Development of Low Cost Cathode Materials for Lithium-ion Batteries

（リチウムイオン電池用低価格正極材料の開発）

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Chapter 1

Introduction
1.1 Introduction

Recently, the rapid advancement of science and technology became the engine for great industrial and economic growth. Through this growth the peoples of developed countries came to enjoy a comfortable and convenient way of life. Electric power is the key energy source in a current and future society, which supports the life of ease and the world’s socioeconomic system. As symbolized by the recent rapid growth in the use of compact portable telephones, computers and other electronic devices, it is also evident that batteries, particularly secondary batteries, have become an essential part of our electricity-dependent day and age. There can be no doubt that society consumption of electricity and dependence upon it will increase in a future. As batteries provide a high added-value energy source which makes life in a networked society even more convenient, there also can be no doubt the use of batteries will likewise increase.

Moreover, we have been more conscious of our environment in the future society. Global warming and environmental degradation as a result of massive consumption of fossil fuels, target figures for greenhouse gas reductions were established. From now on, instead of pursuing greater convenience, it will be crucial for human to pursue technological development that uses limited energy resources more efficiently and therefore reduces the burden on the environment. Secondary battery technology will be no exception. More than this, in the electricity and energy fields, secondary batteries will play a critical role in reducing the environmental burden created by the consumption of fossil fuels, and in enabling the effective utilization of renewable energy and other natural energy sources.

1.2 secondary batteries

Generally, secondary batteries can be categorized to several types, such as: conventional Lead-acid, Ni-Cd, Ni-MH, and Li-ion type secondary batteries.

Lead–acid secondary battery has a long history of about 150 years and is often used in automobiles for the engine ignition. Its low energy density and its environmental burden Pb
Nickel Cadmium (Ni-Cd) batteries were the standard technology for years, but today they are out of date and seldom are used in high-tech portable devices. They are heavy and very prone to suffer from the “Memory Effect”. The memory effect is caused by crystallization of the battery’s substances and can permanently reduce the battery's lifetime, even make it useless. To avoid it, the battery should be completely discharged and then fully recharged again at least once every few weeks. Another drawback of this battery is that it contains cadmium, a toxic material, and should always be recycled or disposed of properly.

Nickel Metal Hydride (Ni-MH) batteries are the cadmium-free replacement for Ni-Cd. They are less affected by the memory effect than Ni-Cd and thus require less maintenance and conditioning. However, they have problems at very high or low room temperatures. And even though they use less hazardous materials (i.e., they do not contain heavy metals), they cannot be fully recycled yet.

Lithium-ion batteries can be formed into a wide variety of shapes and sizes so as to efficiently fill available space in the devices. Li-ion batteries are lighter than other equivalent secondary batteries. The energy is stored in these batteries through the movement of lithium ions. Key advantage of using Li-ion chemistry is the high open circuit voltage that can be obtained in comparison to aqueous batteries (such as lead acid, nickel metal hydride and nickel cadmium). Li-ion batteries do not suffer from the memory effect. They also have a low self-discharge rate of approximately 5% per month, compared with over 30% per month in nickel metal hydride batteries and 10% per month in nickel cadmium batteries.

1.3 Lithium metal battery

The development of lithium ion battery is on the basic of the utilization of lithium metal. Because Li metal is lightest of all metals and possessed a relatively low potential. Obviously, lithium metal as anode can support higher energy density than other anodes. However, lithium metal is easily reacts with water and emits hydrogen gas. Therefore the
aqueous electrolyte cannot be used with lithium metal.

Lithium metal anode primary batteries based on non-aqueous electrolytes like propylene carbonate-lithium perchlorate and lithium negative electrodes were developed in the early 1970’s. A primary lithium cell, Li|LiBF₄/ GBL|(CF)ₖ was reported by M. Fukuda in 1973 [1]. Soon thereafter, another battery, Li|LiClO₄/ DME–PC|MnO₂ is commercialized by Sanyo in 1975. These cells were used for LED fishing floats, cameras and memory backup applications. A strong research effort was then mounted to convert lithium primary cells into rechargeable cells with high energy density. Table 1 [2] lists the various research efforts. In the 1970’s and 1980’s most efforts concentrated on inorganic cathode compounds. Conducting polymer materials such as polyacetylene, etc., were developed as possible negative and positive electrode materials. However, these polymer materials have about the same density as water, and that batteries made with these materials offered no competitive advantage over the then traditional lead rechargeable batteries. The low density conducting polymer cathodes have found use only for coin cells for memory backup.

Table 1.1  Various Rechargeable Lithium Metal Batteries Systems Developed

<table>
<thead>
<tr>
<th>System</th>
<th>Voltage</th>
<th>Wh/kg</th>
<th>Wh/l</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/TiS₂</td>
<td>2.1</td>
<td>130</td>
<td>280</td>
<td>’78 Exxon</td>
</tr>
<tr>
<td>LiAl/TiS₂</td>
<td></td>
<td></td>
<td></td>
<td>’79 Hitachi</td>
</tr>
<tr>
<td>Li/LiAlCl₄-SO₂/C</td>
<td>3.2</td>
<td>63</td>
<td>208</td>
<td>’81-85 Duracell</td>
</tr>
<tr>
<td>Li/CuCl₂</td>
<td>3.2</td>
<td>67</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>Li/V₂O₅</td>
<td>1.5</td>
<td>10</td>
<td>40</td>
<td>’89 Tohsiba</td>
</tr>
<tr>
<td>Li/NbSe₁</td>
<td>2.0</td>
<td>95</td>
<td>250</td>
<td>’83-86 Bell Lab</td>
</tr>
<tr>
<td>LiAl/Polyaniline</td>
<td>3.0</td>
<td>180</td>
<td></td>
<td>’87 Bridgestone</td>
</tr>
<tr>
<td>LiAl/Polypyrolle</td>
<td>3.0</td>
<td>180</td>
<td></td>
<td>’89 Kanebo</td>
</tr>
<tr>
<td>Li/Al/Polyacene</td>
<td>3.0</td>
<td></td>
<td></td>
<td>’91 Kanebo/Seiko</td>
</tr>
<tr>
<td>Li/MoS₂</td>
<td>1.8</td>
<td>52</td>
<td>140</td>
<td>’87 MoLi</td>
</tr>
<tr>
<td>Li/CDMO</td>
<td>3.0</td>
<td></td>
<td></td>
<td>’89 Sanyo</td>
</tr>
<tr>
<td>Li/Li₀.₃MnO₂</td>
<td>3.0</td>
<td>50</td>
<td>140</td>
<td>’89 Tadiran</td>
</tr>
<tr>
<td>Li/VOₓ</td>
<td>3.2</td>
<td>200</td>
<td>300</td>
<td>’90 HydroQuebec</td>
</tr>
</tbody>
</table>

Attempts to develop rechargeable lithium batteries have been carried out from the late 1970’s. In 1976, M. S. Wittingham et al. [3] reported the prototype Li secondary battery
using TiS$_2$ as cathode material. These electrode systems have been proven to have a basic reversible behavior. However, it soon encountered safety problems as secondary battery, the possibility of short circuit is existed because growth of Li metal that deteriorates the Li/separator interfaces and punctures the separator during charge/discharge process. Therefore, the use of the high performance perchlorates electrolytes was discontinued for safety reasons due to dendrite and very reactive fine powder deposits during recharge. In 1989, Moli Energy had a plant fire related to lithium metal in an AA-size cell. There was a shift to Li-Al alloy anode for greater safety in coin cells. However, the metallurgy of the alloy proved unacceptable for wound AA-size cells. Tadiran developed a dioxolane based electrolyte that spontaneously polymerized at temperatures above 110ºC. The polymerized electrolyte had high resistance and shut down cell operation to provide a safety measure for the cells. The lithium metal rechargeable cells are now mainly restricted to small capacity coin cells.

1.4 Lithium Ion batteries

Since lithium metal constituted a safety problem, in 1980 a breakthrough in concept was generated. M. Lazzari and B. Scrosati [4] proposed the “rocking chair battery” based two insertion compounds, Li$_x$WO$_2$ and Li$_y$TiS$_2$. Though this system could solve the problem of safety, it was unable to provide the practical energy required to make it attractive rechargeable system. Table 1 [2] documents the Summary of the early patents of lithium ion battery. Dr. Hironosuki Ikeda of Sanyo was the first to patent an intercalation material such as graphite in his June 1981 Japanese Patent No. 1769661. One year before Ikeda patent on graphite, Goodenough filed his LiCoO$_2$ patent for an intercalation cathode material. Basu of Bell Laboratories filed a patent U.S. Patent 4,423,125, in 1982 based on his finding of lithium intercalation in graphite at room temperature. Previously, Basu had found lithium intercalation into graphite in molten salt electrolytes at high temperatures U.S. Patent 4,304,825. I. Kuribayashi and A. Yoshino developed a new cell design using an intercalation carbon anode and a LiCoO$_2$ cathode and filed patents world wide. In here, the negative carbon electrode acts as “lithium sink” and LiCoO$_2$ electrode acts as a “lithium source” and total electrochemical process of the carbon/LiCoO$_2$ cell involved the cyclic
transfer of lithium ions between the two insertion electrodes:

\[
\text{Discharge} \quad \text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{CoO}_2 \quad \text{Charge} \quad \text{C}_6 + \text{LiCoO}_2 \quad (1-1)
\]

Using a pilot plant developed for rechargeable Li-MnO\(_2\) cells, Sony Energytec Inc. began to produce commercial cells (named as Li-Ion Battery) based on the Asahi patents in 1991. They also introduced electronic circuitry to control the charge-discharge, the use of a current interrupt device to interrupt current flow on buildup of excessive internal cell pressure and the use of a “shut-down” polymer separator.

Table 1.2 Summary of the early patents of lithium ion batteries

<table>
<thead>
<tr>
<th>Patents</th>
<th>Patents No and (application date)</th>
<th>Name</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition metal oxides as cathode, LiCoO(_2)</td>
<td>USP 4,302,518 (1980/3/31)</td>
<td>J.B. Goodenough</td>
<td>United Kingdom Atomic Energy Authority</td>
</tr>
<tr>
<td>Graphite/Li in nonaqueous solvents</td>
<td>US 4,423,125 (1982/9/13)</td>
<td>S. Basu</td>
<td>Bell Telephone Laboratories, Inc.</td>
</tr>
<tr>
<td>Additives for Gr, Vinylene Carbonate</td>
<td>US Pat. 5,626,981 (May 6, 1997)</td>
<td>B. Simon, J-P. Boeuve</td>
<td>Saft</td>
</tr>
</tbody>
</table>
This name, Lithium-Ion, is now widely accepted by the battery community, worldwide, although there is no lithium metal in the cell. Both electrodes operate by intercalation of lithium ions into the structure of the active materials. AT Battery Co., a joint venture of Toshiba Battery Co. and Asahi Chemical Co. was the second to commercialize the technology using Asahi patent portfolio.

![Diagram of lithium ion battery and lithium secondary battery](image)

**Fig. 1.1** Comparison of the model of lithium ion battery and lithium secondary battery.

The basic structure and working principle of lithium ion batteries was illustrated in Fig.1.1. General speaking, one Lithium ion battery consist a cathode, an ion-conductive electrolyte and an anode separated by separator. During charging, lithium ions are extracted
from cathode and go into electrolyte while lithium ions in the electrolyte insert into anode. The charge compensation is fulfilled through external circuit. During discharge, lithium ions de-intercalated from the anode and intercalated into cathode.

High specific energy density (related to both average working voltage and reversible capacity) and long cyclic life (related to the stability of structure and electrode-electrolyte interface) are simultaneously required for a high performance Lithium ion battery. Therefore, some aspects should be considered in the design of new electrode materials for lithium ion batteries. In general, structural and chemical stabilities, safety, and the availability of redox couple at a suitable energy are the primary considerations. Ideally, an electrode material should simultaneously match such conditions list as below:

a) Cathode and anode should have an open structure to permit reversible lithium insertion.

b) The stability of electrode and electrolyte is the requirement for long cycle life. The insertion/extraction reaction has a topotactic character and both insertion and extraction of guest lithium ions into and from host compound should ideally not modify the host structure. On the other hand, the oxidation of electrolyte should be avoided for oxidation and reduction.

c) The equivalent weight of both electrodes must be low in order to assure specific capacity values of practical interest.

d) The mobility of Li$^+$ ions and electrons in both the positive electrode and negative electrode must be high in order to assure fast kinetics of the electrochemical process and thus, fast charge and discharge rates.

e) The cost of battery and the potential influence on environment should be always kept in mind in new battery design. It is one of the future challenges to develop cheaper and hazardless electrode materials with excellent battery performance.
1.5 Trends in development of Li-ion batteries

Since Sony Co. firstly announced the commercialization of battery based on the patent of Asahi Chemical Ind. The Li-ion rechargeable developed by Sony used the layered LiCoO$_2$ intercalation compound as the positive electrode and a form of carbon as negative electrode. Many announcements were made to greatly improve lithium ion battery technology. As shown in Fig. 1.2 and Fig. 1.3, over the last 15 years there has been a great increase in energy density and units sold of lithium ion batteries. Energy density has improved 5.2 times over the last 15 years, a rate of 11.6% a year. If that trend were to continue, a doubling would occur every 7 years. Unfortunately, they don't specify how capacity (kWh) per dollar has improved over time.

![Trends in energy density of batteries](source)

Fig. 1.2. Trends in energy density of batteries.
Fig. 1.3. Growth of lithium ion battery industry in the past 10 years.

Fig. 1.4. Voltage vs. capacity of some electrode materials.
1.6 Cathode materials for lithium ion battery

Up to now, the most popular positive electrodes are these Li-based compounds, as indication in Fig. 1.4[5]. There are 4 type structure in Li-based compounds, which have lithium insertion voltage of above 3V, namely, layered Lithium metal oxides of LiCoO$_2$, LiNiO$_2$, LiCoNiO$_2$ and LiMnNiO$_2$, the zigzag layered structure of LiMnO$_2$, the three-dimensional spinel type, LiMn$_2$O$_4$ and LiNi$_{1/2}$Mn$_{3/2}$O$_4$, and olivine structure of LiMPO$_4$.

1.6.1 Layered Lithium metal oxides

The layered metal oxides with a general formula of LiMO$_2$ (M = Transition metal elements such as Co, Ni and Mn), in which the Li ion and M ion occupy the alternate (111) planes of the rock salt structure. The structure has an oxygen stacking sequence of …ABCABC… along the c axis and the Li and Me ions occupy alternatively the octahedral sites. There are three MO$_2$ sheets per unit cell. This structure can be described as a layered structure with a space group of $R\overline{3}m$, and the unit cell parameters are usually defined in terms of the hexagonal setting [6]. A schematic layered structure is presented in the Fig.1.5. The structure with MO$_2$ layers allows a reversible extraction/insertion of lithium ions from/into the lithium layer.

![Fig. 1.5. Schematic model of an ideal layer LiMO$_2$ structure.](image)
1.6.1.1 Layered LiCoO$_2$ compound

Among the layered metal oxides, LiCoO$_2$ is the one which has attracted particular attention. The LiCoO$_2$ has a hexagonal structure with cell parameters of $a = 2.82$ Å and $c = 14.08$ Å [6, 7]. Its working voltage is about 4V and its theoretical capacity of 274 mAh g$^{-1}$ corresponding to extraction of 1 mole of Li$^+$ from LiCoO$_2$. Complete removal of lithium from LiCoO$_2$ can not be accomplished due to a series of phase transformation between hexagonal and monoclinic is occurred when the cathode charged above 4.2V. Moreover, the capacity fading can be attributed to side reaction, Co dissolute remarkably at higher voltage > 4.2 V, from oxide compound into electrolyte. Therefore, its practical capacity is only 140mAh g$^{-1}$, near to half of its theoretical capacity [8-10]. In order to obtain higher capacity, many researchers reported that substitution of foreign elements such as Mg [11, 12], Al [13, 14], Fe [15-16], Ni [16-17], Cr [19], Mn [20] and Li [21-22] for Co in LiCoO$_2$ can to suppress phase transformation during cycling process. Recently, Zou et al [23] reported that small amount of foreign element can give intercalation/deintercalation process at higher cut-off voltage of 4.5V. Moreover, metal oxide coating on surface of LiCoO$_2$ particle, such as Al$_2$O$_3$ [24], AlPO$_4$ [24, 25], ZrO$_2$ [26], AlF$_3$[27]and ZnO [28], is also an effective methods to improve its cycleability for high voltage application (over 4.2V).

1.6.1.2 Layered LiNiO$_2$ compound

The other well-known member of LiMO$_2$ family is LiNiO$_2$. Nickel is more abundant and cheaper than cobalt. The crystal structure also belongs to hexagonal system with cell constant of $a = 2.88$ Å and $c = 14.18$ Å [29, 30]. Its working voltage is about 3.7 V and theoretical capacity is 275 mAh g$^{-1}$. The maximum reversible capacity of 200 mAh g$^{-1}$ for 4.3V charge, corresponding to about 87% theoretical capacity was removed from LiNiO$_2$. Up to 4.15V, the intercalation reaction appears to be highly revisable, thus giving the particularly achieved specific capacity of about 140 mAh g$^{-1}$. The reaction mechanism is already known to be a topotactic reaction consisting of three single-phase reaction for the 0 $\leq x < 0.75$ in Li$_{1-x}$NiO$_2$ and a two-phase reaction in $0.75 < x < 1$. These phase transformation could cause capacity fading [29, 30].
The drawback of practical application is difficultly prepared because high vapor pressure of lithium oxide at high calcination temperature and the presence of Ni$^{2+}$ at Li and Ni$^{3+}$ positions in LiNiO$_2$, leading to the nonstoichiometric composition $[\text{Li}_{1-x}\text{Ni}_x]_3\text{b}[\text{Ni}_{3\text{a}}\text{O}_2]_6\text{c}$ ($0<x<0.25$) [31]. This process reduces the application properties of the cathode material because the presence of Ni$^{2+}$ ions at lithium positions hinders lithium diffusion.

Another drawback of practical application is its safety problems, which relates to exothermic oxidation of the organic electrolyte with the collapsing delithiated Li$_x$NiO$_2$ structure [32]. Delithiated Li$_x$CoO$_2$ was found to be more thermally stable than its Li$_x$NiO$_2$ counterpart. Thus, substitution of Co for Ni in LiNi$_{1-x}$Co$_x$O$_2$ was adopted to provide a partial solution to the safety concerns surrounding LiNiO$_2$. A number of investigations also show that the partly substitution of small amount of Mn [33], Co [34] and Al [35] for Ni in LiNiO$_2$ can also enhance its thermal stability.

