

Design principles of the cathode materials for multivalent cation batteries

Takuya Mori

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Chapter 1: General introduction

1.1. Background

Since the industrial revolution, human life has relied on fossil fuels to produce chemical products, medicine, vehicle fuel, and electricity. The main problem of fossil fuel use as energy resources is the emission of carbon dioxide, the major cause of climate change, as a result of fossil fuel combustion. To meet the energy demand of modern human life, new clean energy and devices will be required in the coming centuries; for example, smart grid systems using renewable energies such as wind, solar, and wave power, electric vehicles, and plug-in hybrid automobiles. Rechargeable battery technology plays a central role in the application of such technologies. To date, several battery systems have been developed. Fig. 1-1 shows the history of the development of battery technology.¹ The lithium ion battery is the highest performance battery system among the commercialized batteries of today. However, the lithium ion battery does not have sufficient energy density to power the large scale devices mentioned above. Thus the development of a new battery system is necessary.

1.2. Beyond the lithium ion battery technology

Figure 1-2. shows the load maps of the battery reported from the New Energy Development Organization in Japan.² The circles in this figure show the expected energy density of their battery systems. The weights of the theoretical capacity are weights of positive and negative electrodes. The lithium ion battery is unable to break the capacity limits over 200 mAh g^{-1} ; therefore, another battery system is needed to achieve over 1000 Wh kg^{-1} . Three types of battery systems are proposed: metal-air

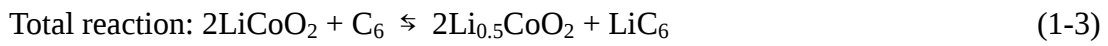
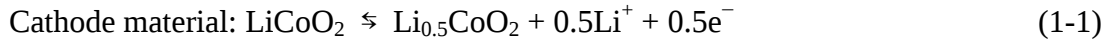
battery, lithium–sulfur battery, and metal anode battery. We focus on the potential of the metal anode battery system as a next generation battery system. These types of battery use the metal electrodes as negative electrodes. A list of the properties of the metal electrodes is shown in Table 1-1. Lithium metal has very attractive features in terms of the capacity, and electrodes potential; however, the terrestrial abundance and the melting points are low. These properties are related to the cost and safety. Moreover, the deposited lithium metal usually has a dendritic morphology, which causes penetration of the cell components and can lead to the battery cell circuit being short circuited.³ Therefore, it is difficult to use lithium metal for the battery anode, and other metals are needed for use as the anode material. Bivalent and trivalent metals such as Ca, Mg, and Al are appropriate anode materials for the battery.^{4, 5} (Table 1-1) as they have high volumetric capacities, relatively low redox potential, low cost, and suitable safety characteristics. These types of the anode use multivalent cations as electron carriers. The multivalent ions simultaneously transfer multiple electrons per ion; therefore, the charge carriers can also have high capacity.

1.3. Multivalent cation battery system

1.3.1. The principles of the current lithium ion battery

In this section, I explain the principles of the current lithium ion battery systems to consider the problems associated with using multivalent cations as the charge carrier. Figure 1-3 shows the schematic illustration of the commercialized lithium ion battery. The core parts of the lithium ion battery are the anode materials, cathode materials, and electrolytes. When this battery is charged, the lithium ions are moved from the cathode materials (for example, LiCoO_2 ⁶) to the anode materials (for example, graphite⁷),

passing through the electrolyte (for example, non-aqueous solvent include lithium salt). The discharge is the backward reaction. The charge/discharge reactions are shown in the equations below:⁸



This reaction mechanism requires the diffusion of the lithium ion into the solid-state phase, which is different from conventional electrochemistry. The elementary steps of the reaction during (dis)charging are divided into the four steps given below and in Fig. 1-4:

- 1) Ionic conduction in the electrolyte
- 2) Charge transfer at the interface between electrode/electrolyte
- 3) Diffusion into the bulk structure
- 4) Compensation of the electron neutrality in the host structure

These steps are related to several measurable values as follows: Step 1) is related to the ionic conductivity of the electrolytes; Step 2) is related to the charge transfer resistances; Step 3) is related to the diffusivity in the solid-state phase; and Step 4) is related to the valence state of the transition metal cation or other anion. In the battery cathode materials, if the guest cations are inserted in the host structures, atoms composing the host structures compensate the charge neutrality in the structures. For

example, when one lithium ion is extracted from LiCoO_2 , the valence states of the Co cations are increased from 3^+ to 4^+ . This valence change causes a change of the ionic radius of the transition metal cations, and also results in larger scale structural change and distortions.

A detailed knowledge of all elementary steps is required to lead the accelerative developments and to improve the actual battery performance. In the case of the lithium ion battery technology, I have also studied various measurement techniques and materials.⁹⁻¹⁶

The feasibility of using multivalent cations as carriers is considered in the following sections. In particular, the features of Mg and Al ions are discussed because these metals have suitable characteristics for use as the anode materials in battery applications.

