will burn. Since
the aluminum current collector melts at above 660 °C. Temperatures above 600 °C are not recommended. Up to ninety-five percent of LMO recovery is estimated by this method.

Analysis of results from several regeneration tests at different conditions lead to the conclusion that a regeneration reaction at 800 °C for 12 hr in air with a heating rate of 2 °C/min and a cooling rate of 1 °C/min produced the best regenerated LMO. It is also observed that the Li:Mn ratio in the regenerated LMO could be exactly controlled by the ratio of the reactants initially taken for the regeneration reaction.

**Recommendations**

The following are the investigations to be done for further study.

1. Effect of regeneration reaction conditions on the particle size and the surface area of the regenerated LMO.

2. The reaction kinetics of the regeneration process in order to generate data for the process design.

3. Chemical reactions involved in the direct combustion of cathode electrode during recovery of LMO.

4. Reasons for slightly higher first cycle capacity loss for the dry process LMO cells compared to the solvent process LMO.

5. Applicability of the same technique of recycling LMO to other Lithium Metal Oxide (lithium cobalt and lithium nickel oxides) cells.
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