### 1.6.2 Spinel LiMn$_2$O$_4$ compound

A spinel LiMn$_2$O$_4$ is a promising cathode material for Li-ion batteries because of less toxicity, cheaper and safety. The structure of stoichiometric LiMn$_2$O$_4$ can been refined with space group Fd$\bar{3}$m, as represented in Fig.1.6. It can be described as a face-centered cubic close-packed oxygen, in which lithium and Mn ions occupy tetrahedral (8a sites) and octahedral (16 sites), respectively. Lithium ion in 8a tetrahedral sites can be reversibly extracted, thus cause LiMn$_2$O$_4$ transforms to $\lambda$-MnO$_2$. On the other hand, the spinel LiMn$_2$O$_4$ is changed to tetragonal Li$_2$Mn$_2$O$_4$ when more lithium ions are inserted into the 16c site at 2.8V. The overall electrochemical reaction is written as follow [36]:

\[
\begin{align*}
\lambda\text{-MnO}_2 + \text{Li}^+ + \text{e}^{-} & \rightarrow \text{LiMn}_2\text{O}_4 \\
\text{Li}_2\text{Mn}_2\text{O}_4 - \text{Li}^+ - \text{e}^{-} & \rightarrow \text{LiMn}_2\text{O}_4
\end{align*}
\] (1-2)

(Cubic)  Discharge  (Cubic)  Discharge  (Tetragonal)
The theoretical capacity of LiMn$_2$O$_4$ is 148 mA g$^{-1}$ when its work voltage is limited more than 3 V. Spinel LiMn$_2$O$_4$ is easy to prepare (compared with the synthesis of LiNiO$_2$) and the overall electrode cost would be minimized among these three kinds of electrode materials because Mn is more abundant and cheaper than Co and Ni. However, the main problem of LiMn$_2$O$_4$ is its severe capacity fading in both room temperature and elevated temperature. The mechanism of capacity degradation in storage or cycle is not clearly identified yet and many possible reasons have been proposed, such as structural instability [36-39], Jahn-Teller distortion [40], Mn dissolution into electrolyte [41-43] and so on.

The substitution of foreign metal ions for part of Mn in LiMn$_2$O$_4$, such as Li, Co, Ni, Al, Mg, Cr, Fe, can improve its cyclic performance with the cost of decline in reversible capacity [44-52]. Moreover, fluorine [53], and sulfur [54] doping at the oxygen site is also an effectively method to enhance its storage and cyclic properties.

![Fig. 1.6. Structure of cubic spinel LiMn$_2$O$_4$.](image)

**1.6.3 Zigzag layered LiMnO$_2$ compound**

Beside all merits that LiMn$_2$O$_4$ has, LiMnO$_2$ has another advantage over LiMn$_2$O$_4$. Its theoretical capacity is 285 mAh g$^{-1}$, higher than that of LiMn$_2$O$_4$. LiMnO$_2$ also has the same crystallographic formula of LiMO$_2$ as LiCoO$_2$ and LiNiO$_2$. Its thermodynamically stable structure, however, is not layered $\alpha$-NaFeO$_2$ type but orthorhombic with space group...
*Pmmn* (o-LiMnO$_2$). As shows Fig.1.7, this structure is an ordered rock-salt structure where LiO$_6$ and MnO$_6$ octahedral are each arranged in corrugated layers. Monoclinic LiMnO$_2$ (m-LiMnO$_2$, space group: C2/m) has cation ordering of the α-NaFeO$_2$ structure type, in which Li ions are located in the octahedral sites between MnO$_6$ sheets. In both polymorphs of LiMnO$_2$, the oxygen array is distorted from ideal cubic-close-packing by the cooperative Jahn-Teller distortion due to high-spin state of Mn$^{3+}$ ion [55, 56]. Monoclinic LiMnO$_2$ has iso-structural with layered LiCoO$_2$, however it is not thermodynamically stable. Therefore it can be prepared by ion exchange from α-NaFeO$_2$. Both polymorphs commonly also undergo phase transformation to spinel during cycling between 2 and 4.3 V.

The main problem of LiMnO$_2$ is its cycling induced phase transition from orthorhombic to spinel [57]. Spinel phase nucleates in the material during the first charge process and transformation to spinel is usually completed within a few charge-discharge cycles. Since the length of 3 V plateau is longer than that of at 4 V, it is usually expected as a 3 V class cathode material. It has been reported that its electrochemical characteristics were related strongly to its particle size [58]. Thus many works have been done to prepare LiMnO$_2$ with small particle size by means of soft chemistry method or mechanical milling [59].

Monoclinic LiMnO$_2$ with layered structure is usually obtained by soft chemical method due to metastable nature, such as ion-exchanged method [60]. The substitution of Al [61], Cr [62] for Mn in LiMnO$_2$ can make the layered structure stable, and this is consistent well with G. Ceder et al. prediction [63]. Nevertheless, the phase transformation to spinel is usually observed. Recently, Ammundsen et al. have reported that the phase transformation can be suppressed by Cr substitution [64].
1.6.4 Possibility of the post iron phospho-olivine cathode

Fig. 1.8. The position of LiMPO₄ (M=Fe, Mn, Ni, Co) in the promoting cathode materials for lithium ion battery.
1.6.4.1 LiMPO\textsubscript{4} compounds

Since LiCoO\textsubscript{2} was commercialized by Sony 15 years ago, a series excellent candidate has been made because of the expensive and oxidative unstable LiCoO\textsubscript{2} for cathode material. Among these materials, the layered rock salt systems \( \text{Li}_x\text{NiO}_2 \) (0\(<\)x\(<1\)), and the manganese spinel framework systems \( \text{Li}_x\text{Mn}_2\text{O}_4 \) are now used commercially as 4V cathode materials because they have been met with these needs in some degree. However, they still exhibit problem inherent to their compositions.

In recent years, the phospho-olivines LiMPO\textsubscript{4} (where M=Fe, Mn, Co, Ni) are now recognized as attractive alternatives. In spite of the same olivine structure for all the samples, the potentials of them are found to be respectively 3.5, 4, 4.8V and 5.2V for Fe, Mn, Co and Ni, respectively. As shown in Fig.1.8, it is observed that the theoretical energy density in (wh/g) of all phospho-olivines are ca. 170mAhg\textsuperscript{-1} and even larger than the LiCoO\textsubscript{2} and LiMn\textsubscript{2}O\textsubscript{4}. In these systems, the overwhelming advantage of Fe-based compound LiFePO\textsubscript{4} has been a focus on its inexpensive and naturally abundant, and less toxic than Co, Ni and Mn. This is first time that Fe-based compound as much promising cathode material was studied. It is well known that Li\textsubscript{x}FeO\textsubscript{2} is quiet unstable because the ratio of ionic radii \( r\text{Fe}^{3+}/r\text{Li}^{+}=0.88 \) (0.77-0.88 for LiMn\textsubscript{2}O\textsubscript{4} and LiNiO\textsubscript{2}) does not suitable for the semiempirical tolerance criterion. In order to overcome this problem, the large polyanions (XO\textsubscript{4}) (X=S, Mo, P, W etc.) with stability structure were studied by Goodenough’s group [65- 71]. The strong X-O covalence supports a relative high voltage. For example, the open –circuit voltages vs. lithium are 3.6V for LiFe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}, 2.8V for Li\textsubscript{3}Fe\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}, etc. Moreover, each sample shows large capacity achieved over 100mAh g\textsuperscript{-1}. As shown in Fig. 1.9 [72]. LiFePO\textsubscript{4} exhibits highest energy density among these cathodes of the lithium ion system in the current electrolyte potential window.
The LiMPO₄ (M=Fe, Mn, Co, Ni) compounds have the ordered olivine structure (shown in Fig.1.10). In fact, olivine is referred to one large family of compounds M₂XO₄, which has the common generalized AB₅O₄ formula as the spinel, and consists of hexagonal close packed (hcp) oxygen array, in which X atoms located 1/8 of tetrahedral sites. While M atoms located in half of the octahedral sites (denoted to M1 and M2). The MO₆ octahedral are linked through shared corners in the bc-plane, The LiO₆ octahedral form edge-sharing chains along the b-axis. One MO₆ octahedron shares edges with two LiO₆ octahedral and a PO₄ tetrahedron. PO₄ groups share one edge with a MO₆ octahedron and two edges with LiO₆ octahedra.

As shown in Fig 1.11, the electronic conductivity of LiFePO₄ is much lower than those of recent lithium storage cathodes recently used, such as LiMn₂O₄ (~10⁻⁴ log sm⁻¹), LiCoO₂ (~10⁻³ log sm⁻¹) [73-75] by a factor of more than 10⁵, only exhibiting values of 10⁻⁹~10⁻¹⁰ at room temperature. Thackeray et al. [76] suggest that the low electronic conductivity of LiFePO₄ may be due to strongly distorted continuous network of FeO₆.
Fig.1.10. Structure representation of LiMPO$_4$.

Fig.1.11. The electronic conductivity of the promising cathode materials.

It is generally accepted that LiCoO$_2$ possesses a two-dimension diffusion plan, While LiMn$_2$O$_4$ possesses a three dimensional channels for diffusion. For LiFePO$_4$, Goodenough
et al. [68] suggest firstly that lithium diffusion in LiFePO$_4$ would be analogues in the LiMO$_2$ layer oxides with M=Co and Ni. As showed in Fig.1.12. This crystal structure provides two spatial diffusion tunnels, running parallel to the c axis and a axis, respectively.

![Fig. 1. 12. Two possible spatial diffusion tunnels for Li ions in structure of LiMPO$_4$.](image)

Most recently, Ouyang et al. [77] concluded that the diffusion in LiFePO$_4$ is one dimension because the other migration pathways have much high-energy barriers resulting in very low possibility of lithium ion migration by first principle calculation. The data of the mean square displacements (MSD) clearly shows that Li ion diffuse only along c direction. Furthermore, they claimed that it lead to low lithium ion diffusion coefficient of LiFePO$_4$.

Based on the mentioned above, low electric conductivity and lithium ion diffusion coefficient have been main problems when LiFePO$_4$ is studied as promising cathode material, which leads to the initial capacity loss and poor rate capability. These problems have been investigated by foreign metal doping [78], mixing with the conductive materials, such as carbon, metal, metal oxide [79-82].

1.6.4.2 Li$_2$MSiO$_4$ compounds

The use of Li$_2$MSiO$_4$ as cathode materials was suggested as early as 1997 in the wake of the emergence of the phosphate electrode. The electrochemistry of Li$_2$FeSiO$_4$ [83], Li$_2$MnSiO$_4$ [84] and Li$_2$CoSiO$_4$ [85] has been reported since showing that these compounds
are able to provide one electron transfer per formula unit at average voltages of ca. 3.1 V, 4.2 V and 4.5V, respectively. Compared with phosphate materials (LiMPO₄) which only one lithium ion can be reversibly cycled, silicate materials (Li₂MSiO₄) would allow reversible extraction of two lithium ions in principle thus it should deliver higher capacity (theoretical capacity of approximately 320 mAh g⁻¹) than phosphates (theoretical capacity of approximately 170 mAh g⁻¹). The structure of Li₂FeSiO₄ is shown in Fig.1.13 [85]. It is an orthorhombic structure with layers of SiO₄ and FeO₄ tetrahedral lying on the ac-plane and linked along the c-axis by LiO₄ tetrahedral. Within these layers each SiO₄ tetrahedron shares its four corners with four neighboring FeO₄ tetrahedral. Lithium ions also occupy tetrahedral sites located between two of the [SiFeO₄] layers, where three of the oxygen atoms of every LiO₄ tetrahedral belong to the same layer and the fourth one to an adjacent layer. A path for lithium migration exists in the structure since the LiO₄ tetrahedral are arranged in rows running along the a-axis by corner-sharing.

However, the main drawback of these materials is their low intrinsic electron conductivity. For example, electronic conductivity of Li₂FeSiO₄ is as low as ~2×10⁻¹² S cm⁻¹ (insulator range) at 60 °C, which is much lower than that of LiFePO₄ (10⁻⁹ S cm⁻¹) at room temperature. In order to improve the electrochemical performance, some researchers have sufficiently reduced the length of solid state transport paths by solution method [84] and decorated such a material with conductive carbon [83-86, 88]. The electrical performance of these materials was firstly reported by Nyten et al [83]. This field is so younger that it needs further study in future. For example, the electrical performance of Li₂NiSiO₄ is still not reported.
Fig. 1.13. Schematic crystal structure of Li$_2$FeSiO$_4$, with Fe–O tetrahedra shown by dark gray (purple), the Si–O tetrahedra by light gray (yellow) and the Li atoms by light (green). The shared O atoms are shown by dark (red). Li ions at sites 1, 2, 3 and 4 are labeled.

1.6.4.3 Li$_2$MPO$_4$F compounds

Some research groups have noticed that fluoride phosphate Li$_2$MPO$_4$F, would be strong candidates for new cathodes with large capacity, as the theoretical capacity of Li$_2$MPO$_4$F is about 310 mAh g$^{-1}$ (if 2Li$^+$ can be reversibly removed), which is twice as large as that of LiMPO$_4$. Although the space groups of LiMPO$_4$ and Li$_2$MPO$_4$F are same, there are remarkable differences between the structures from a crystallographic point of view. LiMPO$_4$ has MO$_6$ octahedra, LiO$_6$ octahedra and PO$_4$ tetrahedra. In contrast, Li$_2$MPO$_4$F has MO$_4$F$_2$ octahedra instead of MO$_6$ octahedra. Okada et al. [89] reported preliminary results confirming the delitiation of Li$_2$CoPO$_4$F with lithium proceeds at 5 V. Similar results were expected with the Li$_2$NiPO$_4$F compound. However, the electrochemical testing of Li$_2$NiPO$_4$F remained unsuccessful most certainly due to electrolyte instability. The open circuit voltage value of Li$_2$NiPO$_4$F was estimated at 5.1 V by calculation [90]. On the other hand, it is difficult to synthesis Li$_2$FePO$_4$F and Li$_2$MnPO$_4$F due to low reactively of LiFePO$_4$ and LiF or LiMnPO$_4$ and LiF.
1.7 Targets of our research

Due to shortage of fossil fuels and environmental concerns, we are convinced that the green energy industry and related industries will become the main stream in the coming 30-50 years. This causes a strong demand of rechargeable batteries. The aim of our research is development of cathode materials with the high-efficiency, long-life, large-capacity and low-cost. Table 1.3 gives a comparison data among the existing cathode materials for lithium ion batteries. It shows that layered Li-Mn-Ni-O system, Li-Co-Ni-Mn-O and Li-Co-Ni-O system still mainly suffer from high cost and safety concern. While, LiFePO₄ (M=Fe and Mn) and Mn-spinel have the good safety characteristics, low cost and environmental friendly. These cathode materials are very suitable for large-scale lithium ion batteries occasions such as EV (Electric vehicles), HEV (Hybrid electric vehicles) and backup of power systems.

In chapter 2, we have verified the quantitative relationship between the capacity of 3.2V discharge plateau and oxygen defect degree of Mn-spinel. To further the insights on the influence of oxygen deficiency, I attempt to correlate the oxygen defect degree to capacity fading in detail.

In chapter 3, we have proposed very simple technique to decrease Mn dissolution and improve cycling performance of Mn-spinel cathode materials at elevated temperature. Here, two heating processes for production are used. High temperature heating in initial step contributes to help the development of crystal growth and leads to decrease in specific surface area. However, resulting intermediate samples belong to oxygen deficient spinel. The oxygen deficiency is repaired in the second step by heating at relatively lower temperature (ca. 600-700 °C) with excess Li salt. Furthermore, the cycling performance of Mn-spinel was also improved by a gas-suspension spray coating method.

In chapter 4, it has been confirmed that the increasing in surface area of LiFePO₄ is an effective way to improve the electrochemical property, which in turn causes the decrease in phase boundary area inside of the particle. In addition, I found that SnO coating can greatly improve a tap density of the LiFePO₄. Moreover, I also prepared P-site doped samples LiFeMₓP₁₋ₓO₄ (M = As, Mo, B) and the improved rate performance will be demonstrated.
Table 1.3 Comparison data among various cathode materials for lithium ion battery.

<table>
<thead>
<tr>
<th>Structure</th>
<th>cathode material</th>
<th>Average voltage</th>
<th>Practical Capacities (mAh g(^{-1}))</th>
<th>Cost</th>
<th>Environmental Concern</th>
<th>Temperature Range</th>
<th>safety</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer</td>
<td>LiCoO(_2)</td>
<td>4V</td>
<td>130~150</td>
<td>high</td>
<td>Acceptable</td>
<td>Decay beyond (-20(^\circ)C to 55(^\circ)C)</td>
<td>Acceptable</td>
</tr>
<tr>
<td></td>
<td>LiNiO(_2)</td>
<td>4V</td>
<td>~220</td>
<td>High</td>
<td>Acceptable</td>
<td></td>
<td>Unstable</td>
</tr>
<tr>
<td></td>
<td>LiNi(<em>{1/3})Co(</em>{1/3})Mn(_{1/3})O(_2)</td>
<td>4V</td>
<td>180~220</td>
<td>high</td>
<td>Acceptable</td>
<td></td>
<td>Acceptable</td>
</tr>
<tr>
<td></td>
<td>LiNi(_{1-x})Co(_y)O(_2)</td>
<td>4V</td>
<td>180~180</td>
<td>high</td>
<td>Acceptable</td>
<td></td>
<td>Acceptable</td>
</tr>
<tr>
<td></td>
<td>LiNi(<em>{0.8})Mn(</em>{0.5})O(_2)</td>
<td>4V</td>
<td>160~200</td>
<td>stable</td>
<td>Acceptable</td>
<td></td>
<td>Acceptable</td>
</tr>
<tr>
<td></td>
<td>Li(<em>{1.2})Cr(</em>{0.4})Mn(_{0.4})O(_2)</td>
<td>4-5V</td>
<td>150~200</td>
<td>Structure change</td>
<td>Acceptable</td>
<td>Dangerous</td>
<td></td>
</tr>
<tr>
<td>Zigzag layer</td>
<td>LiMnO(_2)</td>
<td>3~4V</td>
<td>~200</td>
<td>Structure change</td>
<td>Acceptable</td>
<td></td>
<td>Acceptable</td>
</tr>
<tr>
<td>Spinel</td>
<td>LiMn(_2)O(_4)</td>
<td>4V</td>
<td>130~145</td>
<td>Acceptable</td>
<td>Acceptable</td>
<td>Good</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiCoMnO(_4)</td>
<td>5V</td>
<td>130~145</td>
<td>Stable</td>
<td>Acceptable</td>
<td>Electrolyte decomposition</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiNi(<em>{0.8})Mn(</em>{1.5})O(_4)</td>
<td>5V</td>
<td>125~145</td>
<td>Acceptable</td>
<td>Acceptable</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CoLiVO(_4)</td>
<td>4V</td>
<td>135~145</td>
<td>High</td>
<td>Dangerous</td>
<td></td>
<td>Acceptable</td>
</tr>
<tr>
<td>Olivine</td>
<td>LiFePO(_4)</td>
<td>3.5V</td>
<td>~150</td>
<td>Stable</td>
<td>Low</td>
<td>Friendly</td>
<td>-20(^\circ)C to 70(^\circ)C</td>
</tr>
<tr>
<td></td>
<td>LiMnPO(_4)</td>
<td>4V</td>
<td>~150</td>
<td>Acceptable</td>
<td>Acceptable</td>
<td></td>
<td>Excellent</td>
</tr>
</tbody>
</table>
In chapter 5, the spray dry method was used for the preparation of LiMnPO$_4$ with improved physical properties and electrochemical properties. Furthermore, it is confirmed that the combination of carbon coating technology with the spray dry technique brings further improvement in electrochemical properties of LiMnPO$_4$ cathode.