1.3.2. Problems associated with using multivalent cations as charge carriers in the battery system, compared with the lithium ion case

Multivalent cations such as Mg^{2+} and Al^{3+} have a higher charge density than lithium. This property affects several of the elementary steps of the reactions mentioned above.

In the electrolytes, multivalent cations are solvated by many more solvents or anions than the lithium ion. These factors are related to Step 2). This effect is related to the rate capability of the electrode materials for the battery. Therefore, the development of a suitable electrolyte for the positive and negative electrodes is one of the most important points to address to produce a better battery using multivalent cations as the charge carriers.

The choice of electrode materials is mainly related to the Elementary Steps 3) and 4). Using the multivalent cations as the carrier affects the electrostatic interactions between

guest multivalent cations and the host ion. The electrostatic potential between Ion A and Ion B (V_{AB}) is revealed by the following equation:

$$V_{AB} = \frac{(Z_A e)(Z_B e)}{4\pi\epsilon_0 r_{AB}}, \quad (1-4)$$

where Z_A , Z_B , ϵ_0 , and r_{AB} are charge numbers of Ion A, charge number of Ion B, permittivity of the vacuum, and bond distance between Ions A and B, respectively. Both Mg^{2+} and Al^{3+} have a smaller ionic radius than lithium. Thus the interaction between the cation and anion or, if we use the transition metal oxides, the interaction between carrier cation, such as Mg^{2+} and Al^{3+} , and oxide anion, are up to three times larger than Li. As a result, the diffusion of the multivalent cation into the bulk structure is relatively slow. This is likely to influence Step 3) of the four elementary steps given above. Of course, the electronic interactions also occur between two cations and their interactions cause different effects for the electrode materials (which represent the host).

We compare the differences between the several cations to insert/extract to/from the transition metal layered oxide M_xTMO_2 ($M = Li, Mg, \text{ and } Al, TM = Co, Mn, Ni, \text{ and } Fe$) materials. In the layered oxides, M is located in the octahedral sites of the host structures, which are coordinated by the six oxygen atoms. The key interaction between cation and anion is electrostatic attraction. Therefore, M in this location has the lowest potential wells but no potential barriers. When the carrier ions move within the host structures, they transfer to the next neighboring vacant site. During this movement, the carrier cation exceeds the activation barrier E_a . (Fig.1-5.)¹⁷ This activation barrier is related to the transportation process in the host structure. The diffusion coefficient of this process is revealed by the following equation:

$$D = a^2 v \exp\left(-\frac{E_a}{k_B T}\right), \quad (1-5)$$

where a , v , k_B , and T are hopping distances ($\text{\AA}$), vibration frequency (Hz), Boltzmann constant ($=1.38065 \times 10^{-23} \text{ J K}^{-1}$), and absolute temperature (K), respectively. Figure 1-6(a) shows the cation pathway in the layered oxide structures from one octahedral site to another. In this pathway, the location of the cation has two different possible sites at the intermediate conditions, which are located between three oxygen atoms and a tetrahedral site. The electrostatic repulsion and attraction between carrier cation M and the host structure are considered during diffusion into the host structure. Considering the anion effect, if the bond distance between guest cation and host anion decreases, the attraction between the guest cation and host anion would increase. This localized electrostatic interaction can be cancelled by the decreasing repulsion between other ions to maintain the balance of the electrostatic interaction between ions. This effect is expected to decrease the activation barriers; however, the diffusion of the multivalent cations is relatively slow. We therefore need to consider the interaction between the guest cation and the host cation.

The distances between the guest cation site and the host cation site in the transition metal oxides cannot be shorter than $2.8 \text{ \AA}$. If the guest cation is inserted into the tetrahedral site, the guest cation is located close to the host cation, at a distance of about $2 \text{ \AA}$ (Fig.1-6(b))¹⁷ As a result, the repulsion between these cations is strong, and the diffusion of the guest cation becomes difficult. This phenomenon causes the large activation barrier to move into the next neighboring vacant site. The migration energies of several cations (Li^+ , Mg^{2+} , Zn^{2+} , Ca^{2+} , and Al^{3+}) in the various oxide host materials

(spinel, Mn_2O_4 ; olivine, FePO_4 ; layered NiO_2 ; and orthorhombic $\delta\text{-V}_2\text{O}_5$) were calculated by Rong *et al.*¹⁸ They found that the Al^{3+} ion has the highest activation barrier of the four ions because its high electron density causes a strong interaction with the host structure. Thus selection of an appropriate intercalation host for the aluminum battery cathode materials seems to be difficult. In contrast, the results of Rong *et al.* for the divalent ion species indicate the threshold migration barriers in several host materials based on theoretical calculations. Therefore, the intercalation host materials are able to apply the electrode materials for the battery systems using divalent ions as charge carriers.

