Functional Li-M (Ti, Al, Co, Ni, Mn, Fe)-O Energy Materials

In Yea Kim, Seo Yoon Shin, Jea Hwan Ko, Kang Soo Lee*, Sung Pil Woo*,
Dong Kyu Kim, and Young Soo Yoon[†]

Department of Chemical and Biological Engineering, Gachon University, Seongnam 13120, Korea

**Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea*

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ABSTRACT

Many new functional materials have been studied for efficient production and storage of energy. Many new materials such as sodium-based and sulfide-based materials have been proposed for energy storage, but research on Li batteries is still dominant. Due to the influence of environmental concerns regarding nuclear energy, interest in and research on fusion power are steadily increasing. For the commercialization of nuclear fusion, a design standard based on a considerable level of physical analysis and modeling is proposed. Nevertheless, limitations of existing materials in nuclear fusion environments limit practical applications. Tritium propagation material for continuous fusion reaction is one of the core materials, and therefore research on this material is being carried out intermittently. The key material for Li-based energy storage and tritium generation is the functional material Li-M-O. In this review, a structural description of functional Li-M-O system materials and technical trends for its applications are introduced.

Key words : Li-M-O materials, Cathode, Solid electrolyte, Anode, Nuclear fusion materials

Part 1. Li-M-O Materials for Lithium Secondary Batteries

1. Cathode Materials for Lithium Secondary Batteries

1.1. Introduction

Cathode materials are significant, accounting for about 35% of the lithium secondary battery material cost; these materials are classified according to the crystal structure and the constituents of the metallic salt. Crystalline structures under consideration are divided into layered rock salt, spinel, and olivine type structures. In addition, Co, Ni, Mn, Al, Fe, and others are studied mainly as constituents of metal salts. Fig. 1 shows the three main types of crystal structure under consideration as cathode materials for lithium secondary batteries.

The requirements for the cathode materials of the lithium secondary battery are as follows:

1. High Energy Density
2. High Life Cycle
3. Superb Charge/Discharge Rate
4. Affordable Price
5. Environmentally Friendly

CoO₂, which has a layered rock salt type structure, is the most widely used cathode material for lithium secondary

batteries, and is still the mainstay in the industry today. However, cobalt (Co), which is used in the production of LiCoO₂, is a rare metal with a small amount of reserves; also, areas that can produce this material are limited. Therefore, it is disadvantageous in that the unit price is expensive and in that the material is unstable in terms of supply. For this reason, many studies have been carried out in the direction of not using cobalt or in minimizing its usage. As prime examples, there is LiMn₂O₄, which has a spinel type structure that uses Mn, and the LiNiO₂ layered rock salt structure, which uses Ni. Both Ni and Mn are easily available compared to cobalt. In addition, research on ternary alloy materials using combinations of Ni, Co, and Mn, or Ni, Co, and Al have been actively conducted.²⁾ However, the structure of LiNiO₂ is unstable in the charged state, and the performance of LiMn₂O₄ deteriorates at high temperature. For these reasons, the tritium alloys of Li[Ni, Co, Mn]O₂ are the most actively used materials in industry, and not LiCoO₂. The general characteristics of the aforementioned materials are listed below in Table 1.

1.2. LiCoO₂

LiCoO₂ has a layered rock salt structure called “α-NaFeO₂”, in which oxide ions constitute a (111) plane, and lithium ions and cobalt ions are alternately present between the layers. An attempt to apply such a layered oxide containing lithium ion as a cathode material was made when the Mizushima Corporation discovered in 1980 that LiCoO₂ in a solution of 1 M LiBF₄/PC exhibited a potential of 4 V to lithium metal and that reversible insertion and desorption of lithium ions was possible.^{3,4)}

[†]Corresponding author : Young Soo Yoon
E-mail : benedicto@gachon.ac.kr
Tel : +82-31-750-8988 Fax : +82-31-750-8839

Table 1. Types and Characteristics of Cathode Materials for Lithium Secondary Batteries

Material	LiCoO ₂	LiNiO ₂	LiMn ₂ O ₄	LiFePO ₄	LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂
Crystal Structure	Layered	Layered	Spinel	Olivine	Layered
Operating Voltage	3.7 V	3.5 V	4.0 V	3.2 V	3.6 V
Practical Capacity	145 mAh g ⁻¹	175 mAh g ⁻¹	100 mAh g ⁻¹	150 mAh g ⁻¹	140 mAh g ⁻¹
Stability	high	low	middle	very high	high
Cycle Performance	high	low	low	high	high
Cost	high	middle	middle	low	middle

Fig. 1. Representative crystal structures of cathode materials for lithium secondary batteries: (a) layered LiCoO₂, LiNiO₂, LiMn₂O₄; (b) cubic LiMn₂O₄ spinel; (c) olivine structured LiFePO₄.¹⁾