Reference


[80] Marca M. Doeff, James D. Wilcox, Robert Kostecki, and Grace Lau, J. Power Sources,


Chapter 2

Oxygen Deficiency, a key factor in controlling the cycle performance of Mn-spinel cathode for lithium ion batteries
2.1 Introduction

Spinel type lithium manganese oxides are the most promising cathode materials for lithium ion batteries because they are cheaper, less toxic and more easily prepared than other candidates (lithium nickel oxides and lithium iron orthophosphate). A problem hindering the practical application of Mn spinel is the capacity fading upon cycling in both spinel/Li and spinel/carbon cells, especially at elevated temperature. Several reasons have been suggested to explain its degraded cycling performance, including structural instability [1-3], Jahn-Teller distortion [4] and Mn dissolution into electrolyte [5-7], etc. But no general consensus for the capacity fading mechanism has yet been reached.

Other than the above reasons, Deng et al. [8, 9] recently proposed that oxygen deficiency plays most important role in cycleability. Greatly improved cycling performance could be obtained for Li-rich spinel with oxygen stoichiometry even at elevated temperature. It was also found that oxygen defect degree is reduced as result of Mn dissolution during storage at elevated temperature. Takahashi et al. [10] believed that stabilized structure by reducing the oxygen deficiency contributes to the improvement of 60°C storage performance of the cell.

In fact, to suppress Mn dissolution from spinel surface in the electrolyte, the surface area of spinel can be made small by the means of sintering at rather high temperatures (over 850°C). It is likely that oxygen deficiency often presents in extra-heated spinel samples [11, 12]. In the charge-discharge profiles for this type of samples (as shown in Fig. 2.1), a “fingerprint” 3.2V discharge plateau usually appears. Gao and Dahn have ascribed the 3.2V discharge plateau to oxygen deficiency and suggested to use it as a “qualitative indicator for detecting oxygen deficiency” [12].

We have verified the quantitative relationship between the capacity of 3.2V discharge plateau and oxygen defect degree. To further the insights on the influence of oxygen deficiency, we attempt to correlate the oxygen defect degree to capacity fading in detail. In this study, we have prepared series of Mn-spinel and Al doped Mn-spinel with different oxygen defect degree by strictly controlling the synthesis conditions. The effects of oxygen
deficiency on the structure change as well as the cycle performance have been addressed.

2.2 Experimental

The undoped spinel samples were prepared by melt-impregnation method as follows. The mixture of Mn$_3$O$_4$ (Tosoh, Japan) and LiOH was pre-calcined 500 °C for 5 h in air, and then post-calcined at the temperature range of 700–900 °C in air. The chemical composition of as-prepared samples was determined by chemical analysis, and some results were listed in table 3.1. The details of chemical analysis were described in the previous paper [13].

Two series of Li$_{1+x}$Al$_y$Mn$_{2-x-y}$O$_4$ ± δ (x=0.05, y=0.05, 0.10 and 0.15) samples were prepared by two methods. The detail of syntheses process was described in the Chapter 3.

To investigate the reaction mechanism that occurs in the spinels material, ex situ XRD patterns were collected on the spinel electrodes at selected capacity points during the initial charge. The cells were dismantled in an Ar-filled glove box, and then the spinel electrodes were recovered and washed by DMC solvent to remove the salt. After the evaporation of DMC, the electrodes were covered by a thin transparent waterproof paraffin film and were subjected to XRD measurement. XRD data of spinel electrodes were collected in the range of 2θ = 10–80° with a step of 0.02°
Table 3.1
Chemical composition of oxygen-deficient spinel samples

<table>
<thead>
<tr>
<th>Heating temperature (°C)</th>
<th>Chemical composition (LiMn)$<em>3$O$</em>{4-z}$</th>
<th>z in</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>Li$<em>{1.010}$Mn$</em>{1.990}$O$_{3.995}$</td>
<td>0.005</td>
<td>This study</td>
</tr>
<tr>
<td>750</td>
<td>Li$<em>{1.005}$Mn$</em>{1.994}$O$_{3.994}$</td>
<td>0.006</td>
<td>This study</td>
</tr>
<tr>
<td>800</td>
<td>Li$<em>{1.010}$Mn$</em>{1.990}$O$_{3.988}$</td>
<td>0.012</td>
<td>This study</td>
</tr>
<tr>
<td>800</td>
<td>Li$<em>{1.015}$Mn$</em>{1.985}$O$_{3.997}$</td>
<td>0.003</td>
<td>Ref. [15]</td>
</tr>
<tr>
<td>850</td>
<td>Li$<em>{1.002}$Mn$</em>{1.998}$O$_{3.981}$</td>
<td>0.019</td>
<td>This study</td>
</tr>
<tr>
<td>850</td>
<td>Li$<em>{1.013}$Mn$</em>{1.987}$O$_{3.973}$</td>
<td>0.015</td>
<td>Ref. [15]</td>
</tr>
<tr>
<td>900</td>
<td>Li$<em>{1.013}$Mn$</em>{1.987}$O$_{3.973}$</td>
<td>0.023</td>
<td>Ref. [15]</td>
</tr>
</tbody>
</table>

2.3 Results and Discussion

We consider that the oxygen-defect spinel has schottoky type oxygen defect as shown in Fig. 2.2. Above structure is supported by crystallographic studies [14], one oxygen vacancy give rise to three Mn ions with the coordination number of 5 (MnO$_5$), which links with three MnO$_6$ octahedrons across O atom. Therefore, 1 mol defect oxygen forms 12 Mn atoms (three sets of MnO$_5$–(MnO$_6$)$_3$), which contribute to the two equivalent plateaus at 3.2 and 4.5V. Here, these capacities are expressed as $C_{3.2V}$ and $C_{4.5V}$, respectively. Assume that the molar ratio of Mn$^{3+}$/($\text{Mn}^{3+}+\text{Mn}^{4+}$) is 0.5 and 1 mol Mn$^{3+}$ in LiMn$_2$O$_4$ delivers 148 mAh g$^{-1}$ capacity, we could obtain the following equation for the capacity of 12$\delta$ mole Mn in LiMn$_2$O$_4$ . $\delta$: $C_{3.2V}+C_{4.5V} = 148 \times 12\delta \times 0.5$. Since $C_{3.2V}$ equals to $C_{4.5V}$, $C_{3.2V}$ could be expressed as (1):

$$C_{3.2V}=148 \times 12\delta \times 0.5 \times 0.5=444\delta$$ (1)
In order to further confirm the accuracy of the above equation, based on the data of previous paper [15] and the present work, we plot the $C_{3.2V}$ against $444\delta$ as shown in Fig. 2.3. The linear relationship in this figure would strongly support our suggestion, which is based on the crystallographic reason.
In this work, the relation between cycling performance and oxygen defect degree for Li-Mn-O spinel system can be seen in Fig. 2.4, where the capacity retention after the first 50 cycles along with various oxygen defect degree $\delta$ were described. Besides the four painted circles applied in our previous paper [13], four open circles were added in the present work. All the points are distributed around a straight line. It shows an almost relationship between oxygen defect degree and the capacity fading, and the capacity retention $C_{50}/C_{1}$ could be expressed as follows: $C_{50}/C_{1}=(100 - 2.17 \times 10^{3}\delta)/100$. Moreover, the extrapolation of this line to $\delta = 0$ could give the crossover point of 100%. Therefore, it would indicate that the most important factor for improving cycleability is oxygen stoichiometry in spinel cathode material when the spinel cathode was cycled at room temperature.
The relation between cycling performance and the degree of oxygen defect can be more clearly observed in Fig. 2.5, where the capacity retention after 50 cycles at 60°C is plotted against the oxygen defect degree $\delta$. Beside four painted circles obtained from the present work, four open marks were added in our previous study [8, 9]. Although the kind of doping metal is different, the capacity retentions give a linear line against the oxygen defect degree $\delta$. The capacity retention $C_{50}/C_1$ at 60°C could be reduced as follows: $C_{50}/C_1=(100 - 2.75 \times 10^3 \delta)/100$. It shows that the capacity fading of high temperature is more significant than that of room temperature ($100 - 2.17 \times 10^3 \delta$). When $\delta$ is extrapolated to 0, the capacity retention would achieve ca. 100%, which is very similar to Fig. 2.3. Consequently, we confirm that the oxygen stoichiometry is a determining factor in cycleability improvement in spite of ambient temperature. In fact, Al-doping can help the increase in the oxygen content in the spinel when they were synthesized in the same condition, and it turns to improve the cycling performance of spinel samples.
The lattice parameters are also influenced by oxygen deficiency. Fig. 2.6 shows the relation between lattice parameter and δ in spinel compounds. It is clear that lattice parameters of Li-Mn-O spinel increase with the increase in oxygen content. The intersect point at δ = 0 is 8.237 Å would be the accurate lattice parameter of the ideal LiMn$_2$O$_4$ with oxygen stoichiometry.

The different electrochemical performance, including capacity and recharge-ability might be due to the difference in electrometrical Li$^+$-intercalation mechanisms. To investigate the changes in the crystal structure during charge, XRD examinations were performed on both oxygen stoichiometric spinel and oxygen defect spinel. The cubic lattice parameter for oxygen stoichiometric spinel, lithium rich spinel with oxygen stoichiometry and oxygen defect spinel as a function of lithium content, $z$, in Li$_{1-z}$Mn$_2$O$_4$ are plotted in Fig. 2.7(A), (B) and (C), respectively. It is evident in Fig. 2.7(C) that, in the range of $0<z<0.2$, the $a_o$ retains the constant value of 8.25 Å, which could be considered as the two-phase coexist region. Moreover, two crystal phases with different lattice parameters still present in the range of 0.5<$z<1$. These results show clear evidence of two-phase coexistence regions on both the 4.0 and 4.2V plateau, in agreement with the three cubic model proposed by Yang et al. [16].
Fig. 2.7(A) shows that the $a_0$-axis shrinks almost linearly from 8.247 to 8.125Å in the region for $0<z<0.5$. This is very different from the oxygen defect sample, where two-phase coexistence in the same region. The different unit-cell lattice change patterns during charge and discharge in this region mainly results in the different electrochemical properties between oxygen stoichiometric spinel and oxygen defect spinel. It further confirmed that the capacity fading during cycling for oxygen defect spinel occurs on both 4.0V and 4.2V plateau. In contract, this fading occurs on 4.2V plateau only for the spinel without an oxygen deficiency. These results are in good agreement with the result reported by Xia and Yoshio [2].
On the other hand, Fig. 2.7(B) shows that $a_0$ decreases almost linearly from 8.22Å to 8.15Å in the region of $0<z<0.3$, and then decreases almost linearly from 8.15 Å to 8.05 Å in the region of $0.3<z<0.8$. This can be considered as the one-phase model proposed by Xia and Yoshio for lithium-rich samples [2]. It should be noted that there are no two-phase coexistence in $z>0.55$, which is very different from the Fig. 2.7 (A) and Fig. 2.7 (C). We suggest that excess lithium could suppress the phase transitions at all region. In altering the lithium and oxygen content by different annealed temperature and synthesis procedures, we have successfully reproduced the results for the one-phase, two-phase, and three-phase models. This clearly demonstrates that the structural changes during charge/discharge cycling are determined by the Li/Mn ratio and the oxygen deficiency.

**Fig. 2.8.** The *ex situ* XRD patterns for N-Al015-660 cathode at different charge states.

Fig. 2.8 shows the *ex situ* XRD patterns for N-Al015-660 ($\text{Li}_{1.039}\text{Al}_{0.146}\text{Mn}_{1.815}\text{O}_{4.017}$) cathode during the initial charge from 3.0-4.3V under galvanostatic condition of 0.4 mA/cm². All the diffraction peaks move to higher angles in a continuous fashion during
charge. Further, it is confirmed that the ex situ XRD patterns of Al doped oxygen defect spinel C-Al005-1000 (Li$_{1.033}$Al$_{0.049}$Mn$_{1.918}$O$_{3.990}$) also are similar to those of N-Al-660 during charge process. This behavior is quit different from that of normal Li-Mn-O spinel with oxygen deficiency [2], which gives two-phase mechanism in both low and high voltage regions of charge process. In other words, electrochemical processes of Al doped oxygen defect spinels are completely different from those of normal oxygen defect Li-Mn-O spinel. Moreover, there are no any new peaks during cycling, so it is suggested that the crystal structure is very stable in the charge process.

In order to obtain more detailed information for the structure of two typical spinels, cubic lattice parameters of both samples were calculated and plotted as a function of z in Fig. 2.9. The unit cell sizes of de-lithiated oxygen stoichiometric spinel, Li$_{1.039-z}$Al$_{0.146}$Mn$_{1.815}$O$_{4.017}$, shrink uniformly from 8.17 Å to 8.06Å and the shape of the curve is expressed as one continuous line. Similar results have been also reported in the

![Variation of the a_o-axis lattice parameter for N-Al015-660 and C- Al005-1000 cathode at different charge states.](image-url)

Fig. 2.9. Variation of the a$_o$-axis lattice parameter for N-Al015-660 and C- Al005-1000 cathode at different charge states.
LiMn$_{1.95}$M$_{0.05}$O$_4$ (M=B and Ni) compounds [17]. On the other hand, the curve of oxygen defect spinel, Li$_{1.033-z}$Al$_{0.049}$Mn$_{1.918}$O$_{3.990}$, is composed of two continuous lines divided at ca. \( z=0.4 \). Both lines are roughly parallel with that of oxygen stoichiometric spinel. The cell sizes of oxygen defect spinel in the region of \( z<0.4 \) are 0.04\( \AA \) larger than those of oxygen stoichiometric spinel, however, both spinels give roughly same sizes in the region of \( z>0.5 \). Sudden shrinkage attacks oxygen defect spinel at around \( z=0.4 \). We believe this impact causes the instability of crystal during the cycling. Moreover, the doped spinel with oxygen defect exhibits larger volume change (\( \Delta a_o/\Delta z=0.18 \)) in all region than that of J. Lee’s [17], who reported that the volume change in LiMn$_{1.95}$Al$_{0.05}$O$_4$ is 0.13-0.14 when the sample prepared at relatively low temperature of 800 \(^\circ\)C. Such large volume change is essentially due to larger cell size of oxygen defect spinels because the delithiate products have the same unit cell volume. In fact, volume change of our oxygen stoichiometric spinel is also about 0.13 in all regions. Moreover, a comparison of Fig. 2.9 and Fig. 2.3 reveals that the phase transition evolving at \( x>0.55 \) in undoped spinel is greatly suppressed by Al doping. In the previous paper [1, 2], we have suggested that the structure of spinel collapses due to the lattice stress imposed by the phase transition occurring in all regions for oxygen defect undoped spinel. Therefore, the excellent cycling performance of this sample may also be correlated with the absence of a phase transition.

3.4. Conclusions

In this study, \textit{ex situ} XRD has further indicated the cause of capacity fading in various kinds of spinels. It shows clearly that two-phase coexistence region occurs on both the 4.0 and 4.2V plateau for undoped spinel with oxygen deficiency. This behavior is quite different from the undoped spinel with oxygen stoichiometry, where two-phase coexistence region occurred on the 4.2V plateau region only. However, Al doped spinel with oxygen stoichiometry shrink uniformly from 8.17 \( \AA \) to 8.06\( \AA \) during de-lithiation, which could be considered as one-phase reaction. I have confirmed that the capacity retentions give a linear line against the oxygen defect degree \( \delta \) in normal spinel at room temperature, as well as Al doped spinel at 60 \(^\circ\)C. When \( \delta \) is extrapolated to 0, the capacity retention would achieve ca.
100% in both cases. Furthermore, I determined the accurate lattice parameter of the ideal LiMn$_2$O$_4$ without oxygen deficiency is 8.237Å.

References

Chapter 3

Improved Cycling Performance of Mn-Spinel Cathode Materials at Elevated Temperature
3. 1. Improvement cycling performance of Mn-spinel cathode materials by two-step method

3.1.1 Introduction

Spinel type lithium manganese oxides are the most promising cathode materials for lithium ion batteries because they are cheaper, less toxic and more easily prepared than other candidates (lithium nickel oxides and lithium iron orthophosphate). A problem hindering the practical application of Mn spinel is the capacity fading upon cycling in both the spinel/Li and spinel/carbon cells, especially at elevated temperature. Several reasons have been suggested to explain its degraded cycling performance, including structural instability [1-3], Jahn-Teller distortion [4] and Mn dissolution into electrolyte [5-7], etc.

It has been recognized that partial substitution of Mn with other metal cations, such as Li, Co, Ni, Al, Mg, Cr, Fe and so on [9-17], can improve the cycling performance of spinel cathode. However, the capacity fading mechanism of metal-doped spinel remains not clear. Now, we believe that the oxygen stoichiometry of spinel is the most important factor controlling the capacity retention during cycling [2], and metal doping only plays a role in helping the formation of oxygen stoichiometric spinels.