Step 3) is likely to be affected by the strong interactions between multivalent cations and host ions. However, Step 4) has not yet been mentioned. When the guest cations are intercalated into the host structure, the host transition metal cation compensates the charge to maintain the electrical neutrality of the inserted sites. In the case of multivalent cations, the two or three electron reactions need to occur during redox processes. If the multiple electron reaction occurs, the size of the transition metal cations is drastically changed and the host structure is expected to locally distort.

These issues for the electrode materials lead to low rate capabilities and low storage capacities. To achieve high energy density battery systems, it is necessary to apply cathode materials. The choice of cathode material is important when developing next-generation battery systems. This thesis focuses on the cathode materials. The next section discusses the reported cathode materials for the magnesium and aluminum battery systems.

1.3.3. Reported multivalent cation battery cathode materials

1.3.3.1. Magnesium battery cathode

Magnesium insertion cathode materials have been studied over the past few decades. Lists of the reported cathode materials for the magnesium battery are given in Table 1-2.^{19, 20} In the early days, insertion oxide cathode materials were the main focus of studies. Gregory *et al.* performed galvanostatic cycling of some oxides (e.g., RuO_2 , and Co_3O_4) in the electrolyte containing magnesium salt.²¹ Novak *et al.* suggested vanadium pentoxide (V_2O_5), and molybdenum trioxide (MoO_3) as insertion hosts for the multivalent cations.²²⁻²⁶ However, insertion ability of the magnesium ions is poor for these materials (Table 1-2.) because of the strong interaction between magnesium and the oxygen anions in the lattice structures, as mentioned above.

Next, the sulfide materials were considered as the cathode materials for the magnesium battery because they can be more fully polarized than the oxide anion. The layered structure sulfides, such as TiS_2 and MoS_2 , are well known insertion materials of the cations.^{27, 28} The application of the sulfides as cathode materials for the magnesium battery have also been reported.^{21, 26, 29-31} Among the sulfide cathode materials, chevrel structured cathode materials can be reversibly inserted with two magnesium ions. Use of chevrel structured sulfides (Mo_6S_8) has been reported as an prototype magnesium rechargeable battery systems.³² The crystal structure of the Mo_6S_8 chevrel phase is shown in Fig. 1-7. This structure has 12 insertion sites for the magnesium in the host structures, which are divided into two different sites (the inner site and the outer site; Fig. 1-7.)^{32, 33} Moreover, guest cations can easily move between these sites.³³ As a result, the chevrel phase has a stable structure for several guest cations, and the redistribution of electronic charge easily occurs on such elements during intercalation reactions.³² This

material has a relatively high rate capability, and good cycling ability among the reported cathode materials for the magnesium battery. However, the theoretical capacity and the potential of the cathode are relatively low (ca. 128.8 mAh g⁻¹, 1.1V vs. Mg²⁺/Mg). Thus, exploration of the high capacity and high potential cathode materials is necessary to achieve a high energy density battery system.

One of the candidate materials for the magnesium battery cathode is V₂O₅.^{21, 23, 29, 34} The theoretical capacity of this material is very high (ca, 589 mAh g⁻¹); it has a large space in its crystal structure. The capacity of polycrystalline V₂O₅ as an insertion host for the magnesium battery cathodes is about 150 mAh g⁻¹ (Mg_{0.5}V₂O₅) at 150°C. Unfortunately, this material shows poor reversibility.³⁴

Novak *et al.* found a reversible electrochemical cycling of the V₂O₅ in the electrolytes containing Mg²⁺.²⁶ In their experiments, the electrolyte contains water molecules. The obtained capacity is correlated with the water content in the electrolyte solution.²⁵ The water molecules are solvated for the Mg²⁺ in the electrolyte, and shield the charge of the Mg²⁺. This solvated magnesium is easy to insert into the V₂O₅ large layers and the V₂O₅ materials showed a capacity of near 200 mAh g⁻¹.³⁵ Recently, Imamura *et al.* prepared the composite of the V₂O₅ xero gel with carbon.³⁶ This material shows very large discharge capacities, and relatively good cycle stability. The structure of V₂O₅ xero gel is shown in Fig. 1-8.³⁷ The three-hold lamella structure was constructed from the a-b plane of the orthorhombic V₂O₅ sheets. This lamella packed structure includes water molecules. There are large spaces between layers, of around 11.5Å in distance, and two different insertion sites of the Mg²⁺ (Site-a and Site-b), because of the two step electrochemical reactions.³⁶⁻³⁸ Site-a is located near the center of the square planer oxygen atoms, and Site-b is near the apical oxygen atoms.³⁸