Insertion / desorption proceeds as lithium ions migrate into a two-dimensional plane with a CoO₆ octahedral structure. Since lithium ions are intercalated/deintercalated in a state in which the crystal structure, composed of an oxide and a cobalt ion, is maintained, good characteristics are exhibited in a normal charge/discharge cycle. The fact that expansion/contraction only occurs during the charging/discharging cycle can be advantageous when the battery is built because the use of graphite as an anode leads to the opposite effect. In addition, since the diffusion path of lithium ions is a single layer of a two-dimensional plane, it is advantageous in terms of the characteristics of the battery, which has a larger diffusion coefficient than those of other crystal structures. From the manufacturability aspect, LiCoO₂ also has a great advantage as a cathode material for a lithium secondary battery because a good quality product can be obtained by a relatively simple process.

Although, due to ly used as a cathode material for lithium secondary batteries in the early days, the continuous use of LiCoO₂ has been greatly limited by the increase in unit price due to the scarcity of the source material. Fig. 2 shows charge/discharge curves at C/24 rate in the range of 3.6-4.85 V. The curves show that LiCoO_x has several phases during the range of electrochemical cycling.⁵⁾ In addition, there is a problem of phase change when this material is charged excessively during the charging / discharging process. That is, when the amount of lithium ions desorbed exceeds 0.5, the phase changes from hexagonal to monoclinic, and the structure of LiCoO₂ becomes unstable. In order to prevent such a phenomenon, the charging voltage is limited to about 4.2 V when LiCoO₂ is used as the cathode material of a lith-

Fig. 2. Charge-discharge curves of Li_xCoO₂ at C/24 rate in the range of 3.6 - 4.85 V vs. Li₀/Li₊. The sequence of the several phases is indicated as x varies from 1.0 - 0.05.⁵⁾

ium secondary battery. For this reason, the theoretical capacity of LiCoO₂ is 274 mAh g⁻¹, but the capacity that can actually be used is limited to 130-150 mAh g⁻¹.

The charge / discharge reaction is as follows:

Many studies are being conducted to develop a cathode material for a lithium secondary battery with excellent properties that can compensate for the shortcomings of LiCoO₂. The research is divided into two major categories:

1. Developing a method that can compensate for the flaws of LiCoO₂
2. Finding a new material that can replace LiCoO₂

In order to compensate for the disadvantages of LiCoO₂, many studies on surface coating using metal oxide were conducted. Studies on the surface coating of LiCoO₂ using

Fig. 3. Voltage profile of an Li/LiMn₂O₄ cell discharged at C/24 rate with LMO material synthesized at 700 °C (left). Variation of the lattice parameters as a function of the Li content *x* during charge/discharge in the LMO cathode (right).⁵⁾

ZrO₂, Al₂O₃, MgO, SiO, etc., have been carried out and the life cycle of LiCoO₂ during charging/discharging cycles at potentials of 4.2 V or higher has improved significantly compared to that of LiCoO₂ without metal oxide. This improvement has been due to the suppression of physical phase change, inhibition of elution of cobalt ions, and suppression of increased interfacial resistance.⁶⁾

1.3. LiNiO₂

LiNiO₂, which has the same crystal structure (α -NaFeO₂) as LiCoO₂, has been studied for a long time as a replacement cathode material for LiCoO₂. Because it has a crystal structure identical to that of LiCoO₂, it exhibits characteristics equivalent to those of LiCoO₂ in various aspects. In fact, LiNiO₂ is 1.2 times larger than LiCoO₂ in terms of capacity because the amount of lithium that can be extracted is 0.7 for LiNiO₂, which is higher than the 0.5 extraction value for LiCoO₂. Also, it is easier to supply nickel, due to its low cost, than it is to supply cobalt.

The price of nickel is also cheaper than cobalt, which is superior in terms of supply.

The charge / discharge reaction is as follows:

However, LiNiO₂ has some problems when materials are synthesized. In order for LiNiO₂ to be activated electrochemically, it must stay as Ni³⁺ for the lithium to exist, but it is easy for Ni³⁺ to be reduced to Ni²⁺ during material synthesis. If Ni²⁺ is present instead of Ni³⁺, it is easy for lithium to become Li_{1-x}Ni_{1+x}O₂. This phenomenon leads to the diffusion of lithium ions and to a deterioration in the cycle of charge and discharge. Many synthetic methods have been studied as alternatives, but there is no clear solution yet. Also, when Li is removed from LiNiO₂, the Ni moves to the position of Li. When the number of Li is large, Li occupies

the location of Ni; this deteriorates the charge and discharge rate. Such inversion of Li and Ni, and the low thermal stability, prevent LiNiO₂ from being commercialized.