The spinel cathode materials should be prepared at relatively milder temperature of less than 850°C in order to suppress the formation of oxygen deficiency. Such oxygen stoichiometric spinels prepared by one step calcination have inevitably caused higher specific surface area and low crystallinity. The surfaces of spinel samples possess a certain catalytic activity towards electrolyte oxidation, and then high surface area is likely to trigger the electrolyte oxidation which accompanies dissolution of Mn from spinel. Dissolved Mn ion would destroy SEI film formed on the graphite anode and make the performance of full lithium-ion battery become worse [18]. Especially, such effect becomes more severe at elevated temperature so that ordinary oxygen stoichiometric spinel with high surface area can not be used as cathode material in practical lithium ion batteries.

For the sake of overcoming this problem, many researchers use coating technique [19-23], which would lead to lower rate capability. The spinel cathode materials were
prepared at high temperature (>850 °C) in order to decrease the surface area. Such spinels with lower surface area often present oxygen deficiency. Recently, Takahashi et al. [24] reported that annealing at 800 °C after 1000 °C calcinations can reduce the oxygen defect content in the Mg-doped spinel and they showed improved discharge capacity even after the storage at 60 °C. However, we also noticed that a 3.2V plateau still exits (although very tiny to be perceived) in their modified spinel.

In this paper, I have proposed very simple technique to decrease Mn dissolution and improve cycling performance of spinel cathode materials at elevated temperature. Here, two heating processes are used. High temperature heating in initial step contributes to help the development of crystal growth and leads to decrease in specific surface area. However, resulting intermediate samples belong to oxygen deficient spinel. The oxygen deficiency is repaired in the second step by heating at relatively lower temperature (ca. 600 - 700 °C) with excess Li salt.

We have synthesized a new spinel with Al-doping and “controlled” oxygen stoichiometry with small specific surface area by above new two-step method. These new materials have shown very low Mn dissolution of 3.2 ppm for 2 week storage in electrolyte at 60°C, and greatly improved cycling performance at elevated temperatures compared to those synthesized by conventional method, especially in the full lithium ion battery (graphite/spinel).

3.1.2 Experimental

Various metal-doped Mn-spinels (LiMn_{1.9}M_{0.1}O_4 - δ, M: Li, Mg, Al, Cr, Co, Fe and Ni, δ: oxygen defect content) were synthesized by a conventional solid state reaction from the mixtures of starting materials, such as LiOH (FMC Co.), Mn_3O_4 (Mitsui Mining Co.), MgO (Ube Co.), Al_2O_3 (Showa Electric Co.), Cr_2O_3 (Koujundo Kagaku Co.), Co_3O_4 (Seido Chemical Co.) Fe_2O_3 (Koujundo Kagaku Co.) and NiO (Seido Chemical Co.). They were
fired at 900 ~ 1000 °C for 10 h in air, where the rate of the heating/cooling was controlled to be 100 °C/h.

Two series of Li$_{1+x}$Al$_y$Mn$_{2-x-y}$O$_{4+δ}$ (x=0.05, y=0.05, 0.10 and 0.15) samples were prepared by two different methods, respectively. The N series samples were prepared by a two-step solid state reaction: 1) in the first step; the mixture of LiOH, Mn$_3$O$_4$ and Al$_2$O$_3$ (in the mole ratios of 1: 1.95:0.05, 1: 0.9: 0.10 and 1: 0.85: 0.15 for N-Al005-660, N-Al010-660 and N-Al015-660, respectively) was heated at 500 °C for 5h and then calcinated at 1000 °C for 10 h to get an intermediate product with small surface area; 2) in the second step; the extra LiOH (0.05 for 1.0 LiOH in the starting material) was added into the intermediate product and then annealed at 660 °C for 10h to get the final product. Another C series samples designed as C-Al005-T, C-Al010-T and C-Al015-T (“T” is 800, 850, 900, 950 or 1000 corresponding to the calcination temperature), which have almost the same Al content with N-Al005-660, N-Al010-660 and N-Al015-660, were prepared by the conventional one-step method [2].

The chemical composition of as-prepared samples were determined by chemical analysis and listed in table 3.1.1. The details of chemical analysis were described in the previous paper [8].

The structures of the samples were characterized by XRD (Rigaku Rint 1000) using CuKα radiation. The specific surface area was measured by the BET method (Micromeritics FlowsorbIII). The morphologies of the materials were observed by scanning electron microscopy (SEM).
### Table 3.1.1 Chemical formula of Al-doped spinels

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Chemical composition</th>
<th>Average Mn valance</th>
<th>Prepared method</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Al005-1000</td>
<td>Li$<em>{1.033}$Al$</em>{0.049}$Mn$<em>{1.918}$O$</em>{3.990}$</td>
<td>3.545</td>
<td>One-step method</td>
</tr>
<tr>
<td>C-Al010-1000</td>
<td>Li$<em>{1.035}$Al$</em>{0.110}$Mn$<em>{1.855}$O$</em>{3.994}$</td>
<td>3.570</td>
<td>One-step method</td>
</tr>
<tr>
<td>C-Al015-1000</td>
<td>Li$<em>{1.041}$Al$</em>{0.148}$Mn$<em>{1.811}$O$</em>{3.997}$</td>
<td>3.594</td>
<td>One-step method</td>
</tr>
<tr>
<td>N-Al005-660</td>
<td>Li$<em>{1.035}$Al$</em>{0.053}$Mn$<em>{1.912}$O$</em>{3.993}$</td>
<td>3.552</td>
<td>Two-step method</td>
</tr>
<tr>
<td>N-Al010-660</td>
<td>Li$<em>{1.038}$Al$</em>{0.097}$Mn$<em>{1.865}$O$</em>{3.999}$</td>
<td>3.576</td>
<td>Two-step method</td>
</tr>
<tr>
<td>N-Al015-660</td>
<td>Li$<em>{1.039}$Al$</em>{0.146}$Mn$<em>{1.813}$O$</em>{4.017}$</td>
<td>3.613</td>
<td>Two-step method</td>
</tr>
</tbody>
</table>

The electrochemical performance of spinel was evaluated using CR2032 coin-type cells. Cathodes were prepared by mixing Mn-spinels with 8wt% polyvinylidene fluoride (PVDF) and 4wt% acetylene black (AB). The slurry mixture was coated on an Al foil and then pressed. Unless specified otherwise, lithium metal was used as an anode and glass fiber (GA-100) as the separator (Toyo Roshi Kaish, Ltd., Japan). The electrolyte was 1M LiPF$_6$-ethylene carbonate/dimethyl carbonate (EC/DMC, 1:2 by volume) (Ube Industries, Ltd., Japan). Cells were galvanostatically charged and discharged with a cut-off voltage range of 3V~4.3 V vs. Li/Li$^+$ electrode at room temperature (RT) and 60 °C.

In the lithium ion batteries, the MCMB6-28 anodes were prepared by coating the slurry of 90% MCMB6-28 (Osaka Gas Co., Ltd.) and 10% PVDF (Kureha Co., Ltd.) dissolved in N-methyl pyrrolidone (NMP) is coated onto copper foil. An electrochemical test in the voltage region of 3V~4.2V was performed at a constant charge/discharge rate of 0.4mA/cm$^2$ at room temperature and 60 °C.

The Mn dissolution was determined by ICP after two weeks storage of 3g as-prepared samples in 30ml of electrolyte solution at 60 °C.

### 3.1.3 Results and Discussion

From the previous studies, it was found that oxygen deficiency is always present in extra-heated spinel samples. In the charge–discharge profiles for oxygen-deficient spinel, a 3.2V discharge plateau (C$_{3.2V}$) usually appears, together with 4.5V charge–discharge
plateaus delivering equivalent capacities. The quantitative relationship between the 3.2V plateau capacity and oxygen vacancy degree have been already established in Li-Mn-O spinel compounds [25], where $\delta$ is calculated by $C_{3.2V}/444$. Fig. 3.1.1 shows the effect of various foreign metals doping on the initial discharge capacity of $C_{3.2V}$ for LiMn$_{1.9}M_0.1$O$_4-\delta$, (M: Mg, Al, Fe, Cr, Co, Ni, Li and Mn, $\delta$: oxygen defect content) spinel samples. It is confirmed that all spinel sample prepared at more than 900 °C have oxygen defect. The values of $C_{3.2V}$ in normal metal doped spinel compounds are always increased as the increase in heating temperature. It was found that Mg and Al doping could suppress 3.2 V capacity effectively even at the sintering temperature as high as 900–1000 °C. Moreover, the theoretical capacity of 4V region increases with increased in oxidation number of the doped metal ion in the 16d site of LiMn$_2$O$_4$ at the same doping level in mole fraction. Therefore, Al substituted manganese spinel is expected to be a best cathode material with higher capacity and lower oxygen defect.

![Graph showing the effect of various metal doping on the initial discharge capacity of $C_{3.2V}$ for LiMn$_{1.9}M_0.1$O$_4-\delta$.](image)

Fig. 3.1.1. Initial discharge capacity of the 3.2V plateau ($C_{3.2V}$) for various metal (M) doped spinel samples (LiM$_{0.1}$Mn$_{1.9}$O$_4$) prepared at 900-1000°C in air.
The rate capability of various metal (M) doped spinel samples (LiM₀.₁Mn₁.₉O₄) prepared at (a) 900°C and (b) 950°C has been determined by evaluating the variation of the discharge capacity versus current (Fig. 3.1.2(a)). All the samples analyzed show similar rate capability, the capacity decreases linearly on increasing the current. The likeness in behavior shows that the rate capability does not depend on the dopant cations. On the other hand, the slope of capacities against rate for the various metal doped spinel sample prepared at 900°C is smaller than that of the sample prepared at 950°C, which would be related with the comparable particle size of the samples.

Fig. 3.1.3 shows the relation between the calcinations temperature of Li₁.₀₅Al₀.₁₅Mn₀.₈O₄ by conventional method and C₃.₂V determined by the coin-type cells. As expected, the C₃.₂V decreased with the decrease in the calcinations temperature. It has been also found that the C₃.₂V plateau disappears at calcination temperature of 800°C, which means that Li₁.₀₅Al₀.₁₅Mn₀.₈O₄ with oxygen stoichiometry can be synthesized at the relatively lower calcination temperature.
Fig. 3.1.3. Relation between calcinations temperature and $C_{3.2V}$ for C-Al015-T (T=800, 900, 950 and 1000).

Fig. 3.1.4 shows the relation between capacity retention after two cycle and the capacity of 3.2V discharge plateau in LiM$_{0.1}$Mn$_{1.9}$O$_4$ prepared at 900 °C and 950 °C. Although the kind of doping metal is different, the capacity retentions give approximately a linear line against the $C_{3.2V}$ values. Consequently, I can confirm that the oxygen stoichiometry in foreign metal ion doped spinel compounds is also a determining factor in cyclability improvement at the elevated temperature.

Fig. 3.1.4. Dependence of capacity retention after first 50cycles on $C_{3.2V}$ values for LiM$_{0.1}$Mn$_{1.9}$O$_4$ prepared at 950 °C and 900 °C. Current density: 0.4 mA cm$^{-2}$; voltage range: 3.0 - 4.3V; operation temperature: 60 °C.
Fig. 3.1.5 XRD patterns for the Li$_{1.05}$Al$_y$Mn$_{1.95-y}$O$_4$ ($y=0.05, 0.10, 0.15$) materials prepared by covenantal one-step method (a, b, c) and two-step method (d, e, f).

Fig. 3.1.5 shows the XRD patterns of spinel samples Li$_{1.05}$Al$_y$Mn$_{1.95-y}$O$_4$±$\delta$ ($y=0.05, 0.10, 0.15$) prepared by conventional method and two-step method. All the diffraction peaks can be indexed on the cubic structure with the space group $Fd\bar{3}m$ and there are no peaks of impurity phase. Although the XRD profiles of these samples are almost the same, their lattice parameters are slightly different. The calculated cubic lattice parameters ($a_0$) for two series of spinel samples (Li$_{1.05}$Al$_y$Mn$_{1.95-y}$O$_4$±$\delta$) are plotted as a function of composition $y$ in Fig. 3.1.6. I found the following trends: (i) the increase of $y$ value in Li$_{1.05}$Al$_y$Mn$_{1.95-y}$O$_4$±$\delta$ is accompanied by a decrease of the lattice parameter as report before [16], because the ionic radius of Al$^{3+}$ (0.57Å) is smaller than that of Mn$^{3+}$ (0.66Å). However, there is no linearity in the plots, which are different from the case of doped Mn-spinel samples prepared at low temperature (<850°C) [26, 27], where the lattice parameter decreased
lineally with the increase in the value of $x$ in LiM$_{x}$Mn$_{2-x}$O$_4$. I suggest that the substitution of Mn$^{3+}$ by Al$^{3+}$ can not only decrease the distance of Mn-O but also lead to the decrease in the degree of oxygen vacancy even under the condition of high calcinations temperature. (ii) The lattice parameters of C series spinel samples (a in Fig. 3.1.6) are larger than those of N series spinel samples (b in Fig. 3.1.6), which should be attributed to the different oxygen content in both series samples. I believe that the higher content of oxygen vacancy in the samples prepared by the conventional method leads to a greater increase in Mn-O distance, which may influence on the structure stability of spinel during cycling. (iii) A sudden decrease in the lattice constant at $y = 0.15$ for samples prepared by two-step method would be related to the fact that there is almost no oxygen-deficiency when Al doping amount exceeds $y = 0.15$.

Fig. 3.1.6. The calculated cubic lattice parameter vs. $y$ in spinel samples prepared by two different methods: (a) C series sample prepared by conventional method (b) N series sample prepared by two-step method.

Fig. 3.1.7 shows the initial two charge/discharge curves of Li/Li$_{1.05}$Al$_{y}$Mn$_{1.95-y}$O$_{4}$ ± δ cells using the two series of samples as cathode materials. A plateau at 3.2V correlated with oxygen deficiency was observed for C-Al005-1000 (Li$_{1.033}$Al$_{0.049}$Mn$_{1.918}$O$_{3.990}$), C-Al010-1000 (Li$_{1.035}$Al$_{0.110}$Mn$_{1.855}$O$_{3.994}$), C-Al015-1000 (Li$_{1.041}$Al$_{0.148}$Mn$_{1.811}$O$_{3.997}$) and N-Al005-660 (Li$_{1.035}$Al$_{0.053}$Mn$_{1.912}$O$_{3.993}$). This means that the oxygen deficiency still exists when the
doping Al content < 0.15 for all samples prepared by conventional one-step method. However, oxygen deficient spinel for N series samples was found only in the case of $y = 0.05$. When $y$ is 0.15, the chemical formula of N-Al015-660 based on chemical analysis is $\text{Li}_{1.039}\text{Al}_{0.146}\text{Mn}_{1.815}\text{O}_{4.017}$, then it could be classified into oxygen stoichiometric spinels with cation vacancies in 16d site and rewritten as $[\text{Li}]_{8a}[\text{Li}_{0.035}\text{Al}_{0.145}\text{Mn}_{1.807}\text{□}_{0.013}]_{16d}[\text{O}_4]_{32e}$ (□ denotes vacancies), where subscripts “8a”, “16d” and “32e” are the sites in $Fd3m$. This formula indicates that heating with additional LiOH at 660 °C can repair the oxygen deficiency originating from sintering at high temperature. It is also noted that the polarization of samples prepared by two-step is smaller than those of samples prepared by the conventional one-step method.

![Charge/discharge curves](image)

Fig. 3.1. 7. Charge/discharge curves at room temperature of $\text{Li}_{1.05}\text{Al}_y\text{Mn}_{1.95-y}\text{O}_4 (y=0.05, 0.10$ and $0.15)$ (a) C series sample by conventional method (b) N series sample prepared by two-step method. The current density: 0.1 mAcm$^2$. 

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The cycling performance of N-Al015-660 and N-Al010-660 cathodes were examined and shown in Fig. 3.1.8. For comparison, the two controlled materials, C-Al015-1000 and C-Al010-1000, with almost the same metal doping content as N-Al015-660 or N-Al010-660, are shown in the same figure. The capacities of C-series samples fade more rapidly than those of N-series samples with no oxygen deficiency. Oxygen stoichiometric sample, N-Al015-660, exhibits excellent cycleability, and loses only 0.66% of the initial capacity during 50 cycles, whereas the C-Al015-1000 sample with slight oxygen deficiency loses 8% of initial capacity, although they have almost the same Al content and specific surface area. C-Al010-1000 with the largest oxygen deficiency exhibits the poorest cycling performance among the four samples; it loses ca. 15% of initial capacity. On the other hand, N-Al010-660 exhibits better cycling behavior although the Al doping content of C-Al015-1000 is higher than that of N-Al010-660, since the chemical analysis shows that $\delta$ value in $(\text{Li, Al, Mn})_3\text{O}_{4+\delta}$ (oxygen contents) is 3.999 for N-Al010-660 (which can be considered as oxygen stoichiometric spinels) and 3.997 for C-Al015-1000, respectively. It would be concluded that oxygen content in spinel samples is most important factor.

![Fig. 3.1.8. The cycling performance of N-Al015-660, C-Al010-1000, C-Al015-1000 and N-Al010660 and C-Al015-800 cathodes at 60°C (0.4mA/m²).](image)
However, oxygen stoichiometric C-Al015-800 sample shows a larger capacity lose of 6%. This might be due to the catalytic activity of the spinel surface towards electrolyte oxidation or dissolution of Mn ion from the surface of spinel. As shown in Fig. 3.1.9, the specific surface area is reduced to about one forth by increasing calcination temperature from 800 °C (1.4 m² g⁻¹) to 1000 °C (0.4 m² g⁻¹). The SEM images of these materials were measured and shown in Fig. 3.1.10, where the morphology of these primary particles of spinels was octahedral shape and surrounded by the flat surface. It is likely that the spinel samples prepared at high temperature have been highly crystallized to the cubic spinel structure. The average particle size of the C-Al-015-T fired at 800 °C was ca. 0.3µm and it increases to ca. 1µm after calcination at 1000 °C. In addition, the SEM image of N-Al015-600 was also shown in Fig. 3.1.10. It shows that the morphology and particle size of N-Al015-600 are similar with C-Al-015-1000.