The V_2O_5 xero gel shows very high capacity as a cathode material for the magnesium battery.³⁸ However, the water in this material constitutes a severe problem for the application in the magnesium battery system since the magnesium metal anode is easily oxidized by water and passivated for the active species in the electrolyte.³⁹ Moreover, other large spacing materials have been studied, such as hollandite type MnO_2 .⁴⁰ Unfortunately, this material forms inactive MgO during discharge reaction.⁴¹

Another approach to explore the high capacity cathode materials is to use nano structured materials.⁴²⁻⁴⁶ The nano-sheet structures show the adsorption/desorption of the guest cation during discharging/charging. This mechanism does not require an intercalation site in the active materials, and does not suffer from the slow diffusivity of the magnesium cations. Liang *et al.* shows the 2.0 V, and *ca.* 150 mAh g^{-1} by using graphene-like MoS_2 for the cathode materials.⁴⁶ Compared with other high energy density battery systems, the capacity and voltage remains low.

In recent years, other oxide host materials have been considered as the cathode materials for magnesium ion batteries. Other possible intercalation host materials include spinel type oxides and polyanionic compounds.

The spinel oxide type materials have been used as an excellent cathode material for lithium ion batteries.^{47, 48} The crystal structure of the spinel oxide $LiMn_2O_4$ is shown in Fig.1-9. This structure has three dimensional zigzag diffusion pathways in its structure in the lithium ion battery case.⁴⁷ The DFT (Density Functional Theory) calculations suggest that this spinel oxide intercalation host is suitable for magnesium ion batteries in terms of the migration of the cations in the host structures.¹⁸ In addition, computed energy densities can achieve better values than the lithium ion battery.⁴⁴ The insertion reaction of the magnesium into the spinel host was first reported by Luis *et al.* who

performed the galvanostatic measurements for the mixed manganese-cobalt oxide spinel.¹⁹ This host material shows a relatively high potential (*ca.* 2.9 V vs. Li^+/Li) and good reversibility. However, the obtained capacity was only 30 mAh g^{-1} . Recently, the Mn_2O_4 spinel oxide host indicates a large capacity in aqueous solution (*ca.* 545.6 mAh g^{-1} in 0.5 mol dm^{-3} MgCl_2 in H_2O).^{49, 50} Moreover, a spinel oxide host using several transition metal cations inserted the magnesium ions in the molten salt type electrolyte, based on the salt of the bis(trifluoromethanesulfonyl) imide.⁵¹

The other potential oxide host is the polyanion compounds. These types of materials are also applied for the cathode materials of the lithium ion battery. Olivine-type LiFePO_4 is a commercialized cathode material for lithium ion batteries, and all lithium can be removed from the host structure because of the material's high structural stability.⁵² The structure of the olivine-type LiFePO_4 is shown in Fig.1-10. This material belongs to the *Pnma* space group and is composed of PO_4^{4-} tetrahedra, with Fe^{2+} occupying corner-shared octahedral positions, and the Li^+ located in chains of edge-sharing octahedral sites. This structural stability is expected to be maintained during magnesium insertion/extraction. Moreover, the polyanion units, such as PO_4 , cause the inductive effect for the transition metals and these types of the materials show relatively high potentials. The mechanisms of these inductive effects are shown in Fig.1-11,⁵³ and are caused by the characteristics of the bond between transition metal M and ligand X. When the ionic character increased between M-X bonds, the energy of the orbital of the transition metal decreased. Next, the open circuit potential of these materials was increased from the nominal transition metal oxide materials. The obtained potential values are tuned by the electronegativity of the polyanion species.⁵³ Thus the application of polyanionic compounds has some advantages for the cathode materials.

To date, several materials have been suggested for the magnesium battery. Makino *et al.* suggested $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ as an insertion host of the magnesium ions.⁵⁴ This material can insert 1.2 magnesium ions (*ca.* 160 mAh g⁻¹) in the 1 mol dm⁻³ Mg (ClO₄)₂ / propylene carbonate electrolytes. However, the extraction properties have not been reported and the redox potential of Ti is relatively low. For the application of the cathode materials, Nuli *et al.* reported the olivine-type MgMSiO_4 (M = Mn, Fe, and Co)⁵⁵⁻⁶² and found reversible charge–discharge behavior. The obtained average voltage was near 1.8 V, which is different from the theoretical calculation performed by Ling *et al.*⁶³ Thus the potential of the olivine-type MgMSiO_4 (M = Mn, Fe, and Co) as a cathode material for the magnesium battery has not yet been clarified. Finally, Orikasa *et al.* reported the high performance of a cathode material of MgFeSiO_4 prepared by ion exchange methods.⁶⁴ This material shows the high capacity, and good cycle stability. Therefore, the polyanionic compounds have been found to be feasible for the application as the magnesium battery cathode.