1.4. LiMn₂O₄

The spinel structure generally has the form of AB₂X₄. LiMn₂O₄ generally has this spinel structure and Mn ion occupies the 16d octahedral site, while Li ion occupies the 8a tetrahedral site. The 16c octahedral site, which is near the 8a tetrahedral site (occupied by Li ion), is empty; this path is necessary for Li ion to diffuse inside LiMn₂O₄. Fig. 3 provides the voltage profile of an Li/LiMn₂O₄ cell discharged at C/24 rate with LMO material synthesized at 700°C.⁵⁾ During the process of charging and discharging, a flat section appears in the region of 3 V and 4 V. However, in the 3 V region, Li ions are further inserted into the 16c site; this generates Li₂Mn₂O₄, which results in degradation in the cycles due to volumetric expansion.⁷⁾

Compared to other cathode materials, LiMn₂O₄ has a small capacity. It also has problems during charge and discharge cycles in the 4 V region. The leading causes for these problems include dissolution of Mn in the organic electrolytes,^{8,9)} structural instability,^{10,11)} and the Jahn-Teller Effect.¹²⁾ For these reasons, studies are underway to improve the cycle of charging and discharging by replacing a part of the Mn with another metal.

The charge / discharge reaction is as follows:

1.5. LiFePO₄

LiFePO₄, an olivine-type compound, is an excellent cathode material due to its high capacity and the low cost of its raw material. In particular, due to its excellent cycle of charging / discharging, and its thermal stability, it is attracting attention from many researchers in the industry

as a cathode material for batteries of large-sized electric vehicles. LiFePO_4 has been studied continuously since the Goodenough Corp. used a polyanion in the form of XO_4^{y-} ($\text{X} = \text{S}, \text{P}, \text{As}, \text{Mo}, \text{W}, y=2, 3$) to develop an Fe compound with an operating voltage of 3.4 V.^{13,14} LiFePO_4 is a cheap material with outstanding life cycle and thermal stability; it is also environmentally friendly. Despite these advantages, the use of this material is still limited. This is because this material is difficult to charge and discharge rapidly due to its low electrical conductivity ($10^{-10} \text{ S cm}^{-1}$). In order to solve these problems, two approaches are under study. The first is to increase the surface area of the sample that will be used in the reaction by inserting particles with large specific surface area into the nanostructure. The second method is to coat a conductive material such as carbon onto the surface of the particles. A variety of studies have been conducted using these two methods, and a lot of progress has been made until now.¹⁵⁻¹⁹

The charge / discharge reaction is as follows:

1.6. $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$

$\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ is a ternary cathode material with a crystal structure identical to that of LiCoO_2 ; its capacity and operating voltage are similar to those of LiCoO_2 . According to the research, it is possible to charge and discharge this material with a high capacity of 200 mAh g^{-1} when the voltage is raised to 4.6 V.²⁰ $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ has a high thermal stability compared to that of LiNiO_2 , and it uses a 3 times lower amount of Co compared to LiCoO_2 . Many studies have been done on the possibility that a solid solution compound of the transition metal can be used to take advantage of existing materials and mitigate the mentioned disadvantages. Among potential materials, $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ is one of the few solid solution compounds that is actually being used in the industry, and it is the closest to becoming commercialized.

2. Solid Electrolyte Materials for Lithium Secondary Batteries

2.1. Introduction

Secondary batteries provide high energy for various electronic devices, but they are subject to flame hazard because they use volatile and highly reactive liquid electrolytes. Next generation secondary batteries will use solid electrolytes instead of liquid electrolytes, and research is underway to fabricate batteries with low flame hazard.^{21,22} Advantages of batteries manufactured using solid electrolytes (also known as "all solid-state batteries") are that they do not use liquid electrolytes, so there is little risk of fire,

and that there is no leakage of liquid. In addition, such batteries are safe for use at high temperature and pressure, and their low self-discharge rate enables long-term storage. Unlike liquid electrolytes, solid electrolytes do not leak, so there is no restriction on packing, and this means the battery can be miniaturized. In order to manufacture all solid-state batteries with these advantages, it is important to develop a new solid electrolyte with excellent electrolyte performance. The performance of the battery is affected by the internal movement of Li ions. Therefore, the higher the ionic conductivity of the solid electrolyte is, the better the performance of the battery is.²³⁻²⁵

The following are additional requirements for solid-state batteries:

1. Interfacial stability between anode and cathode
2. High chemical structural stability
3. Large working windows of voltage and current
4. Stability over a wide temperature range
5. Low corrosion and high thermal mechanical strength (for demanding environments)
6. Economically and environmentally friendly

The solid electrolytes that are being studied recently are LiSiCON , NASiCON , the Garnet type, the Perovskite type, the anti-perovskite type, and more. A lot of the research that has been conducted has mainly focused on the wide range of chemical compositions and crystal structures. Fig. 4 shows several types of solid electrolytes with good ion conductivity for use in lithium secondary batteries.