![Fig. 3.1.9. The variation of BET specific surface area of C-Al015-T materials with the calcination temperature.](image-url)
Fig. 3.1.10. SEM image for the C-Al015-T spinel prepared by calcination at different temperature. (a)C-Al-015-800 (b) C-Al-015-900 (c) C-Al-015-950 (d)C-Al-015-1000(e) N-Al-015-660

It has been believed that the dissolved Mn ions in the electrolyte can be deposited on the carbon surface which leads to not only a capacity fading of cathode spinel but also deteriorates the performance of anode carbon at elevated temperature [18]. Thus the degradation of the cycle performance becomes more severe. Finally, reduction of Mn dissolution is a very important factor in the full lithium-ion batteries (spinel/C). Moreover, because dissolution of Mn ions can be reduced Mn metal, which leads to the possibility of short circuit, it could encounter safety problems, Fig. 3.1.11 shows the Mn dissolution from the spinel samples fired at various temperatures by conventional one-step method. The Mn dissolution for C-Al015-800 is about 14 ppm, which is much smaller than that of the undoped spinel (100 ppm) [28, 29], on the other hand, that of C-Al015-1000 is reduced to
6.1ppm. So it can be clearly seen that Mn dissolution is closely related with the surface area of spinel samples (contact interface between the cathode and organic electrolyte). However, it is noted that Mn dissolution from C-Al015-1000 is larger than those from C-Al015-900 and C-Al015-950, although they have almost the same specific surface area. Moreover, the Mn dissolution of N-Al015-660 was reduced to 3.2ppm. Therefore, we may suggest that C-Al015-1000 with oxygen deficiency would have some kind of surface defect, and it leads to structure instability and accelerate the Mn dissolution. It is very similar with the result reported by Takahashi et al. in the case of Mg doped spinel [24]. The above results show that the reduction of the Mn dissolution with a small surface area, the stabilization of the spinel structure without the oxygen deficiency and the increase in the crystallinity contribute to the improvement of the 60°C storage performance.

![Fig. 3.1.11. The relation between calcinations temperature and Mn dissolution for C-Al015-T and Mn dissolution of N-Al015-660.](image)

In order to compare the performance of lithium ion batteries based on the cathode materials C-Al015-800 (spinel with oxygen stoichiometric prepared at low temperature of <850 °C), C-Al015-1000 (slightly oxygen deficiency) and N-Al015-660 (spinel with oxygen stoichiometric prepared at high temperature of > 900 °C), they were assembled together with MCMB6-28 anodes to fabricate coin-type lithium-ion batteries. The high-temperature cycling performances of lithium-ion batteries were shown in Fig. 3.1.12. Almost no capacity fading was observed after 50 cycles in the case of lithium ion batteries using N-Al015-660 cathode at room temperature. However, a slight capacity loss still
occurred at elevated temperature for the lithium-ion batteries. The capacity loss over the 50 cycles varied from about 16% of the initial capacity for sample N-Al015-660 to 41% and 36% for sample C-Al015-800 and C-Al015-1000 in full cells, respectively. Although oxygen-stoichiometric spinel prepared at low temperature (<850 °C) has excellent cycling performance in half-cell (spinel/Li) (the capacity loss is Ca. 6%), it is unsuitable to be a promising cathode material for full-lithium-ion batteries for the sake of its high surface area and low crystallinity. A similar result was also found for Mn-spinel samples with slight oxygen deficiency, which exhibits a severe capacity fading which can be attributed to structure instability, which leads to Mn dissolution into electrolyte during the cycling. On the other hand, the cycling performance of lithium ion batteries based on N-Al015-660 (84% capacity retention of initial cycle) is better than that of LiCoO₂ at 60 °C [30, 31]. It indicates that the new Al doped spinel is a promising cathode materials for practical applications.

![Discharge capacity (mAh/g) vs. cycle number](image)

Fig. 3.1.12. The variation of discharged capacity for lithium ion batteries based on N-Al015-660 and C-Al015-T with cycle number at 0.4 mA/cm². The specific capacity calculated based on cathode material weight.

### 3.1.4. Conclusions

Among the various foreign metals (Mg, Li, Co, Ni, Al, Cr, Fe), I found that Al and Mg doping could suppress 3.2V capacity effectively even at sintering temperature as high as 900-1000°C. Moreover, we have successfully prepared oxygen-stoichiometric spinel by
sintering a mixture of Mn$_3$O$_4$, LiOH and Al$_2$O$_3$ at 1000°C and then annealed intermediate product at lower temperature together with extra LiOH. Compared with spinel prepared by the conventional method, the new samples exhibit superior capacity retention and lower Mn dissolution. These improvements are attributed to their oxygen stoichiometry and small BET surface area. The capacity retention of the new kind of oxygen-stoichiometric spinel is about 99.34% at 60°C in the half-cell after 50 cycles. To the best of our knowledge, this is the best value among the reported papers. We believe that the new kind of Al doped spinel is a promising cathode materials for practical applications.
3.2. Improvement of cycling performance by spray dry coating method.

Modification of the surface properties of the cathode materials by coating with some metal oxides has been recognized as one of the most reliable techniques [31–35]. The advantage of this technique is that side reactions on the surface with electrolyte are avoided and structural breakage of Mn-spinel during charge–discharge cycling can be moderated. In this study, I have developed new coating technique, named as spray coating method, and the effect of the coating on the cycle stabilities of Mn-spinel cathode are investigated.

3.2.1 Experimental

Commercial Mn-spinel powder was used as the raw material for ZnO coating. ZnO-coated Mn-spinel was prepared by a gas-suspension spray coating method. The coating solution, Zn(CH$_3$COO)$_2$ was prepared by dissolving dissolved into a mixture of distilled ethanol. The coating solution that was sprayed through a nozzle, into fluid bed, made by spinel particle and airflow heated. The wetted powders were extensively dried through solvent evaporation at 80 °C. The repeated motion of the powders through the spray zone allowed a continuous coating of material to build up and, finally, uniform ZnO coated powders could be prepared. The amount of ZnO coated on the Mn-spinel could be controlled from 1 to 6 wt.% as ZnO by adjusting the spraying time. The Mn-spinel powders coated with metal solution were calcined at 400 °C- 700 °C for 3 h under an air atmosphere.

3.2.2 Results and discussion

Fig. 3.2.1. shows the SEM images of bare and ZnO coated Mn-spinel. Obviously the surfaces of bare Mn spinel particles are very smooth and seems rather “clean” without any radicals. After coating, the surfaces of Mn spinel particles are covered with a uniform layer of ZnO. The ZnO content in the final Mn spinel was calculated to be 5-6 wt. %.
Fig. 3.2.1. SEM photographs of (a) bare and (b) ZnO coated Mn-spinel (5-6%).

Fig. 3.2.2 shows charge/discharge curves of bare and ZnO coated Mn-spinel with different coating amount on first cycle. The cell voltage was changed from 4.3 to 3V at 0.4mA/cm$^2$. ZnO coated (1-2%) Mn-spinel shows the smaller polarization than the bare Mn-spinel. However, a high amount (5-6%) of ZnO coating brought about decreased capacity. It is thought that the high amount of ZnO which is electrically insulating and inactive for Li intercalation/deintercalation covers the surface of Mn-spinel particles so that migration of Li$^+$ ions from the host structure would be hindered, leading to decrease in the specific discharge capacity.

![Charge-discharge curves](image)

Fig. 3.2.2. Charge-discharge curves of bare and ZnO-coated Mn-spinel with different ZnO content at the first cycle.
Cycling performance of bare and 5-6% ZnO coated Mn-spinel cathode at 60°C presented in Fig. 3.2.3. The discharge capacity of bare Mn-spinel decreases to 85% of initial capacity. Although ZnO-coated Mn-spinel annealed at 400°C exhibits a capacity retention after cycling which is superior to the bare counterpart, the improvement of cyclability was more obvious as the coating temperature is increased. For example, the capacity retention was about 99% for the ZnO coated Mn-spinel annealed at 600°C.

As shown in Fig. 3.2.2, a low amount of ZnO coating will give a large discharge capacity and small polarization. In order to obtain best electrochemical performance, the cycling performance of 1-2% ZnO-coated Mn-spinel with different coating temperature was also elevated (as shown in Fig. 3.2.4). It shows that the 1-2% ZnO-coated Mn-spinel annealed at 700°C exhibits a large discharge capacity of 105mAh g⁻¹ and excellent cycling performance of 98% even after 150 cycles.

![Fig. 3.2.3. Cycling performance of bare and 5-6% ZnO-coated Mn-spinel with different coating temperature at 60°C (0.4mAcm⁻²).](image)
Fig. 3.2.4. Cycling performance of bare and 1-2% ZnO-coated Mn-spinel with different coating temperature at 60°C (0.4mAcm⁻²).

As shown in Fig. 3.2.5, bare Mn-spinel and ZnO coated Mn-spinel exhibit similar rate capability. In other words, a small amount of ZnO coating (such as 1-2%) can’t influence the rate capability of Mn-spinel cathode material.

Fig. 3.2.5. Comparison of the rate capabilities of bare Mn-spinel and ZnO-coated Mn-spinel.
3.2.3 Conclusions

SEM image shows that ZnO is coated uniformly on the surface of Mn-spinel particles by a spray dry coating method. Significant improvement of the electrochemical performance of Mn-spinels is achieved by coating ZnO. Increasing the amount of the coated ZnO, the discharge capacity of Mn-spinel a decreases slightly, but the cycleability of Mn-spinel at elevated temperature is improved obviously. In view of discharge capacity and cycleability, the 1-2% coated sample shows optimum cathodic behaviors.

References


Chapter 4

Improved Electrochemical Performance of LiFePO$_4$
Cathode Materials for Lithium Ion Batteries
4.1 Improved Electrochemical Performance of LiFePO$_4$ by Increasing Its Specific Surface Area

4.1.1 Introduction

Recently, the possible applications of large-scale Li ion batteries for the backup of power systems and hybrid electric vehicles (HEV) have been extensively studied [1, 2, 3, and 4]. However, it is difficult to use LiCoO$_2$ as the cathode material in large-scale lithium ion batteries because of its safety problem and high cost, although it is successfully commercialized in small size lithium ion batteries. Therefore, it is the best choice to use LiFePO$_4$ as the cathode material of large-scale lithium ion batteries from its safety and cost points of view. Moreover, LiFePO$_4$ has many other advantages such as its high theoretical capacity of 170 mAh g$^{-1}$, acceptable voltage of 3.5V and excellent cycling performance.

Padhi et al. [5] firstly reported the electrochemical performance of LiFePO$_4$ and pointed out that the disadvantage of its poor electronic conductivity, which leads to its lower discharge capacity, high polarization and poor rate capability becomes the main obstacle for its practical application in lithium ion batteries. Many ways have been tried to improve the rate capability of LiFePO$_4$. For example, Huang et al. [8] and other groups have improved the reversible capacity to reach about 140 mAh g$^{-1}$ at 1C by various carbon coating technology [6-11]. Park et al. also reported that the initial discharge capacity of LiFePO$_4$ increased from 121 mAh g$^{-1}$ to 139 mAh g$^{-1}$ by silver coating (1 wt %) at 1/5C [12]. Chung et al. have succeeded in increasing bulk electronic conductivity of LiFePO$_4$ by doping the foreign elements (Mg, Nb and etc.) and reported ca. 130 mAh g$^{-1}$ of the reversible capacity at 1/2C rate [13].

Some authors have believed that the slow diffusion of lithium ions between two phases is also a key factor to affect the rate capability of LiFePO$_4$ [14]. The increasing of the specific surface area in active material speeds up the diffusion of lithium ions in LiFePO$_4$ and improves the rate capability of the sample. It is believed that the addition of the carbon particles can suppress the crystal growth of LiFePO$_4$ and produce the samples with a large
surface area [7- 9], furthermore, as Chen and Dahn [7] have already reported, small particle size is more important factor than carbon coating itself.

In this paper, the effect of specific surface area on the rate capability of LiFePO$_4$ without carbon coating will be investigated in detail. Moreover, the excellent cycling performance of LiFePO$_4$ in lithium ion batteries at high temperature has been confirmed.

4.1.2. Experimental

The LiFePO$_4$ cathode material was prepared by solid-state reaction method using LiCH$_3$COO$\cdot$2H$_2$O, FeC$_2$O$_4$$\cdot$2H$_2$O, and (NH$_4$)$_2$HPO$_4$ as starting materials (method A). The starting materials were mixed and ground with planetary ball mill for 1h, 6h, and 12h in acetone under an argon atmospheres. Then the mixture was initially preheated at 350 °C for 3h and followed with sintering at 470 °C - 610 °C for 8h under an argon gas flow (100 ml min$^{-1}$). Sample is prepared from Li$_2$CO$_3$, FeC$_2$O$_4$$\cdot$2H$_2$O, and (NH$_4$)$_2$HPO$_4$, using same preparation procedure (method B).

The structures of the samples were characterized by XRD (Rigaku Rint 1000) with Cu target tumble. The specific surface area was measured by BET method (Micromeritics FlowsorbIII). The morphologies of materials were also observed by scanning electron microscopy (SEM).

The electrochemical performance of LiFePO$_4$ was evaluated using CR2032 coin-type cells. The cathode was prepared by the following process. First, the active materials were mixed with teflonized acetylene black (33 wt % polytetrafluoroethylene, 66wt % acetylene black and 1wt% surface active reagent) at a weight ratio of 4:3, 2:1 and 4:1. 20mg of the mixture of cathode material and TAB-2 was pressed on 150mm$^2$ stainless steel mesh used as the current collector under a pressure of 300 kg cm$^{-2}$. The thickness of obtained electrode pellets is about 200µm, and then it dried at 170 °C for 5 hours under vacuum. The lithium metal was used as an anode, and glass fiber (GA-100) as separator (Toyo Roshi Kaish, Ltd. Japan). The electrolyte is 1M LiPF$_6$-ethylene carbonate / dimethyl carbonate (EC/DMC, 1:2 by volume) (Ube Industries, Ltd., Japan). Cells were charged and discharged galvanostatically with cutoff voltage range of 2.5 V~4.3 V vs Li/Li$^+$ at room temperature.
(RT) and 60°C.

In the lithium ion batteries, the MCMB6-28 anodes were prepared by slurry coating of commercially available MCMB6-28 material produced by Osaka Gas Co., Ltd. Cycling performance was measured at a constant charge/discharge rate of 0.4 mA cm⁻² and 60°C.

4.1.3 Results and Discussion

Fig. 4.1.1. TG/DSC curves of the starting materials composition of LiCH₃COO • 2H₂O, FeC₂O₄ • 2H₂O, and (NH₄)₂HPO₄.

Fig. 4.1.1 shows the TG/DSC curves of the starting materials composition of LiCH₃COO • 2H₂O, FeC₂O₄ • 2H₂O, and (NH₄)₂HPO₄ (1:1:1 in mole). The measurement was done at temperature range from room temperature to 800°C and a heating rate of 5°C/min in Argon. Five endothermic peaks (1, 2, 3, 6, 5) at 60°C, 154°C, 154°C, 165°C and 260°C in the DCS curve are observed. Peak 1, 3 corresponds to the losing lattice water of LiCH₃COO • 2H₂O, FeC₂O₄ • 2H₂O. Peak 3, 6 and 5 corresponds to the composition of (NH₄)₂HPO₄, LiCH₃COO and FeC₂O₄. From 170 to 450°C, two exothermic peaks appear at
175 and 260°C in DSC curve, corresponding to the reaction of Li₂O and H₃PO₄ and the reaction of LiH₂PO₄ and FeO. The above reaction process can be presented as:

\[
\begin{align*}
\text{LiCH₃COO} \cdot 2\text{H₂O} & \longrightarrow \text{LiCH₃COO} + 2\text{H₂O} \quad (1) \\
(\text{NH₄})₂\text{HPO₄} & \longrightarrow 2\text{NH₃} + \text{H₃PO₄} \quad (2) \\
\text{LiCH₃COO} + \text{H₃PO₄} & \longrightarrow \text{CO₂} + \text{H₂O} + \text{LiH₂PO₄} \quad \text{(intermediate)} \quad (3) \\
\text{FeC₂O₄} \cdot 2\text{H₂O} & \longrightarrow \text{FeC₂O₄} + 2\text{H₂O} \quad (4) \\
\text{FeC₂O₄} & \longrightarrow \text{FeO} + 2\text{CO} + \text{CO₂} \quad (5) \\
\text{FeO} + \text{LiH₂PO₄} & \longrightarrow \text{LiFePO₄} + \text{H₂O} \quad (6)
\end{align*}
\]

From 470°C to 700°C, we hardly observed the weight losing form TG curve, which should correspond to the formation of LiFePO₄. On the other hand, the practical size grows with increasing the sintering temperature, which in turn leads to the decrease in the rate capability. Therefore, 470°C, 510°C and 570°C as experiment temperature were further studied.

The first charge-discharge curves of a series of LiFePO₄ samples (which prepared by method A) with the milling time of 12h prepared at 470 °C, 510 °C, 570 °C and 610°C are shown in Fig. 4.1.2. All the samples exhibited flat voltage plateau at ca. 3.5 V, which is the characteristics of the two phase’s reaction of LiFePO₄. The discharge capacities are larger than the charge capacities in the initial cycle for the samples prepared at 470 °C (about ca. 5 mAh g⁻¹) and 510 °C (about ca. 2 mAh g⁻¹), and this phenomenon disappears in the second cycle. Such excess discharge capacities indicated that the amorphous residuals such as FePO₄ are formed as an impurity phase because we cannot find any impure peak from XRD, which is reported by Yamada et al. using the Mossbauer spectroscopy [16]. They suggested that the inactive Fe³⁺ would be reduced to active Fe²⁺ at high temperature to form LiFePO₄. It is found that a tendency of the excess capacity gradually decreases with the increase of the sintering temperature in our LiFePO₄ samples. The excess capacity in the initial discharge process is not observed for the sample prepared at 570 °C and 610°C, which
means that the pure sample could be obtained as the sintering temperature \( \geq 570 ^\circ C \). Moreover, in the range of 470\(^\circ\)C to 570\(^\circ\)C, the initial discharge capacities of LiFePO\(_4\) increase with the increasing of sintering temperature. The sample prepared at 570\(^\circ\)C delivers 160mAh g\(^{-1}\), which corresponds to 93\% of the theoretical capacity.