1.3.3.2. Aluminum battery cathode

As mentioned above, the aluminum cations are strongly polarized, thus the insertion reaction is difficult to use as the electrode reaction. Several researchers have tried to apply the intercalation host for the aluminum battery electrodes. For example, V_2O_5 ^{65, 66}, VO_2 (B)⁶⁷, and fluorinated graphite⁶⁸ have been considered as insertion hosts of the aluminum ions. However, these cathode materials show a relatively low redox potential, which does not correspond with the insertion reaction of the lithium. Furthermore, evidence of the successful insertion of the aluminum ions has not been given. The chevrel structure has been reported as the only possible insertion host for the aluminum

ions.⁶⁹ However, this material has a relatively low redox potential and capacity. Hence, developing the cathode materials using the intercalation reaction is difficult because of the high charge density of the aluminum ions.

A possible approach has been suggested that involves the use of intercalation reactions for the aluminum battery systems. A possible solution is to use aluminate anion (e.g., AlCl_4^-) as a charge carrier for the battery. Cathodes composed of graphite⁷⁰,⁷¹, and polymer active materials⁷²⁻⁷⁷, have been developed. The large anion species have a small charge density, and weak interactions between the guest ion and the host structure. This concept leads to fast charge–discharge properties; the required time for a full charge or discharge is about 43s.⁷¹ However, the theoretical capacity of these materials remains low due to the large molecule size of the anion.

Studies have shown that the intercalation host is difficult to use as the aluminum battery cathode. Recently, other types of reactions have been described as electrode reactions for the battery cathode for lithium ion battery technology. This reaction is called a conversion reaction. Fig. 1-12 shows the schematic diagram of the reaction mechanisms of the conversion reaction compared with the intercalation reaction.¹ The conversion reaction mainly occurs at the surface of the particles, and therefore does not need insertion sites in the electrode materials. When the MX (M = transition metal, X = anion, such as oxides, sulfides, fluoride, chloride) reacted with the guest cation during discharging, nano-sized metal particles and amorphous compounds of the guest cation with anion X were produced.^{78, 79} After charging, the nano-sized MX was generated. In this mechanism, the theoretical capacity is high because the weights of the material are light and multi-electron reactions can be utilized.⁸⁰ The nano-sized materials created using the conversion reaction show a relatively high reversibility for lithium ion battery

electrode materials.⁷⁸⁻⁸¹ Therefore, these conversion reactions are expected to show high performances as cathode materials for the aluminum secondary battery.

The applications of the conversion reactions for the aluminum battery cathode have been reported in early studies; for example, chlorides (FeCl₃) and sulfides (FeS₂, Ni₂S₃) were suggested.⁸²⁻⁸⁴ Iron-based pyrite (FeS₂) is one of the potential cathode materials, as it not only exhibits a high theoretical capacity (894 mAh g⁻¹, 4470 mAh cm⁻³) but is also naturally abundant. Moreover, the energy density of the FeS₂ are 462.7 Wh kg⁻¹, and 1939.0 Wh L⁻¹ from the thermodynamic calculations.⁸⁵ The crystal structure of the FeS₂ is shown in Fig. 1-13. This material has dumbbell-shaped S₂²⁻ in its crystal structures. In previous studies, FeS₂ has been suggested as a cathode material for aluminum rechargeable batteries.⁸⁶ Koura *et al.* first demonstrated the feasibility of FeS₂ as a cathode material for aluminum rechargeable battery systems operating at elevated temperatures around 240°C and also investigated the charge–discharge reaction mechanism.⁸⁷ The following reactions were reported at 240°C:



For the practical application of aluminum rechargeable batteries, the charge–discharge reaction should be operated at ambient temperatures. While the use of FeS₂ to aluminum rechargeable battery cathodes at near ambient temperatures was also reported by Koura *et al.*⁸⁸, the underlying mechanisms are not yet well understood.

1.4. Objectives

The previous sections have shown that several cathode materials for the multivalent

cation batteries, such as magnesium and aluminum ions using as carrier of the electron, have been reported for some decades. However, systematic knowledge of these materials remains limited. This study investigates the reaction mechanisms of several cathode materials as model electrodes to reveal the systematic design principles for the cathode of a multivalent cation battery. Analytical techniques and considerable knowledge of the insertion type and conversion type cathode materials have been developed for the lithium ion battery. This thesis reflects on the application of these technologies to the multivalent cation battery, compared with the case of the lithium ion battery. The previously accumulated knowledge provides the development rules for use of the cathode materials in the multivalent cation battery. Moreover, this study aims to develop new types of cathode materials.

1.5. Thesis Outline

This thesis consists of two parts, and seven chapters, presenting the design principles of the cathode materials for multivalent cation batteries. In particular, this thesis focuses on the battery system using aluminum and magnesium ions as carriers of the electrons.