In order to understand Li-M-O solid electrolytes, this chapter mainly focuses on their structure and material properties. Also, this chapter will discuss the pros and cons of these electrolytes, and how we will overcome their flaws.

Fig. 4. Reported total lithium ion conductivity as function of temperature.²⁶⁾

2.2. NASICON type solid electrolyte

The general structure of the NASICON (Na super ionic conductor) solid electrolyte is expressed as $AM_1M_2P_3O_{12}$ / $AM_1M_2(PO_4)_3$. One AO_6 octahedron and the PO_4 tetrahedrons share six oxygen atoms at the edges to form a three dimensional skeleton. Three-dimensional channels (M_1 , $M_{1/2}$, M_2) are formed in the crystal lattice and the conduction of ions become possible. B-alumina, $Na_3Zr_2Si_2PO_{12}$, and $NaZr_2(PO_4)_3$ are materials representative of the NASICON structure (Fig. 5).²⁸⁾ Many studies have been conducted on $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) ($0 \leq x \leq 0.4$, LATP), in which Na and Zn are replaced by Li and Ti ions and some Al.²⁹⁾ $NaZr_2(PO_4)_3$ shows a low ionic conductivity of about $10^{-5} \text{ S cm}^{-1}$ at 300°C , but it has been reported that this ionic conductivity increases tenfold when Na is replaced with Li.³⁰⁾ When Zr^{4+} ions are replaced by Ti^{4+} ions, which are small in size, the ionic conductivity improves due to the formation of a channel that is more suitable for ions to move in, while the skeletal structure of NASICON is maintained. Many studies have been conducted on $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) ($0 \leq x \leq 0.4$, LATP), in which Na and Zn are replaced by Li and Ti ions and some Al.^{31,32)} The structure of LATP depends on the amount of lithium inserted; the ionic conductivity of $Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$ was at its highest (10^{-2} - $10^{-3} \text{ S cm}^{-1}$) when the x value was 0.3. Research on the synthesis of LATP is continuously being performed using various methods such as solid state reaction, sol-gel reaction, hydrothermal reaction, and more. Studies have reported that the ionic conductivity increased with the replacement of Ti^{4+} and P^{5+} ions with trivalent cations (Al, Ga, Sc, In, Y) in the LATP structure.^{33,34)} However, when LATP comes in contact with Li metal, which is used as a cathode, Ti^{4+} is reduced to Ti^{3+} and it becomes difficult to apply these methods to all solid-state batteries. LAGP substitutes Ge^{4+} for Ti^{4+} ; therefore, LAGP is attracting more attention than LATP as a solid electrolyte because LAGP makes Li more stable by replacing Ti^{4+} with Ge^{4+} .³⁵⁾

Fig. 5. Crystal structure of $NaZr_2(PO_4)_3$. The solid box indicates the unit cell.²⁷⁾

2.3. Garnet type solid electrolyte

The general structure of a garnet type solid electrolyte is expressed as $A_3B_3C_2O_{12}$, which forms as a tetrahedron (site A), a dodecahedron (site B), and an octahedron (site C), and coordinating oxygen atoms.^{36,37)} Fig. 6 shows the crystal structure of $Li_5La_3M_2O_{12}$ ($M=Nb/Ta$). Among the garnet type solid electrolytes, Lithium Lanthanum Zirconia Oxide (LLZO), which was studied by Weppner's group in 2007, has been the most studied compound. LLZO has cubic and tetragonal structures, with ionic conductivity values of $\sim 5 \times 10^{-4} \text{ S cm}^{-1}$ in the cubic structure and $1.6 \times 10^{-6} \text{ S cm}^{-1}$ in the

Fig. 6. Crystal structure of $Li_5La_3M_2O_{12}$ ($M = Nb/Ta$) (a). Details of 3D lithium ion migration pathway in $Li_5La_3M_2O_{12}$ ($M=Nb/T$) (b).²⁷⁾

Fig. 7. Crystal structures of $\text{Li}_2\text{ZnGeO}_4$ (a) and $\text{Li}_{3.5}\text{Zn}_{0.25}\text{GeO}_4$ (LISICON) (b). The remaining lithium occupies the interstitial sites within the rigid network of LISICON.²⁷⁾

tetragonal structure.^{38,39)} In previous research, a method of synthesizing LLZO by adding Al^+ to form a stable cubic structure has been studied.^{40,41)} Ever since then, many synthesis studies were performed by adding a variety of cations.^{40,42)} Other garnet compound includes lithium lanthanum metal oxide (Metal = Nb, Ta); $\text{Li}_6\text{AlLa}_2\text{M}_2\text{O}_{12}$ with Ca, Sr, and Ba (position A) has ionic conductivity of $4 \times 10^{-5} \text{ S cm}^{-1}$.⁴³⁾ In order to synthesize a solid electrolyte with a garnet structure, the material must be made to remain at a high temperature of 1100°C for a long period. During this process, Li^+ ions become volatile and either the garnet structure collapses or a solid electrolyte with low ionic conductivity is synthesized. Experiments are underway to synthesize solid electrolytes with excellent properties.