![Graph showing first charge-discharge curves of LiFePO\(_4\) samples prepared at different temperatures.](image)

Fig. 4.1.2. The first charge-discharge curves of the LiFePO\(_4\) samples prepared at (1) 470 \(^\circ\)C, (2) 510 \(^\circ\)C and (3) 570 \(^\circ\)C. The current density was 0.1C (15mA g\(^{-1}\)), at room temperature.

It is reported that the electrochemical performance of LiFePO\(_4\) could be significantly improved by adding a mount of conductive materials in the cathodes [6-10]. We examine how much conductive carbon is enough to keep the excellent electrochemical performance of LiFePO\(_4\). Fig. 4.1.3 shows the effects of the content of acetylene black (AB) on the discharge capacity of LiFePO\(_4\) at 1C rate. Although there is obvious increase in discharge capacity as increasing the AB content from 6.5wt\% to 13wt\%, no obvious effects of AB content on the electrochemical performance of LiFePO\(_4\) was observed when the conductive carbon content is over 13wt\%. It indicated that 13 wt\% is enough for a connection between LiFePO\(_4\) particle and conductor, even though LiFePO\(_4\) is fine particle with surface area surface of 24 m\(^2\) g\(^{-1}\).
Fig. 4.1.3. The effect of acetylene black (AB) content on the discharge capacity of LiFePO₄ at 1C.

The effect of sintering temperature on the rate capability of LiFePO₄ is shown in Fig. 4.1.4. BET measurements indicated that all samples prepared at 470°C, 510°C, 570°C and 610°C exhibit the higher specific surface area with 24.6 m² g⁻¹, 26.3 m² g⁻¹, 24.1 m² g⁻¹ and 16.4 m² g⁻¹ respectively, which are more than two times bigger than that (ca. 6 ~ 9 m² g⁻¹) reported by Prosini et al. [16]. The BET surface area of sample keep roughly constant value for the sintering until 570°C, however, it decreased rapidly beyond this critical heating temperature. The LiFePO₄ prepared at 610°C exhibits the nearly same discharge capacity with the one prepared at 570°C at very low rate of C/10, which indicates that they have almost same purity. Although the rate capability of LiFePO₄ has been improved with the increasing of the sintering temperature from 470°C to 570°C, it decreased as the sample prepared at 610°C because of a rapid decrease in the surface area.

On the other hand, although surface area of the sample prepared at 470°C is much higher than that prepared at 610°C, the rate capability results show exactly the opposite. It is well known that the practical size of the LiFePO₄ materials increases with increasing the
sintering temperatures, so the poor high rate performance of the sample prepared at 470°C cannot be ascribed to the particle size. As mention in discussions on the Fig. 4.1.2, we strongly suggest that some impurities existing in the bulk of this sample should responsible for the deteriorated performance, although it cannot be detected for the limitation of the XRD machine. The sample prepared at 570°C has the excellent rate capability and its discharge capacity still attains to more than 120mAh g⁻¹ even at 5C rate. Therefore, it is believed that pure LiFePO₄ prepared at 570°C with large surface area has the best electrochemical performance.

![Graph](image)

**Fig. 4.1.4.** The rate capability of the LiFePO₄ samples prepared at (a) 470 °C, (b) 510 °C, (c) 570 °C and (d) 610 °C at room temperature. The cathode loading of LiFePO₄ was ca. 9 mg cm⁻².

Fig. 4.1.5 shows the XRD patterns of the samples with the mixing time of 1h, 6h and 12h before preheating at 350°C and final sintering at 570°C. In order to express these samples clearly, they are abbreviated as LFP1hbm, LFP6hbm and LFP12hbm, respectively. All diffraction peaks can be indexed on the orthorhombic structure with a space group Pnmb, so there are no peaks of impurity phase. The peak width of the sample in XRD profiles
becomes larger with the elongation of the ball milling time. For example, the (111) peak width of LFP12hbm is obviously wider than that of LFP6hbm, which means that the longer ball milling time causes the decrease in the crystalline grain-size of the samples.

The lattice parameters, the full width at half maximum (FWHM) and calculated grain-size (D) according to the (111) and (131) diffraction peaks for three samples are summarized in Table 4.1.1. The grain-size was calculated by Scherer formula: 

$$D = \frac{k \lambda}{\beta \cos \theta}$$

where k is 0.9, λ is 1.5406 Å and β is the full width at half maximum length of diffraction peak on a 2θ scale, respectively. Though the lattice parameters of all samples have almost the same values, the D values calculated from (111) and (131) peak width are in the range of 30~40 nm (LFP12hbm) and 50~80 nm (LFP1hbm). Main difference in three samples is the gain size.

Fig. 4.1.5. XRD patterns of LFP1hbm, LFP6hbm and LFP12hbm.
Table 4.1.1. The lattice parameters, full width at half maximum (FWHM) and calculated grain size (D) of the (111) and (131) diffraction peaks for LFP1hbm, LFP6hbm and LFP12hbm.

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>FWHM (°)</th>
<th>D_{111} (nm)</th>
<th>D_{131} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(111)</td>
<td>(131)</td>
<td></td>
</tr>
<tr>
<td>LFP1hbm</td>
<td>10.32</td>
<td>5.996</td>
<td>4.689</td>
<td>0.17</td>
<td>0.13</td>
<td>52</td>
</tr>
<tr>
<td>LFP6hbm</td>
<td>10.31</td>
<td>5.997</td>
<td>4.691</td>
<td>0.20</td>
<td>0.16</td>
<td>44</td>
</tr>
<tr>
<td>LFP12hbm</td>
<td>10.31</td>
<td>5.997</td>
<td>4.686</td>
<td>0.23</td>
<td>0.28</td>
<td>38</td>
</tr>
</tbody>
</table>

Fig. 4.1.6 shows SEM images of the powders. The average particle sizes of the LiFePO$_4$ samples obviously decrease with the extension of the ball milling time from ca. 300-500 nm of LFP1hbm, 200-400 nm of LFP6hbm to ca. 100 nm of LFP12hbm. Correspondingly, the specific surface areas of the samples increased from 4.6 m$^2$ g$^{-1}$ (LFP1hbm), 14.2 m$^2$ g$^{-1}$ (LFP6hbm) to 24.1 m$^2$ g$^{-1}$ (LFP12hbm).

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Fig. 4.1.6. SEM micrograph of (A) LFP1hbm, (B) LFP6hbm and (C) LFP12hbm. (D) Sample B
Fig. 4.1.7 shows the cyclic voltammograms of LiFePO$_4$ measured at a sweep rate of 0.1mv/s at room temperature. These CV show one pair of peaks, consisting of a cathode peak and an anode peak, occurred at about 3.5V domain, which corresponded to the two-phase charge-discharge reaction of Fe$^{2+}$/Fe$^{3+}$ redox couple. LFP1hb m electrode has broad peaks in CV curves. In contrast, LFP12hb m electrode demonstrates sharp redox peaks. This could attribute to an improvement in kinetics of lithium intercalation/deintercalaction at the electrode/electrolyte interface and/or the rate of lithium diffusion in film with increasing the specific surface area.

Fig. 4.1.7. Cvs of LFP1hb m, LFP6hb m and LFP12hb m electrodes.

Fig. 4.1.8 also shows the rate capabilities of the LFP1hb m, LFP6hb m and LFP12hb m measured at room temperature. The rate capability of LiFePO$_4$ has the obvious improvement with the extension of the starting materials milling time. The discharge capacity increases from 76mAh g$^{-1}$ of LFP1hb m to 134 mAh g$^{-1}$ of LFP12hb m at the charge/discharge rate of 2.4C. Experimental results shows that milling time of the starting materials can increase the specific surface area of the final products and has no effects on
the structure of the LiFePO$_4$. It means that the improvement of rate capability is ascribed to the increasing of specific surface area caused by extension of milling time.

Fig. 4.1.8. The rate capability of LiFePO$_4$ at room temperature

We have also examined the effects of the different starting materials on the electrochemical performances of LiFePO$_4$, as shown in Fig. 4.1.9. Data of BET measurement indicates that the lower specific surface area of the sample B (SEM picture as shown in Fig. 4.1.6) is 12.5 m$^2$ g$^{-1}$. The rate capability of the sample B is obviously inferior to that of LFP12hbm. The sample A has 116mAh g$^{-1}$ of the discharge capacity at 5C rate, while the discharge capacity of the sample B is only 80mAh g$^{-1}$ at the same rate. It is further demonstrated that the electrochemical performance of LiFePO$_4$ is closely related with its specific surface area, which turn to the effect of the ratio of grain contacted with electrolyte.
Fig. 4.1.9. The rate capabilities of LFP12hbm samples prepared by method A and B. (A) sample A, (B) sample B.

Fig. 4.1.10 shows the cycling performance of LFP12hbm at high temperature (60 °C) and room temperature. The initial discharge capacity of LiFePO₄ increases from 145mAh g⁻¹ at room temperature to 160mAh g⁻¹ at 60°C even at 1C rate. The vibration of the discharge capacities could reflect the effect of temperature on the electrochemical performance, such phenomenon has been often observed for the cathode materials in lithium battery [17, 18]. It shows that the discharge capacity of LiFePO₄ is very sensitive to the surrounding temperature and suitable to be used at elevated temperature. The capacity retention of LiFePO₄ is almost 100% even after 50 cycles, which indicated that our LiFePO₄ has the excellent cycling performance as a cathode in lithium batteries.

Fig. 4.1.10. The cycling performance of LFP12hbm at room temperature and 60°C. The discharge/charge current density is 1C.
Fig. 4.1.11 shows charge-discharge characteristics of LFP12hbm/MCMB at room temperature. The cell was charged to 4.2V and discharged to 2V at charge current 0.5C and discharge current range from 0.1C to 5C at room temperature. A flat charge-discharge voltage curve was observed at about 3.3V since LiFePO$_4$ evolved two-phase reaction process and low potential of MCMB anode. It is worth noting that a large irreversible capacity was observed at initial cycle, this irreversible capacity loss could attribute to the formation of solid electrolyte interface (SEI). As respected, the lithium intercalation capacity decreased with increasing current density of discharge. Despite the LiFePO$_4$ cathode strongly depends on the rate C in half-cell, The LiFePO$_4$/MCMB also shows the excellent rate capability and exhibits about 108mA g$^{-1}$ of discharge capacity even at 5C. Moreover, the average voltage for the discharge decreased from 3.3V (0.1) to the 2.8V (5C) with increase the C, which may attribute to the low potential and excellent rate capability of MCMB. From
these results, it believed that MCMB is a suitable anode material for LiFePO$_4$/C lithium ion battery.

Fig. 4.1.12. The cycling performance of the LiFePO$_4$/MCMB6-28 at room temperature.

Fig. 4.1.12 shows the cycling performance of LiFePO$_4$/MCMB6-28 at room temperature. The first 7 cycle correspond to the various rate discharge capacity of LiFePO$_4$/MCMB. It exhibits excellent cycling performance, and retains 93.7% of the 9th cycle after the 100th cycle at room temperature. As shown in Fig 4.1.2. The average columbic efficiency of this cell was about 99.75% (from 9th to 100th cycle), compared with the data of K. Zaghib et al. [19], their LiFePO4/natural graphite cell shows about 99.4% of the average columbic efficiency, and retains 80% of initial capacity after 100$^{th}$ cycle. It clearly identified that higher efficiency supports higher capacity retention. We believe that Decomposition of electrolyte plays an important role in determining the capacity fading of lithium ion battery. Based on these results, it is further confirmed that MCMB is a suitable anode active material for LiFePO$_4$/C lithium ion battery system.

Another excellent candidate of low-cost cathode material for large-scale Li-ion batteries, LiMn$_2$O$_4$ was been also widely studied because it’s inexpensive and environmentally
benign. It is accepted generally that the dissolved Mn in the electrolyte can be deposited on the carbon surface and then lead to the capacity fading at high temperature. For instant, Amine et al.[20] reported the Al doped spinel material, although this material has excellent cycling performance in lithium half cell (85% capacity retention after 100 cycle), a severe capacity fading (50% capacity retention after 100 cycle) was still observed in the full lithium ion cell despite the limited Mn dissolution (less than 5ppm) in electrolyte. As shown in Fig. 4.1.13, the capacity retention of a LiFePO$_4$/MCMB cell attains to 83% of the initial discharge capacity at 60°C after 200 cycles. It indicates that a lithium ion battery used LiFePO$_4$ as cathode materials exhibit the excellent cycling performance even at 60°C although it has the higher specific surface area.

![Graph showing cycling performance of LiFePO$_4$/MCMB cell at 60°C.](image)

**Fig. 4.1.13.** The cycling performance between a LiFePO$_4$/MCMB cell at 60°C.

### 4.1.4 Conclusion

LiFePO$_4$ with the excellent rate capability has been successfully synthesized by a simple solid-state reaction. The electrochemical performances of LiFePO$_4$ have been improved with the increasing of sintering temperature from 470°C to 570°C. It is beneficial to the rate
capability of LiFePO$_4$ by the extension of milling time. The LiFePO$_4$ sample prepared at $570\,^\circ\text{C}$ for milling time 12h has delivered 145 and 115 mAh g$^{-1}$ of the reversible capacity at the rates of 1C and 5C, respectively. It also exhibits the excellent cycling performance at room temperature as well as at 60 °C. It has been confirmed that it is an effective way to improve the electrochemical performance of LiFePO$_4$ by the increasing of its surface area accompanying the ratio of grain contacted with electrolyte.
4.2 Improved Electrochemical Performance of LiFePO$_4$ by SnO-coating.

4.2.1 Introduction

It seems that the particle coated by a large amount of carbon is necessary for improvement of electrochemical performance of LiFePO$_4$. For instance, Hang et al. [8] reported 15wt% carbon coated LiFePO$_4$ showed a reversible capacity of about 120 mAh g$^{-1}$ at very high rate of 5C. S-T. Mynng et al. [22] made LiFePO$_4$/C by emulsion drying method (27.7wt% of carbon), which exhibited a discharge capacity of about 125mAh g$^{-1}$ at 20mA g$^{-1}$. However, the tap density and rate capability is very important factor for practical application in the cathode materials of lithium ion batteries. Dahn et al. [23] suggested that it was important for LiFePO$_4$ to carefully note effect of carbon coating on capacity, rate capability and tap density. A large amount of carbon will decrease the energy density of material significantly due to its inactive and bulky character. Theoretically, it would be found minimizing of coating material amount or maximizing particle size of active material provided acceptable rate capability for application. Unfortunately, it is difficult to realize this ideal electrode due to the diffusion limited and low electric conductively of LiFePO$_4$ and low effective carbon coating. We intend to devote finding a high effective coating material to substitute for carbon. In addition, Park et al. [12] have confirmed that about 1 wt.% silver coating could preserve the LiFePO4 capacity even at high current densities. Moreover, the density of silver is 10 g cm$^{-3}$, which is much higher than carbon. Therefore, a little electronic conductive Ag coating could be effective to achieve better electrochemical performance.

It is well known that SnO is very easily reduced by small amount of Fe$^{3+}$ and C under a reduction atmosphere. I consider that SnO coating can not only reduce the possibility of Fe$^{3+}$ in LiFePO$_4$ but also improve the rate capability of LiFePO$_4$ cathode material due to existence of Sn. In our work, a novel coating material SnO was successfully coated on LiFePO$_4$ product by solution method. The effect of coating temperature on the particle morphology, rate capability and tap density will be discussed.
4.2.2 Experimental

LiFePO$_4$ samples were synthesized by solid-state method from LiCH$_3$COO • 2H$_2$O, FeC$_2$O$_4$ • 2H$_2$O, and (NH$_4$)$_2$HPO$_4$. The materials were mixed and ground with planetary ball mill for 12h in acetone under an argon atmosphere. The mixture was initially preheated at 350 °C for 3h and then sintered at 620°C for 8h under an argon gas flow (100 ml min$^{-1}$).

Sn(C$_2$O$_4$) was added in distilled water until it was dissolved in the water adjust the pH by NH$_3$.H$_2$O and CH$_3$COOH,. The synthesized LiFePO$_4$ was slowly added in this solution and mixed, the weight rate of LiFePO$_4$:SnC$_2$O$_4$ is 1:0.077, which correspond to 5% SnO in final product of LiFePO$_4$. Subsequently, it was dried at 100°C for 2h, and annealed at 600, 700, 800 for 3h.

4.2.3 Result and discussion

(a) bare LFP620(x 7500)          (b) bare LFP620(x 500)
Fig. 4.2.1. SEM morphology of (a) bare LFP620 (b) SnO-coated LFP620 prepared at 600°C (C) Sno-coated LFP620 prepared at 700°C.

Fig. 4.2.1 shows the effect of coating temperature on the morphology of LiFePO$_4$. Although there is no significant change in pristine particle, large aggregation was observed for SnO-coated LiFePO$_4$; even about 30µm particle size was shown for the SnO-coated sample prepared at 700°C. There is clear evidence that coating by the SnO solution method promoted the aggregate of pristine particle. In other words, it would help samples to increase the tap density.
As shown in Fig. 4.2.2, it is clearly seen that SnO-coated LFP620 prepared at 600°C and 700°C have better rate capability than prepared at 500°C, which maybe due to the SnO coating layer annealed at 600°C and 700°C may have better crystallinity and adhesion on LiFePO₄, in comparison with coating layer annealed at 500°C. These results clearly indicates that SnO-coating layer annealed at 600°C or 700°C is suitable for enhancing the battery performance of LiFePO₄ in comparison to the sample annealed at 500°C. In addition, because the increase in the annealed temperature reduces the tap density, the SnO-coated LiFePO₄ prepared at 700°C shows the tap density of about 1.32g cm⁻³, which is about 42% than the bare sample (0.93g cm⁻³). Therefore, 700°C was selected as coating temperature. We considered that SnO coated LiFePO₄ annealed at 700°C has larger tap density and worth for further studying.

4.2.4. Conclusion

The SnO-coated LiFePO₄ have been successfully synthesized by solution method. I found that SnO would help increase the tap density. When sample coating at 700°C shows the tap density of about 1.32g cm⁻³, which is 42% than the bare sample (0.93g cm⁻³). Moreover, the coated LiFePO₄ has still retained the excellent rate capability.
4.3 Improved Rate Capability of LiFePO$_4$ by P-site Doping

4.3.1 Introduction

As mentioned in introduction of 4.1, LiFePO$_4$ shows significant advantages, such as high safety and low cost. However, poor rate performance limited its practical application in high power density batteries. In order to solve this problem, much effort has been paid by several groups, including carbon coating to improve the electrical contact of active particles \[6,8,21–29\], super-valence ion doping in Li-site to enhance intrinsic electronic conductivity \[13\], and two-valence ion doing in Fe-site enhance the rate performance \[26, 30\].