In chapter 1, I described the problems for multivalent cation battery systems, and the aim of this study was revealed. The cathode materials were selected as a target for this study because cathode materials inhibit the increase of the energy density of these battery systems above their potential capacities. These limitations are expected to derive from the diffusivity in the solid-state and difficulty of the charge compensation mechanisms. Many cathode materials have been reported over the past decades; however, the design principles for the cathode materials have not yet been determined. In this thesis, the design principles of the multivalent cation batteries are shown based

on the knowledge of the reaction mechanisms of the several model electrodes which were selected. I explored the sulfide and oxide compounds and investigate the crystal and electronic structures.

In Part 1 of this thesis, I focus on the sulfide cathode materials for the multivalent cation battery system.

In chapter 2, I focus on FeS_2 as a model electrode for the aluminum rechargeable battery. Nano FeS_2 particles were prepared by ball milling to improve the material utilization of the FeS_2 cathode material for an aluminum battery at ambient temperature. The reaction mechanism, including the crystal structure and the electronic structure changes, were investigated by X-ray diffraction and X-ray absorption spectroscopy (XAS).

In chapter 3, I investigate the electronic and local structural change of the Mo_6S_8 chevrel phase during discharging by Mo K -edge, Mo L_{III} -edge, and S K -edge X-ray absorption fine structure (XAFS) measurements, and consider the insertion mechanisms of the magnesium ions into the Mo_6S_8 chevrel phase. The charge compensation mechanisms were investigated using the X-ray absorption near edge structure (XANES) and local structure of the absorbing atoms were also investigated from the extended X-ray absorption fine structure (EXAFS).

In Part 2 of this thesis, we focus on the oxide cathode materials for the multivalent cation battery system.

In chapter 4, I investigate the structural change of the MnO_2 nano sheet reacted with magnesium ions by XAS. The nano sheet structure achieved very short diffusion length and able to analysed the difference of the effect of the structural change between magnesium ion and lithium ion as charge carriers. Analysis of the EXAFS spectra is

used to investigate the local structural change and their bond length and distortions. Moreover, local structural change after absorption of the magnesium ions was compared with that of the lithium, and the effect of the bivalent ions for the local structural distortions is discussed.

In chapter 5, I investigate the correlation between performance and anti-site defects in the crystal structure of MgMnSiO_4 . Crystal structure of MgMnSiO_4 shows an olivine type structure. The olivine type structure, LiFePO_4 , in the Lithium ion battery has a one-dimensional (1D) path,^{89, 90} and the rate performance in LiFePO_4 is significantly affected by anti-site mixing, which occurs between lithium and iron.^{91, 92} For intercalation materials with 1D frameworks, a smooth path through which ions transit would be favorable. We discuss the correlations between electrochemical performances and anti-site mixing ratio of MgMnSiO_4 .

In chapter 6, I discuss the electrochemical performances of MgFePO_4F as a feasible cathode material, which has three dimensional diffusion pathways in the crystal structure. We demonstrate the charge–discharge measurements in the Mg-ion cells, and investigate the potential performances for the magnesium ion battery cathode.

In chapter 7, I investigate the feasibility of using electrochemically delithiated $\text{V}_2(\text{PO}_4)_3$ as a promising magnesium ion (de)-intercalation host and provide promising high voltage cathode host material contenders for magnesium batteries. This material shows reversible magnesium ions (de)-intercalation into (from) the host frameworks, and a high potential. We develop the high potential cathode materials for the magnesium ion battery.

In chapter 8, the general conclusions of the research in which we consider the knowledge gained from the present studies and present the future prospects for the multivalent cation battery system.

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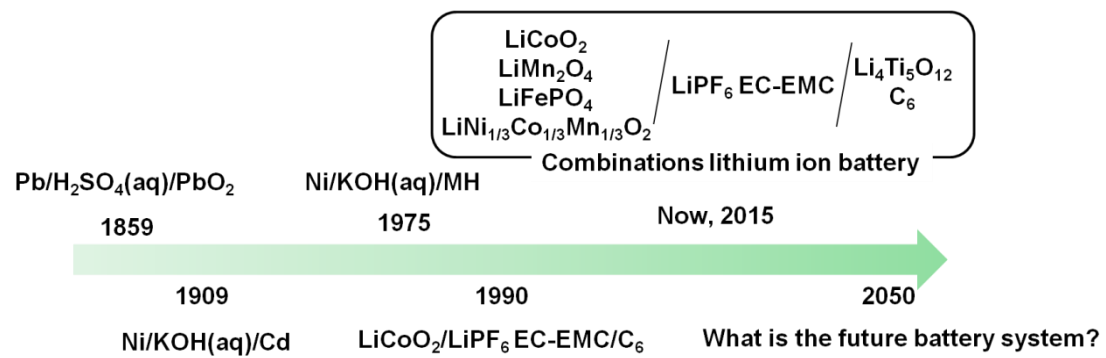


Fig.1-1. History and projections of batteries.