2.4. LISICON-type solid electrolyte

LISICON, which was introduced by Bruce and West, is an abbreviation of “Lithium Super Ionic Conductor”; its structural formula is $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$.⁴⁴⁾ Due to its structure, lithium ions are distributed between two different octahedron sites (Li_1 and Li_2 sites inside the lattice) and move between them. $\text{Li}_{3.5}\text{Zn}_{0.25}\text{GeO}_4$ has a high ionic conductivity of $1.2 \times 10^{-1} \text{ S cm}^{-1}$ at 300°C , but a low ionic conductivity of $10^{-7} \text{ S cm}^{-1}$ at room temperature.⁴⁵⁾ The Li-rich $\text{Li}_{3.5}\text{Zn}_{0.25}\text{GeO}_4$ structure octahedron sites are shown in Fig. 7. The use of $\text{Li}_{3.5}\text{Zn}_{0.25}\text{GeO}_4$ for batteries is limited at room temperature. On the other hand, thio-LISICON (e.g. Li_4GeS_4 , Li_3PS_4 , Li_5AlS_4), in which oxygen is replaced by sulfur, has an ion conductivity value that is 100 times higher than that of oxide type LISICON.^{46,47)} In particular, $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ has a high ionic conductivity of $2.2 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. Therefore, in the case of LISICON-type solid electrolytes, researchers are developing methods to replace the oxygen in thio-LISICON with sulfur.

2.5. Perovskite type solid electrolyte

Perovskite is also known to have a formula of ABO_3 ; the

Fig. 8. Crystal structure of tetragonal $\text{Li}_3\text{La}_{3/2}\text{TiO}_3$ (a). Lithium, lanthanum, and vacancies are distributed at the A-sites. Schematic representation of 3D mobility of lithium ions in the perovskite structure (b).²⁷⁾

BO_3 surrounding the A-site ions becomes the frame of the crystal structure.^{48,49)} The perovskite structure (ex. tetragonal $\text{Li}_{3x}\text{La}_{3/2-x}\text{TiO}_3$) is shown in Fig. 8. The first research into the Li-M-O type perovskite material was conducted after a study on the A-site deficiency structure was undertaken by Latie and Belous; in this study, $\text{La}_{2/3}\text{TiO}_3$ was replaced with Li^+ instead of replacing it with La^{3+} .^{50,51)} After that study, a variety of materials have been studied. As of now, the most widely studied material is $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_{2.94}$ (LLTO); its ionic conductivity is $2 \times 10^{-5} \text{ S cm}^{-1}$, which is relatively high compared to the values of other materials.⁵²⁾ LLTO has high ionic conductivity because its structure deforms when there are not a sufficient number of A-site ions. However, the ionic conductivity of LLTO differs between its total ion conductivity ($2 \times 10^{-5} \text{ S cm}^{-1}$) and bulk ion conductivity ($1 \times 10^{-3} \text{ S cm}^{-1}$). This shows that the movement of Li^+ ions is restricted by contact resistance generated at the grain boundaries.⁵³⁾ In

order to solve this issue, many studies have examined the effect of the heat treatment temperature in order to determine an optimum temperature. It was also necessary to reduce the activation energy and, for that reason, a variety of ions were studied as substitutions ($\text{La}^{3+}=\text{Pr}$, Nb , Sm).⁵⁴⁾ LLTO has excellent ionic conductivity, but the intercalation of lithium causes Ti^{4+} to be substituted with Ti^{3+} , resulting in a deterioration in the performance, which limits the use of this material as a solid electrolyte. Various studies have been carried out to improve the ionic conductivity of perovskite structure materials. For example, Martin et al. obtained an ion conductivity of $4.3 \times 10^{-5} \text{ S cm}^{-1}$ by replacing TiO_3 with NbO_3 .⁴⁹⁾