Besides these strategies, we believed that P-site doping may also be an effective way. In this paper, we prepared P-site doped samples LiFeM$_x$P$_{1-x}$O$_4$ (M = As, Mo, B) and the improved rate performance and cyclic stability will be demonstrated below.

4.3.2 Experimental

LiFePO$_4$ samples were synthesized from LiCH$_3$COO $\cdot$ 2H$_2$O, FeC$_2$O$_4$ $\cdot$ 2 H$_2$O, and (NH$_4$)$_2$HPO$_4$ by solid-state method. The materials were mixed and ground with planetary ball mill for 12h in acetone under an argon atmosphere. The mixture was calcinated in a tube furnace with flowing argon at 350 $\degree$C for 4 h. After cooled down to room temperature, the samples were reground and sintered at 650 $\degree$C for 12 h and cooled down to room temperature in the tube furnace under the same atmosphere. The samples of LiFeM$_x$P$_{1-x}$O$_4$ (M = Mo, B, As) were prepared by the same procedures. Mo$_2$O$_5$, B$_2$O$_3$ and As$_2$O$_3$ were used as precursor, respectively, for doped samples.

The structures of the samples were characterized by XRD (Rigaku Rint 1000) with Cu target tumble. The specific surface area was measured by BET method (Micromeritics Flowsorb). The morphologies of materials were also observed by scanning electron microscopy (SEM).

Rate performance of the samples LiFePO$_4$ or LiFeM$_x$P$_{1-x}$O$_4$ was evaluated using CR2032 coin-type cells. The cathode was prepared by the following process. First, the active materials were mixed with teflonized acetylene black (33 wt % polytetrafluoroethylene, 66wt % acetylene black and 1wt% surface active reagent) at a
weight ratio of 2:1. 20mg of the mixture of cathode material and TAB-2 was pressed on 150mm\(^2\) stainless steel mesh used as the current collector under a pressure of 300 kg cm\(^{-2}\). The thickness of obtained electrode pellets is about 200µm, and then it dried at 170 °C for 5 hours under vacuum. The lithium metal was used as an anode, and glass fiber (GA-100) as separator (Toyo Roshi Kaish, Ltd. Japan). The electrolyte is 1M LiPF\(_6\)-ethylene carbonate / dimethyl carbonate (EC/DMC, 1:2 by volume) (Ube Industries, Ltd., Japan).

4.3.3 Result and discussion

The XRD patterns of the prepared LiFePO\(_4\) and LiFeM\(_x\)P\(_{1-x}\)O\(_4\) (M = B and As, x=0.01, 0.03 and 0.05) were shown in Fig. 4.3.1. LiFePO\(_4\) and LiFeB\(_x\)P\(_{1-x}\)O\(_4\) (x=0.01, 0.03 and 0.05) samples are pure phases with an ordered olivine structure indexed in orthorhombic \(P_{nmb}\). However, an increase of the peak (\(2\theta \approx 43\)) in XRD was observed for As doped LiFePO\(_4\), which is similar with XRD data of LiFe\(_x\)Mn\(_{1-x}\)PO\(_4\) [31, 32]. It suggested that LiFeAS\(_x\)P\(_{1-x}\)O\(_4\) (x=0.01, 0.03 and 0.05) exhibit an ordered olivine structure by different space group. Above results indicate that the prepared samples are pure olivine compounds without any obvious impurities, such as Fe\(_2\)P and Li\(_3\)PO\(_4\) [33, 34].

![XRD patterns](image-url)

Fig.4.3.1. The XRD patterns of the prepared LiFePO\(_4\) and LiFeM\(_x\)P\(_{1-x}\)O\(_4\) (M = B and As, x=0.01, 0.03 and 0.05)
The lattice volumes of doped samples LiFePO$_4$ and LiFeM$_x$P$_{1-x}$O$_4$ ($M = B$ and As, $x=0.01, 0.03$ and $0.05$) are showed in Fig.4.3.2. I remark that the increase of the content of the As and B cation is cause by an increase and decrease of the lattice parameters, and the linear variation in the lattice volume, which indicates that the P$^{5+}$ ions would be substituted by B$^{3+}$ and As$^{5+}$ ions. On the other hand, a slight change in lattice volume only occurs at $x=0.01$ in LiFeMo$_x$P$_{1-x}$O$_4$, and does not change lattice volume increase in the content of Mo from 0.03 to 0.05, which means maximum doping level of Mo would be Ca. 1%. It may be related to the fact that P$^{5+}$ (0.34Å) can not be substituted by Mo$^{6+}$ (0.62Å) due to its large atomic radium.

Fig. 4.3.2. The calculated lattice parameter of LiFeM$_x$P$_{1-x}$O$_4$ samples ($M = $ Mo, B, As, $x=0.01, 0.03$ and $0.05$).

Fig.4.3.3 shows the SEM micrographs for LiFePO$_4$ and LiFeM$_{0.03}$P$_{0.97}$O$_4$ ($M = B$ and As). As shown in Fig. 4.3.3(a, b, c), the samples LiFePO$_4$, LiFeAs$_{0.03}$P$_{0.97}$O$_4$ and LiFeB$_{0.03}$P$_{0.97}$O$_4$ have a uniform and narrow particle size distribution with regular particle
shape about 0.25µm. As shown in Fig. 4.3.3 (d), adding MoO3 can promote the aggregate of pristine particle.

Fig. 4.3.3. SEM morphology of (a) LiFePO₄, (b) LiFeP₀.₉₇₉B₀.₀₃O₄, (C) LiFeP₀.₉₇As₀.₀₃O₄, and (d)LiFeP₀.₉₇Mo₀.₀₃O₄.
In order to further study the effects of B, As, and Mo-dopant on the physical properties of LiFePO$_4$ cathode materials, we have measured their specific surface areas, the data is plotted against dopant content in Fig. 4.3.4. It is found that B and Mo dopant can reduce the specific surface area of LiFePO$_4$. Particularly, the specific surface areas of the samples decreased from 13.5 m$^2$ g$^{-1}$ to 10.2 m$^2$ g$^{-1}$ when $x=0.05$ in LiFeMo$_x$P$_{1-x}$O$_4$. On the other hand, As dopant leads to increase the SSA of LiFePO$_4$ from 13.5 m$^2$ g$^{-1}$ to 15.6 m$^2$ g$^{-1}$ when $x=0.05$ in LiFeAs$_x$P$_{1-x}$O$_4$.

![Graph showing specific surface area (SSA) of LiFeM$_x$P$_{1-x}$O$_4$ (M = Mo, B, As, $x=0$, 0.01, 0.03 and 0.05).](image)

Fig. 4.3.4. The specific surface area (SSA) of LiFeM$_x$P$_{1-x}$O$_4$ (M = Mo, B, As, $x=0$, 0.01, 0.03 and 0.05).

Fig. 4.3.5 shows the charge-discharge curves of LiFeM$_x$P$_{1-x}$O$_4$ (M = Mo, B, As, $x=0.01$, 0.03 and 0.05). It is noted that a 4.3V plateau occurs for As and Mo doped LiFePO$_4$ smaples. Moreover, the capacity of 4.3V plateau ($C_{4.3V}$) increases with increasing the amount of As and Mo. For example, about ca.30 mAh g$^{-1}$ of $C_{4.3V}$ was delivered when $x$ is 0.05 in LiFeAs$_x$P$_{1-x}$O$_4$. In fact, such phenomenon also exists at the sample prepared at low temperature of 470℃, which mentioned in Fig.4.1.1. The reason for this phenomenon is not clear.
Fig. 4.3.5 The charge-discharge curves of LiFeM$_x$P$_{1-x}$O$_4$ (M = Mo, B, As, x = 0.01, 0.03 and 0.05) at various current rates. (a) M = Mo, (b) M = B, (c) M = As.
Fig. 4.3.6 shows the rate capability of LiFeM\textsubscript{x}P\textsubscript{1-x}O\textsubscript{4} (M = Mo, B, As, x= 0.01, 0.03 and 0.05) at various current rates. LiFePO\textsubscript{4} samples show a discharge capacity of 142 mAh g\textsuperscript{-1} under 0.2mA cm\textsuperscript{-2}. However, only 67 mAh g\textsuperscript{-1} at 5mA cm\textsuperscript{-2} can be obtained for LiFePO\textsubscript{4}. LiFeAs\textsubscript{x}P\textsubscript{1-x}O\textsubscript{4} exhibit b shows the capacity of 76 and 74 mAh g\textsuperscript{-1} for x=0.01 and x=0.03 under 5mA cm\textsuperscript{-2}. LiFeB\textsubscript{0.01}P\textsubscript{0.99}O\textsubscript{4} exhibits the best high-rate performance among the doped samples. About 86 mAh g\textsuperscript{-1} of discharge capacity can be still delivered under 5mA cm\textsuperscript{-2}. All of Mo doped LiFePO\textsubscript{4} samples exhibits smallest discharge capacity under all current rates, which should be consider that Mo compound was existed as an impurity in LiFePO\textsubscript{4} and its low specific surface area.

![Graph](image)

**Fig. 4.3.6** The rate capability of LiFeM\textsubscript{x}P\textsubscript{1-x}O\textsubscript{4} at various current rates.

**4.2.4. Conclusion**

In this study, we confirm that the P\textsuperscript{5+} ions of LiFePO\textsubscript{4} can be substituted by B\textsuperscript{3+} and As\textsuperscript{5+} ions. However, Mo compound was only existed as an impurity in LiFePO\textsubscript{4} because Mo cannot dope in P-site. LiFeB\textsubscript{0.01}P\textsubscript{0.99}O\textsubscript{4} exhibits the best high-rate performance among the doped samples. About 86 mAh g\textsuperscript{-1} of discharge capacity can be still delivered under 5mA cm\textsuperscript{-2}. All of Mo doped LiFePO\textsubscript{4} samples exhibit smallest discharge capacity under all current rates, which should be considered that Mo compound was existed as an impurity in LiFePO\textsubscript{4} and its low specific surface area.
cm². On the other hand, only 67mAh g⁻¹ at 5mA cm⁻² can be obtained for LiFePO₄.

References


Chapter 5

Improved Electrochemical Performance of LiMnPO$_4$/C Composite as the Cathode for Lithium-ion Batteries
5.1. Introduction

Lithium-ion batteries have been widely used as power sources from portable electronic devices to electric vehicles due to their excellent cycling performance and high energy density among the commercialized secondary battery systems. Many compounds have been studied as possible cathode materials for lithium-ion batteries, such as LiCoO$_2$, LiNiO$_2$, LiMnO$_2$, LiMn$_2$O$_4$, LiFePO$_4$, LiNi$_0.5$Mn$_0.5$O$_2$ and their derivatives [1-6].

The olivine-type LiMnPO$_4$ (M= Fe, Mn) compounds are some of the most promising cathode materials for large-scale lithium-ion batteries because of their high theoretical capacity, excellent thermal stability, low cost and no toxicity. However, their electric conductivity is relatively poor [5], so various carbon coating techniques have been developed to improve the electrochemical performance of LiFePO$_4$ [7-11]. The other problem of these materials is slow kinetics and internal friction during charge/discharge [12]. This can be solved by minimizing the particle size of the materials, thereby reducing the diffusion path length for lithium ions in the cathode material and establishing an excellent electric contact with the carbon conductor. This attempt has already been achieved by carbon coating, in the other words fine LiFePO$_4$ particles have been successfully prepared and their excellent electrochemical performances have been reported by many researchers [8-11, 13-14].

The carbon coating technique is now widely used and applied to LiMnPO$_4$ materials. The discharge capacities of various LiMnPO$_4$ materials are summarized in Table 1. An excellent material with a discharge capacity of 150 mAh g$^{-1}$, which is extremely close to the theoretical one (171 mAh g$^{-1}$), has been successfully prepared using carbon coating technique [15]. The most popular carbon coating technique is post ball-milling of active material and electric conductor, such as acetylene black, carbon black material, etc. Though this method is useful, this process is composed of two steps, in which one is preparation of LiMnPO$_4$ and the other is ball-milling.
Table 5.1. Composition and utilization of cathode with LiMnPO$_4$ made by different synthesis methods

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Carbon content (%)</th>
<th>Test condition</th>
<th>Dis-capacity (mAhg$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two step: Solid state method + ball-milling with carbon</td>
<td>10</td>
<td>Charge: charging to full charge, Discharge: 0.16 C; 2-4.5 V.</td>
<td>120</td>
<td>[12]</td>
</tr>
<tr>
<td>Two step: Solid state method + ball-milling with carbon</td>
<td>6</td>
<td>Charge: CCCV, 4.5V 0.017mA/cm$^2$ Discharge: 0.28 mA/cm$^2$; 4.5-2 V.</td>
<td>150</td>
<td>[15]</td>
</tr>
<tr>
<td>Two step: Precipitation method + balling milling with AB</td>
<td>16.7</td>
<td>1/20 C, 2-5 V.</td>
<td>95</td>
<td>[16]</td>
</tr>
<tr>
<td>Two step: Hydrothermal method + balling milling with AB</td>
<td>20</td>
<td>1.5 mAg$^{-1}$, 3-4.5 V.</td>
<td>70</td>
<td>[17]</td>
</tr>
<tr>
<td>One step: So-gel method</td>
<td>3</td>
<td>1/20 C, 2.5-4.5 V.</td>
<td>40</td>
<td>[18]</td>
</tr>
</tbody>
</table>

In this study, we have tried the one step preparation of LiMnPO$_4$/C materials. Such a method has been reported by R. Dominco et al. [18], whose sample prepared by the sol-gel technique shows the lower discharge capacity of 40 mAh g$^{-1}$ and porous texture, which leads to a lower density. We combined our original spray dry technique [19-22] with the carbon coating technique to prepare the dense LiMnPO$_4$/C material. Here, it is found that our samples with a larger cell volume give a higher discharge capacity and showed the characteristic IR spectrum which is different from those prepared by solid state method.

5.2. Experimental

The starting materials, CH$_3$COOLi•2H$_2$O (98%, Wako Co.), NH$_4$H$_2$PO$_4$ (99%, Katayama Co.) and Mn (CH$_3$COO)$_2$•4H$_2$O (99%, WaKo Co.) were dissolved in water to obtain a homogenous solution. A desirable amount of malic acid was added to this solution as a carbon source. The resulting transfer solution was pumped into a spray-drying instrument (GB32 Pulvis Mini-Spray, Yamato, Japan) to produce a solid state precursor. The precursor was initially decomposed at 350°C in an Ar atmosphere and then ground after cooling. The decomposed intermediate was finally sintered in an Ar atmosphere at desirable temperature for 8hrs. Here, the pure LiMnPO$_4$ sample was finally sintered at a temperature of 550°C.
and was called sample A. The final heating temperature of the LiMnPO₄/C materials is 500 – 800 °C.

For comparison, LiMnPO₄ samples were also prepared by a solid-state reaction method using the same starting materials. They were mixed and ground using a planetary ball mill for 2hrs in acetone. The mixture was initially preheated at 350 °C for 3hrs and then sintered under the same condition as sample A. The samples prepared by the solid state method are marked as sample B.

Powder X-ray diffraction (XRD, Rint-1000, Rigaku, Japan) measurement using Cu Kα radiation was employed to identify the crystalline phase of the synthesized material. The XRD data (2θ = 15-70°) had a step size of 0.02°. The specific surface areas of the samples were determined by the BET method (Micromeritics Flowsorb III). The as-prepared powders were observed using a scanning electron microscope (SEM, JSM 5200, JEOL, Japan) in order to observe their morphology. TG/DTA measurements were conducted using a Thermal Analysis Station (TAS100) at the scan rate of 5 °C/min from 30 to 800°C in air. The tap density of the LiMnPO₄ powder was determined by a self-made instrument (The details were described elsewhere [23]).

The charge/discharge tests were carried out using the CR2032 coin-type cell, which consists of a cathode and lithium metal anode separated by a Celgard 2400 porous polypropylene film. The cathode contains a mixture of 20 mg of accurately weighed active materials and 15 mg of a conducting binder. The mixture was pressed onto a stainless screen and dried at 140 °C for 8 hrs under vacuum. The cells were assembled in a glove box filled with dried argon gas. The electrolyte was 1 M LiPF₆ in ethylene carbonate / dimethyl carbonate (EC / DMC, 1:2 in volume).

A three-electrode glass cell was used for the cyclic voltammetry (CV) measurement. The CV measurements were performed at the sweep rate of 3 mV/min with a cutoff voltage of 2.0-5.0 V.
5.3. Results and discussion

5.3.1 Pure LiMnPO₄ prepared by the spray dry technique

Fig. 5.1 shows the powder X-ray diffraction patterns of the LiMnPO₄ prepared by the spray dry method (sample A) and prepared by the conventional solid-state method (sample B). All diffraction peaks of both samples can be indexed on the orthorhombic structure with the space group Pnmb, and there are no peaks of any impurity phases in the XRD diffraction patterns. All peaks in sample A are located at a lower angle than those in sample B, which means that the lattice volume of sample A would be larger than that of Sample B.

![X-ray diffraction patterns](image)

Fig. 5.1. The powder X-ray diffraction patterns of sample A (top) and sample B (bottom).

The lattice parameters of two LiMnPO₄ samples are calculated and summarized together with the reported values in Table 5.2. The values of the lattice parameters for sample B agree well with the reported values [7, 15, and 24]. On the other hand, our sample A shows slightly higher values in all of the a, b and c axes. The cell volume of sample A is 7% higher than that of sample B. The lattice parameters of our sample are closer to those calculated by the density functional theory and it’s modified one [24-26].
Table 5.2. Lattice parameters of the LiMnPO$_4$ prepared by various methods.