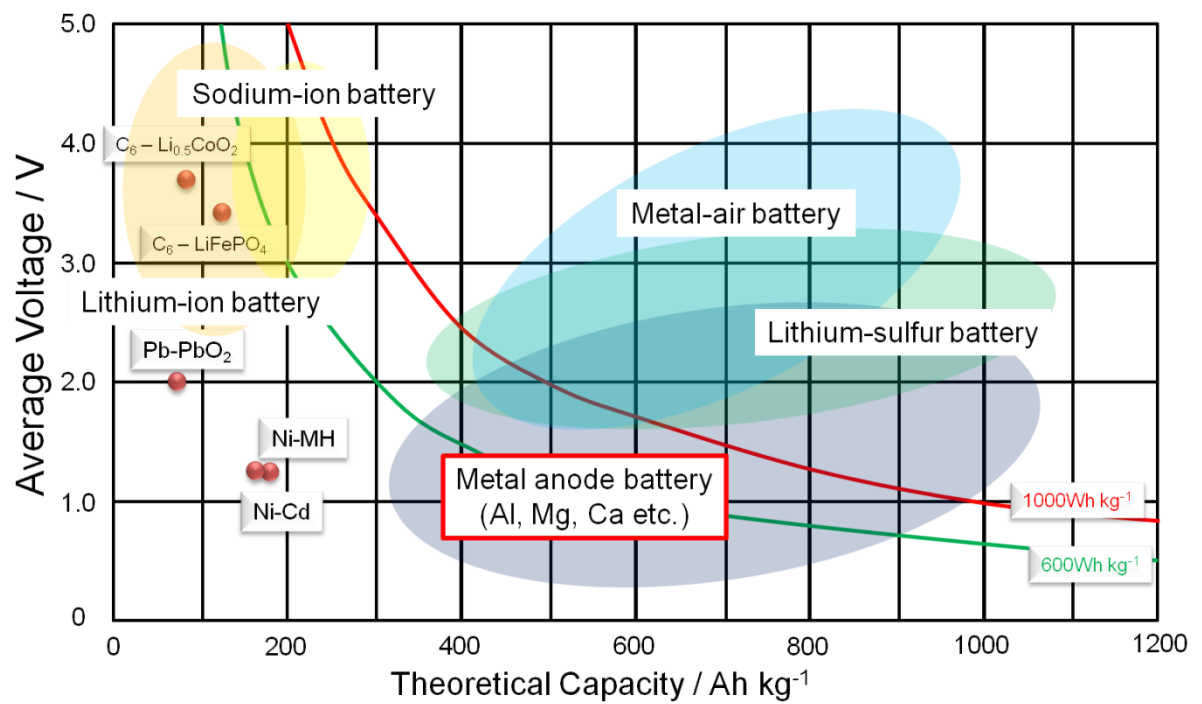


Fig. 1-2. Load maps of the next generation battery systems proposed by the New Energy Development Organization in Japan.²

Table 1-1. Characteristics of the various metal and graphite anode materials.

Electrodes	Atomic weight	Charge	Capacity [mA h g ⁻¹ , mA h cm ⁻³]	Electrodes potential [V vs. SHE]	Terrestrial abundance	Melting points(°C)
Li	6.94	1	3862, 2062	-3.05	0.006	180.5
LiC ₆			372, 855	-2.9		
K	39.1	1	685, 587	-2.925	2.40	63.7
Na	22.99	1	1166, 1132	-2.71	2.64	97.7
Ca	40.08	2	1337, 2073	-2.866	3.39	842.0
Mg	24.31	2	2205, 3837	-2.38	1.94	650.0
Al	26.98	3	2980, 8043	-1.662	7.56	660.3