2.6. Anti-perovskite type solid electrolyte

The anti-perovskite structure is a typical ABO_3 perovskite structure, in which A is a monovalent metal cation, B is a divalent metal cation, and O is a negative monovalent anion. This structure is created when an anion element in the conventional perovskite structure is replaced with a cation metal. Zhao et al. were the first to study Li_3OA (A = halogen) anti-perovskites.^{23,24,55,56)} The most basic material of this structure is Li_3OCl , which has a high ionic conductivity ($0.85 \times 10^{-3} \text{ S cm}^{-1}$) and low activation energy. Fig. 9 shows the structure of Li_3ClO . This material has a structure of Li^+ ion at the octahedral corner, O_2 anion at the center, and Cl at the center of the Li_6O octahedron. Recently, in Braga et al., a material with a glass-liquid transition of $\text{Li}_{3-2x}\text{M}_x\text{AO}$ ($\text{M} = \text{Mg}^{2+}$, Ca^{2+} , Ba^{2+} , A = halogen) was synthesized in order to increase the ionic conductivity and obtain a high ionic conductivity of $2.5 \times 10^{-2} \text{ S cm}^{-1}$.⁵⁷⁾ However, despite the good performance of this anti-perovskite, it is necessary to study the mechanism of ion conduction up to date. In addition, studies conducted so far have mainly focused on the stability of the phase. Further, studies on defects and movements of ions in Li_3OCl have been carried out through simulation.⁵⁶⁾ It is necessary to study the applicability of anti-perovskite materials as solid electrolytes using various types of experiments and by subjecting results to verification.

3. Anode Materials for Lithium Secondary Batteries

3.1. Introduction

A battery's energy density increases as the charging voltage of the cathode increases (e.g. $4.1 \text{ V} \rightarrow 4.3 \text{ V}$), as the result the performance of the anode improves. When amorphous carbon was replaced with graphite, the voltage flatness improved and the anode capacity increased from 260 mA h g^{-1} to 360 mA h g^{-1} . This value (360 mA h g^{-1}) is very close to the theoretical capacity of graphite (C_6Li) of 372 mA h g^{-1} . However, it is still necessary to improve the performance of this anode active material. In order to improve the performance of lithium ion secondary batteries, the following tasks must be accomplished:

Fig. 9. Unit cell of cubic anti-perovskite.⁵⁸⁾

1. The anode material must be replaced.
2. Electrode coating technology must be improved.
3. Electrode packing technology needs to be improved.
4. The Li ion absorption rate of the anode must be higher.

The ideas in three (2 ~ 4) of the four statements listed above have reached their limit through space optimization within cell design and packaging. Therefore, it is necessary to increase the capacity of the anodic active material by developing a new anode material and changing the structure itself.

The most noteworthy candidates for replacement of anode materials in the research so far are the following, including metal (M: Si, Sn, Sb, Al), M-O (M: Sn, Fe, Co, Ti, Ni), Li-M-O (M: Sn, Ti, V), $\text{Li}_x\text{M}_y\text{N}_z$ (M: Co).⁵⁹⁻⁶¹⁾ These materials have higher capacity than that of commercialized graphite. Compared to graphite, which is a commercial cathode material, high-capacity metal-based materials go through rapid volume expansion during the alloying/dealloying process with Li ions. For example, Si has a theoretical capacity ($4,010 \text{ mA h g}^{-1}$) that is 10 or more times higher than that of the theoretical capacity of graphite (372 mA h g^{-1}). However, the volume of Si increases by 300 ~ 400 % (theoretically), while the volume of graphite only increases by 12 %. The following phenomenon also occurs in MO type anodic active materials; it is a problem that must be solved before it will be possible to replace graphite. On the other hand, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (titanium based Li oxide) only goes through a slight change in crystal lattice of about 0.1 to 0.2 % during the reaction with Li ions; it also has excellent power and high cycle life, and is safe. However, the disadvantage of Si is that its capacity is low because its reaction potential is high (higher than that of commercialized graphite).

3.2. Li-Ti-O (LTO)

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), which has a cubic spinel structure, has been intensively studied by a number of researchers over the last 20 years. The performance of LTO has been improved through approaches such as changing the size (micro and nano) of the crystalline particles, changing the

shapes, creating different composites with other cathode materials, and carbon coating. LTO, which has a spinel structure (a type of crystal structure), has high electrochemical output due to its three-dimensional diffusion of Li ions. Jung *et al.* prepared carbon coated LTO anodes with high electrochemical performance. Because of its spherical shape and good electronic conductivity, a C coated LTO (5.2 wt %) exhibited outstanding cyclability up to 100 cycles under 1, 5, and 10 C-rates with voltage windows in the range of 1 - 3 V (Li vs. Li⁺), as shown in Fig. 10.⁶²⁾

The advantage of LTO is that it does not form an SEI (Solid-Electrolyte Interphase) because it reacts at a relatively high reaction potential (~1.5 V).⁶³⁾ LTO, because it is thermally stable during the charging/discharging process, is receiving a lot of attention from researchers as an anode material for high output medium- to large- sized batteries. It is thermally stable because there is no exothermic reaction while the SEI on the electrode surface is being decomposed. However, the low energy density that results from the high reaction voltage, and the high cost, make it difficult to commercialize this material.⁶⁴⁾