<table>
<thead>
<tr>
<th>samples</th>
<th>a axis(Å)</th>
<th>b axis(Å)</th>
<th>c axis(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>10.64</td>
<td>6.203</td>
<td>4.871</td>
</tr>
<tr>
<td>Sample B</td>
<td>10.41</td>
<td>6.094</td>
<td>4.732</td>
</tr>
<tr>
<td>Yonemura et al. [7]</td>
<td>10.44</td>
<td>6.103</td>
<td>4.744</td>
</tr>
<tr>
<td>Osorio-Guillén et al. [25]</td>
<td>10.86</td>
<td>6.28</td>
<td>4.85</td>
</tr>
<tr>
<td>Zhou et al. [26]</td>
<td>10.62</td>
<td>6.17</td>
<td>4.80</td>
</tr>
</tbody>
</table>

Infrared and Raman spectroscopy are widely used for the characterization of LiFePO$_4$ and LiMnPO$_4$ [21, 24, 26]. The spectra of LiMnPO$_4$ and LiFePO$_4$ are composed of two frequency regions [24]. The peaks that appeared in the region of 800 - 1200 cm$^{-1}$ are assigned to be intra-molecular stretching modes of phosphate ($\nu_1$ and $\nu_3$) and those in the range of 400 – 700 cm$^{-1}$ correspond to the bending modes [27-29]. The infrared spectra of samples A and B are shown in Fig. 5.2 a (800 – 1200 cm$^{-1}$) and b (400 – 700 cm$^{-1}$). Three strong peaks appear in the $\nu_3$ region and two peaks with different intensities appears in the $\nu_1$ region as shown in Fig. 5.2(a). The spectrum of sample B agrees well with that already reported [26]. On the other hand, the two peaks of sample A are different from those of sample B. One peak (1051 cm$^{-1}$) belongs to the $\nu_3$ region and the other one (984 cm$^{-1}$) $\nu_1$ region. It is found that the common wave numbers of the two peaks in both samples agree with those of LiFePO$_4$. 

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Fig. 5.2 (a). FTIR absorption spectra of $\nu_1$ and $\nu_3$ for sample A and sample B.

Fig. 5.2(b) shows the FTIR spectra for the $\nu_4$ and Li$^+$ cage modes [29]. Three bands in the range from 550 cm$^{-1}$ to 635 cm$^{-1}$ would be assigned to be asymmetric bending vibrations of PO$_3^{4-}$($\nu_4$). The bands at ca. 500 and 465 cm$^{-1}$ are assigned to the Li$^+$ ion “cage modes”. Finally, both samples A and B had similar spectra in this region.

Fig. 5.2 (b). FTIR absorption spectral of $\nu_4$ for sample A and sample B.
Figure 5.3 shows SEM images of the powders (sample A and B). Though sample A has a relatively homogeneous distribution in particle sizes, it is mainly composed of two types of particles. One is isolated spherical primary particles of less than 0.5 µm and the other is sintered secondary one with smooth surface and the larger size of 3-5 µm. Such a LiMnPO₄ with smooth surface has been prepared by hydrothermal method [17], while sample B has many large agglomerated particles with a heterogeneous size distribution. Such extreme differences in morphology would lead to the differences in the tap density and BET surface area. These values for sample A are 0.93 g cm⁻³ and 7.2 m² g⁻¹, respectively. On the other hand, those of sample B are 0.81 g cm⁻³ and 4.7 m² g⁻¹, respectively. Both the higher tap density and higher surface area of sample A are desirable characteristics for an electrode material. The higher surface area of sample A may be due to the presence of smaller isolated particles.

Since our sample is prepared from an acetate compound, the carbon content in sample A is also analyzed by the DTA and TG. As there is no exothermic peak for sample A at 300 – 450 °C, it would be pure LiMnPO₄.

Figure 5.4 shows the charge-discharge curves of samples A and B at room temperature. The cell is charged to 4.6V at the 0.1C rate, and kept at 4.6V until the current density decreased to 0.01mA cm⁻², and then discharged to 2V at 0.1C. Though sample B can be charged to ca. 50 mAh g⁻¹, it delivers only 10 mAh g⁻¹ for the discharge capacity, which is
similar to the value reported in the literature [5]. On the contrary, sample A gives a dramatic increase in the initial charge and discharge capacities. Its charge and discharge capacities are 126 and 90 mAh g\(^{-1}\), respectively. The charge capacity corresponds to 76% of the theoretical value and the columbic efficiency reached 71%. The discharge curve of sample A is composed of two regions, in which one is a constant voltage area at ca. 4 V with the capacity of ca. 40 mA h g\(^{-1}\), and the other is a sloping curve with the capacity of ca. 50 mAh g\(^{-1}\). The appearance of the flat voltage area is related with two phase mechanism of electrochemical reaction as already reported [15]. The improved electrochemical performance of the sample A may be partly ascribed to the high surface area, which leads to the short length of the Li\(^+\) diffusion path. Since the difference in the BET surface area of both samples is only 40%, we believe that the expanded lattice volume would serve fast lithium ion diffusion, and improvement in the charge/discharge capacities.

Fig. 5.4. Initial charge-discharge curves of sample A and sample B.

5.3.2 LiMnPO\(_4\)/C composite prepared by spray dry technique

It is believed that the carbon coating is very effective to improve the electrochemical performance of LiMPO\(_4\) (M=Mn, Fe) cathode materials with a low electric conductivity [15-20]. The carbon coating technique was applied for further improvement in the electrochemical performance of our LiMnPO\(_4\) prepared by the spray dry method. Malic acid (20 wt%) is used as the carbon source and added the source solution. The precursors
obtained by the spray dry process formed a conductive carbon during the decomposition and final heating processes. TG-DTA analysis shown in Fig. 5.5 was used to determine the carbon content of the 700 °C annealed LiMnPO₄/C materials. The weight loss in the TG curve begins at 300°C and reaches the local minimum value of 15 wt% at 400°C. Since this weight loss accompanies an exothermic peak in the DTA curve, it could be due to the combustion reaction of the carbonaceous material. From 421 to 470 °C, the weight slightly increases (2.1%). In the case of LiFePO₄, the Fe₂P phase easily occurs among the LiFePO₄/C materials when they were prepared relatively high-annealing temperature [30, 31]. Therefore, such behavior may be attributed to the oxidative decomposition of Mn₂P in air though it can’t be detected from the XRD (As shown in Fig. 5.6). The second weigh loss is 4% when the temperature increases to 550 °C, which is also assumed to be combustion of carbon in the sample. Finally, the weigh loss by the combustion of carbon would be determined by taking the weight gain of the sample into consideration as 18-21 wt% for the 700 °C annealed sample.

Fig. 5.5 Thermal analysis of LiMnPO₄ at the heating rate of 5°C/min in air.

Fig. 5.6 shows the powder X-ray diffraction patterns of LiMnPO₄/C materials annealed at 500 – 800 °C. There are no peaks of impurity phase in XRD diffraction patterns. The lattice parameters of four samples are nearly the same as that of sample A as expected from their peak position.
Fig. 5.6. The powder X-ray diffraction patterns for LiMnPO₄ prepared by spray dry method at different temperatures: (a) 500°C, (b) 600°C, (c) 700°C and (d) 800°C.

Fig. 5.7 shows an SEM image of LiMnPO₄/C material prepared at 700 °C. The primary particle sizes are slightly smaller than that of isolated one in sample A. It indicates that the addition of the carbon can prevent the growth of the particle. Therefore, carbon coating is not only increasing the electronic conductivity but also decreasing the particle sizes of the samples. Such a texture can improve the diffusion of lithium ions in the LiMnPO₄. According to our experiences, the lithium ion diffusion would have stronger effects on the electrochemical performance of the LiMPO₄ (M=Mn, Fe).

Fig. 5.7. SEM of carbon-coated LiMnPO₄ sintered at 700°C.
Fig. 5.8 shows the effect of the final preparation temperature on the BET surface area of the LiMnPO$_4$/C materials. The specific surface area of the sample is significantly reduced from ca. 47.1 m$^2$ g$^{-1}$ at 500 °C to 35.6 m$^2$ g$^{-1}$ at 700 °C and kept constant until 800 °C. As the crystalline size determined by Scherrer’s equation is roughly 90 nm and the SEM images of 500-800 °C samples also resemble each other, the large difference in the BET surface area of samples would originate mainly from carbon in LiMnPO$_4$/C materials. This consideration would be supported by the fact that carbonization rate of pyrene derivatives determined by gas evolution is fastest in the temperature range of 400-550 °C [32], in the other words carbonization proceeds in these temperature range and the physicochemical property of carbon formed at 500-600 °C would change extremely.

Fig. 5.8 The effect of the sintering temperature on the BET surface area of the carbon coated LiMnPO$_4$.

Fig. 5.9 shows the initial discharge curves of the samples prepared at 500 – 800 °C. It is noted that the discharge capacities of the samples increase with the increasing in the sintered temperature. XRD data indicate that all samples have the pure olivine structure with constant lattice parameters, which means that the effect of the sintering temperature on the discharge capacity of LiMnPO$_4$ did not originate from the structural reason. However, the obvious change in the BET surface area in LiMnPO$_4$/C materials would indicate that the
characteristics of carbon in samples have changed such as its morphology, electronic conductivity and etc. Therefore, we believe that the increase in the discharge capacity with the sintering temperature is related to the change of carbon properties of LiMnPO$_4$/C materials. With a further increase in the sintering temperature, the discharge capacity of LiMnPO$_4$ decreases from the maximum value of 140mAh g$^{-1}$ at 700 °C to 120mAh g$^{-1}$ at 800 °C. The reason for the lower capacity of the 800 °C samples is not clear.

![Graph showing discharge curves of LiMnPO$_4$](image)

Fig. 5.9 The discharge curves of LiMnPO$_4$ prepared at (A) 500 °C, (B) 600 °C, (C) 700 °C and (D) 800 °C.

The rate capability of carbon coated LiMnPO$_4$/C material is shown in Fig. 5.10. The cell was charged to 4.6 V at a 0.25 C rate, kept at 4.6 V until the current density decreased to 0.012mA cm$^{-2}$, and then discharged to 2 V at various rate. More than 100 mAh g$^{-1}$ discharge capacity was still delivered even at the discharge rate of 1 C. The rate capability of the LiMnPO$_4$/C materials should be further improved for practical applications.
Fig. 5.10. The rate capability of carbon-coated LiMnPO$_4$ sample.

Fig. 5.11 shows the cycling performance of LiMnPO$_4$/C sample at a 0.25 C rate in the range of 2.5-5 V. Although a slight capacity fading (ca. 10mAh g$^{-1}$) was found after the 2$^{nd}$ cycle, the discharge capacity is still 112 mAh g$^{-1}$ even after 55 cycles. It is confirmed that the LiMnPO$_4$/C composition shows a good cyclability.

Fig. 5.11. The cycling performance of LiMnPO$_4$ sample at room temperature in the voltage range of 2.5-5V at 0.25C rate.
Fig. 5.12 shows the cyclic voltammograms of the LiMnPO$_4$/C sample (700 ºC) measured at a sweep rate of 3 mV min$^{-1}$ at room temperature and 60 ºC. A pair of peaks was observed in the 4 V region, which corresponds to the oxidation-reduction reaction of Mn$^{2+}$/Mn$^{3+}$ redox couple. There is one wide peak between 3.0 V and 3.7 V measured at room temperature, which was clearly observed during the first reduction process and it decreased with the increasing cycle number. The appearance of the wide peak might be related to the slow diffusion of lithium ion in LiMnPO$_4$, which cause the large polarization of the LiMnPO$_4$ electrode. The wide reduction a peak disappears at 60 ºC, which indicates that the increasing temperature promotes both the diffusion of lithium ions and the electrochemical reaction of Mn$^{2+}$/Mn$^{3+}$. It would lead to the appearance of one pair sharp peaks at 60 ºC. Finally, it means that the LiMnPO$_4$/C sample has higher a capacity and smaller polarization at elevated temperature.

Fig. 5.12. Cyclic voltammograms of LiMnPO$_4$ measured at room temperature and 60 ºC.

5.4. Conclusions
The spray dry method was used for the preparation of LiMnPO$_4$ with improved physical properties and electrochemical properties. The pure LiMnPO$_4$ with the olivine structure is composed of the uniform and dispersed spherical-like particles of 0.5µm~1µm. The
LiMnPO₄ prepared by the spray dry method delivers higher reversible capacity of 90mAh⁻¹ at 0.1 C, on the other hand, that by the conventional solid state method 10mAh⁻¹. Furthermore, it is confirmed that the combination of carbon coating technology with the spray dry technique brings further improvement in electrochemical properties of LiMnPO₄ cathode. SEM images show that the presence of carbon prevents crystal growth, and it is confirmed that the final sintering temperature gives an obvious effect on the electrochemical performance of the LiMnPO₄/C materials. The sample sintered at 700 °C shows the highest discharge capacity and a relatively good rate capability with more than 100mAh⁻¹ at a rate of 1 C.

References:
Chapter 6

General conclusions
General conclusions

LiMPO₄ and Mn-spinel are considered as the most promising cathode materials because they are cheaper, less toxic and safe, but some problem hinder the practical application. For example, Mn-spinel suffers the capacity fading upon cycling in both spinel/Li and spinel/carbon cells, especially at elevated temperature. Olivine LiMPO₄ (M=Fe, Mn) with low electronic conductivity and lithium ion diffusion coefficient leads to its lower discharge capacity, high polarization and poor rate capability. In order to overcome these problems, I have systematically investigated the effect of foreign metal ions doping on structure and electrochemical characteristics of Mn-spinel and have optimized syntheses condition (e.g. Syntheses temperature, the starting materials, syntheses method and so on) for LiMPO₄. Main conclusions are summarized as following:

1. We have verified the quantitative relationship between the capacity of 3.2V discharge plateau and oxygen defect degree using both theoretical method and experimental method. It could be expressed as: \( C_{3.2V} = 148 \times 126 \times 0.5 \times 0.44 \delta \). \textit{Ex situ} XRD has further indicated the cause of capacity fading in various kinds of spinels. It shows clearly that two-phase coexistence region occurs on both the 4.0 and 4.2V plateau forum doped spinel with oxygen deficiency. This behavior is quite different from the undoped spinel with oxygen stoichiometry, where two-phase coexistence region occurred on the 4.2V plateau region only. However, Al doped spinel with oxygen stoichiometry shrink uniformly from 8.17 Å to 8.06Å during de-lithiation, which could be considered as one-phase reaction. Furthermore, we have confirmed that the capacity retentions give a linear line against the oxygen defect degree \( \delta \) in normal spinel at room temperature, as well as Al doped spinel at 60 °C. When \( \delta \) is extrapolated to 0, the capacity retention would achieve ca. 100% in both cases. Consequently, we confirm that the oxygen stoichiometry is a determining factor in cycleability improvement in spite of ambient temperature. Moreover, we determine the accurate lattice parameter of the ideal LiMn₂O₄ without oxygen deficiency is 8.237Å.
2. Among the various foreign metals (Mg, Li, Co, Ni, Al, Cr, Fe), Al doping is expected to be a best cathode material because not only it could suppress 3.2V capacity effectively even at sintering temperature as high as 900-1000°C, but also the theoretical capacity of 4V region increased with increase in oxidation number of the doped metal ion in the 16d site of LiMn$_2$O$_4$ at the same doping level in mole fraction. Moreover, we have successfully prepared oxygen-stoichiometric Al doped spinel by new two-step method. Compared with spinel prepared by the conventional method, the new samples exhibit superior capacity retention and lower Mn dissolution. These improvements are attributed to their oxygen stoichiometry and small BET surface area. The capacity retention of the new kind of oxygen-stoichiometric spinel is about 99.34% at 60°C in the half-cell after 50 cycles. To the best of our knowledge, this is the best value among the reported papers. We believe that the new kind of Al doped spinel is a promising cathode materials for practical applications.

3. ZnO is coated uniformly on the surface of Mn-spinel particles by a gas-suspension spray coating method. Significant improvement of the electrochemical performance of Mn-spinels is achieved by coating ZnO. Increasing the amount of the coated ZnO, the discharge capacity of Mn-spinel a decreases slightly, but the cycleability of Mn-spinel at elevated temperature is improved obviously. In view of discharge capacity and cycleability, the 1-2% coated sample shows optimum cathodic behaviors. Moreover, The ZnO coating is favorable to improving the cycleability of Mn-spinel at elevated temperatures.

4. LiFePO$_4$ with the excellent rate capability has been successfully synthesized by a simple solid-state reaction. The electrochemical performances of LiFePO$_4$ have been improved with the increasing of sintering temperature from 470°C to 570°C. It is beneficial to the rate capability of LiFePO$_4$ by the extension of milling time. The LiFePO$_4$ sample prepared at 570°C for milling time 12h has delivered 145 and115 mAh g$^{-1}$ of the reversible capacity at the rates of 1C and 5C, respectively. It also exhibits the excellent cycling performance at room temperature as well as at 60 °C. It has been confirmed that it is an effective way to improve the electrochemical performance of LiFePO$_4$ by the
increasing of its surface are accompanying the ratio of grain contacted with electrolyte. Moreover, The SnO-coated LiFePO$_4$ have been successfully synthesized by so-gel method, prepared at 700°C shows the tap density of about 1.32g cm$^{-3}$, higher about 40% than the bare sample (0.93g cm$^{-3}$). Moreover, the coated LiFePO$_4$ has still retained the excellent rate capability.

5. We confirm that the P$^{5+}$ ions of LiFePO$_4$ can be substituted by B$^{3+}$ and As$^{5+}$ ions. However, Mo compound was only existed as an impurity in LiFePO$_4$ because Mo can not dope in P-site. LiFeB$_{0.01}$P$_{0.99}$O$_4$ exhibits the best high-rate performance among the doped samples. About 86 mAh g$^{-1}$ of discharge capacity can be still delivered under 5mA cm$^{-2}$. On the other hand, only 67mAh g$^{-1}$ at 5mA cm$^{-2}$ can be obtained for LiFePO$_4$.

6. The spray dry method was used for the preparation of LiMnPO$_4$ with improved physical properties and electrochemical properties. The pure LiMnPO$_4$ with the olivine structure is composed of the uniform and dispersed spherical-like particles of 0.5µm~1µm. The LiMnPO$_4$ prepared by the spray dry method delivers higher reversible capacity of 90mAhg$^{-1}$ at 0.1 C, on the other hand, that by the conventional solid state method 10mAhg$^{-1}$. Furthermore, it is confirmed that the combination of carbon coating technology with the spray dry technique brings further improvement in electrochemical properties of LiMnP O$_4$ cathode. SEM images show that the presence of carbon prevents crystal growth, and it is confirmed that the final sintering temperature gives an obvious effect on the electrochemical performance of the LiMnPO$_4$/C materials. The sample sintered at 700 °C shows the highest discharge capacity and a relatively good rate capability with more than 100mAhg$^{-1}$ at a rate of 1 C.
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