Fig. 10. (a) Rate capacity ability of 5.2 wt % C-coated Li₄Ti₅O₁₂ and (b) cycle performances of 5.2 wt % C-coated Li₄Ti₅O₁₂ from 1C rate (0.17 A g⁻¹) to 10C rate (1.7 A g⁻¹) compared with performance of carbon free Li₄Ti₅O₁₂ at 1C rate (0.15 A g⁻¹) between 1.0 and 3 V (Li vs. Li⁺).⁶²⁾

3.3. Li-Co-N

NTT and Panasonic discovered Li_{2.6}Co_{0.4}N is a nitride anode synthesized using a general ceramic method. A full cell test was carried out with various cathode materials having a high capacity of 900 mA h g⁻¹ as well as low reaction potentials ranging from 0.1 to 1.4 V.⁶⁵⁾ However, this material has limitations for use as a commercial cathode material due to its low life cycle.

3.4. Li-V-O

Vanadium-based Oxide (Li_{1.1}V_{0.9}O₂) is an anodic active material that has a theoretical volume energy density of ~1000 mA h cc⁻¹; this is because it reacts with Li ion at a low potential of 0.3 V. For this reason, it is expected to be applicable to batteries with high energy density. However, in order to commercialize this material, it will be necessary to develop a way to increase the low initial reversible capacity and prevent the volume from changing (~30 %) during electrochemical reactions.⁶⁶⁾

3.5. Li-Ti-Nb-O

LiTiNbO₅ (layered structure) was synthesized by Collin through the ion exchange method.⁶⁷⁾ An electrode containing 0.8 mol of Li was found to have a charge/discharge cut-off range of 1.67 (Li vs. Li⁺) and a capacitance value of ~115 mA h g⁻¹ in the first cycle. When the charge/discharge test was performed at a C-rate of 0.1, LiTiNbO₅ became a low cycle material due a capacity decrease to ~90 mA h g⁻¹ after 40 cycles.

3.6. Li-Ti-P-O

Cathode materials that are composed of LiTi₂P₃O₁₂, which has a framework structure of NASICON (sodium superionic conductor) type have recently been studied using various synthesis methods.⁶⁸⁾ As a result of electrochemical analysis, the main reduction and oxidation have been found to take place between 2.38 and 2.6 V, and the material has been found to have a reversible capacity of ~120 mA h g⁻¹ at 0.1 C. These traits are similar to those of TiP₂O₇, and further research is necessary in order to lower the reaction potential by alloying and compounding this material with other materials.

Part 2. Li-M-O Materials for Nuclear Fusion

1. Introduction

Nuclear fusion is a phenomenon in which two light nuclei gather to form a single heavy nucleus. In order for nuclear fusion to take place, it is necessary to have a very high temperature and a large amount of energy that can separate the electrons from the atom.⁶⁹⁾ Plasma is a hot ionized gas consisting of atoms with separate electrons and nuclei (ions); plasma is considered a fourth state of matter after solid, liquid, and gas. All plasmas are ionized, but that does not mean that all ionized gases are plasmas. In order to cre-

ate a plasma, it is necessary to ionize deuterium and tritium (These isotopes are capable of nuclear fusion).⁷⁰⁻⁷²⁾

The following conditions are required for nuclear fusion:

1. Plasma at 100 million degrees Celsius
2. A device that can safely operate the plasma at 100 million degrees Celsius
3. Seawater, which is rich in deuterium (1 L of seawater contains about 0.03 g of deuterium)

As mentioned above, nuclear fusion involves using a magnetic field to confine a high-temperature (about 100 million degrees Celsius) plasma in a device called a “tokamak” to generate stable helium molecules, neutrons, and thermal energy after collisions between deuterium and tritium at high energy.^{73,74)} This device is expected to be a next-generation energy source that can generate electric energy. As a representative sample, there is the International Thermonuclear Experimental Reactor (ITER), which obtains energy from the D-T (Deuterium-Tritium) fusion reaction.⁷⁵⁻⁷⁷⁾ Fig. 11 shows the inner and outer fuel cycle of a fusion reactor.

In this case, “D” represents deuterium, “T” represents tritium, and “n” represents neutrons. In Korea, KSTAR (Korea Superconducting Tokamak Advanced Research) is a nuclear fusion research institute that has developed its own tokamak.⁷⁸⁾ In addition, there are various nuclear fusion research institutes such as the Jet program of the European Union, JT-60U in Japan, EAST in China, W-7X in Germany, the US TFTR, the TOCE-SUPRA of France, and the SST-1 of India.

Fig. 11. Schematic diagram of fuel cycle system of nuclear fusion reactor.⁷⁹⁾

In a fusion reactor that uses a tokamak, there is a blanket that absorbs the generated neutrons. Inside the blanket, there is a tritium breeder, a ceramic material containing lithium, which produces tritium through a nuclear reaction of tritium breeders and neutrons.^{80,81)} This process is shown in the schematic diagram of the lithium transfer step of the solid breeder material, in Fig. 12.

Thus, the breeder of a nuclear fusion reactor is the key component in producing tritium; the role of lithium in the fusion reaction is to generate tritium via a nuclear reaction. Furthermore, the breeder must simultaneously convert nuclear energy to thermal energy while shielding the neutrons.⁸³⁾ The tritium breeder should have the following conditions.^{84,85)}

1. It must contain a lot of lithium.
2. It must have high thermal conductivity and a low thermal expansion coefficient.
3. It must be mechanically and chemically stable.
4. The emission rate of tritium must be high
5. The structure must be stable under irradiation

Materials those satisfy the conditions above include oxide ceramic materials such as Li_2O , Li_2TiO_3 , Li_2ZrO_3 , LiAlO_2 , and Li_4SiO_4 , which are lithium-based compounds capable of generating tritium.⁸⁶⁾

2. Characteristics of Nuclear Fusion Materials

Li_2O has a high lithium atom density, high thermal conductivity, low tritium solubility, and high tritium growth rate, but has disadvantages such as high water reactivity and high lithium vapor pressure.⁸⁷⁾ LiAlO_2 has a high melting point and low reactivity with water; it has a wide temperature range for use, and has excellent radiation properties, but has a poor tritium emission rate.⁸⁸⁾ Li_4SiO_4

Fig. 12. Schematic diagram of the lithium transfer step in the solid breeder material.⁸²⁾

has good tritium diffusivity and excellent chemical stability, but it is easily fragmented by radiation due to the anisotropy of its thermal expansion coefficient.⁸⁹⁾ Li_2ZrO_3 is chemically and mechanically stable and has a high tritium emission rate, but there is an issue of zirconium becoming excited when heat is radiated after irradiation.⁹⁰⁾ Among researchers, Li_2TiO_3 became a popular material as a breeder due to its excellent maneuverability of tritium, its chemical stability, and its low activation energy.^{91,92)} The physical properties of these lithium-based oxides are closely related to their physical properties such as their porosity, particle size, particle shape, and microstructure. Therefore, optimization of the manufacturing process of breeders plays an important role in controlling the physical properties. Since the characteristics of the initial powder in the preparation of an oxide sintered body have great influence on the physical properties of the sintered body, optimization of the initial powder plays a very important role in the manufacturing process.⁹³⁾ In addition, the breeder is present in the form of pebbles; these pebbles can easily relax the thermo-adaptive force morphologically, and reduce the possibility of cracking and swelling due to irradiation.^{94,95)} In terms of TBR (Tritium breeding ratio), pebbles should have spherical shapes of about 1 mm diameter or more, and should have enough strength to maintain a certain density. Fig. 13 shows TiO_2 Pebbles (Used to make Li_2TiO_3 Pebbles) before rolling process, after 6 h of rolling process, and after 20 h of rolling process. With the increased rolling time, the pebbles became spherical.

Since the porosity has an important influence on the heat conductivity of the pebbles, it is important for the breeder to have an appropriate porosity.^{97,98)} In order to synthesize various tritium breeders, a variety of methods are being used to produce powders.⁹⁹⁾ Generally, a high-temperature solid phase method and a high-energy ball mill method in which calcination and sintering proceed through a mixing process among ceramic manufacturing methods are used. Recently, liquid phase methods such as hydrothermal synthesis, the sol-gel process, the precipitation method, the hydrolysis method, the precipitation method, and the micro-emulsion method have also been used. When the liquid phase method is used, a fine powder with high purity can be obtained, and the composition and particle size of the product can be controlled. NFRI Korea ITER and the Material Development Department of KAERI are pursuing world trends by focusing the research direction of the nuclear fusion tritium breeder on the ITER DEMO. In Korea, research and development is mainly focused on Li_2TiO_3 through the ITER project at NFRI. However, KSTAR's research has been mainly focused on tritium breeders composed of lithium oxide, and there has not been much progress. In order to develop domestic technology such as KSTAR in the future, it will be necessary to conduct research on breeders through various synthesis methods and optimization. It will be possible for Korea to join the ranks of the advanced countries once Korea acquires essential nuclear fusion technology.

Fig. 13. (a) TiO_2 Pebbles (Used to make Li_2TiO_3 Pebbles) before rolling process, (b) after 6 h of rolling process, (c) after 20 hours of rolling process.⁹⁶⁾

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