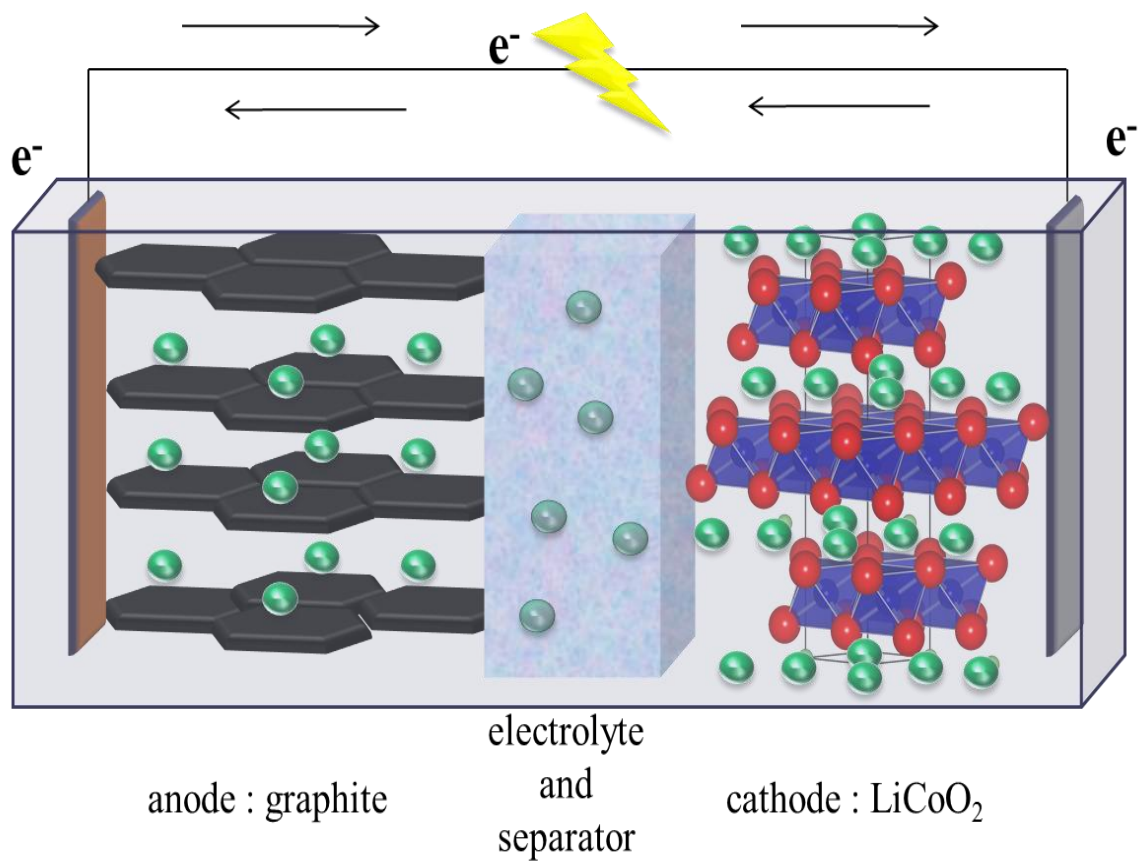


Fig. 1-3. Schematic diagram of the lithium ion battery.

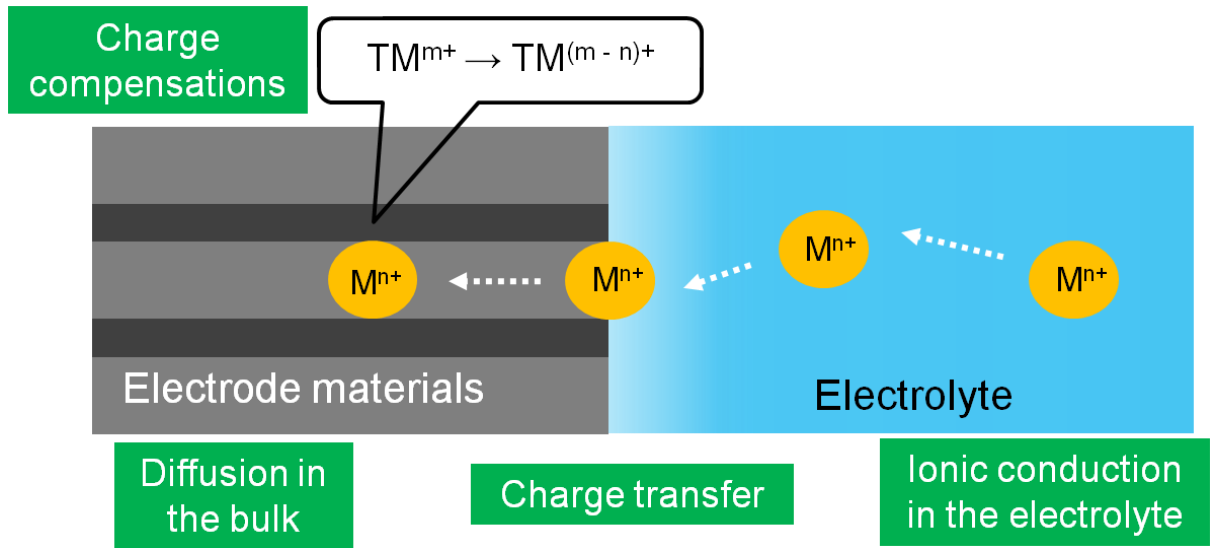


Fig. 1-4. Elementary steps for the electrode reactions in the battery.

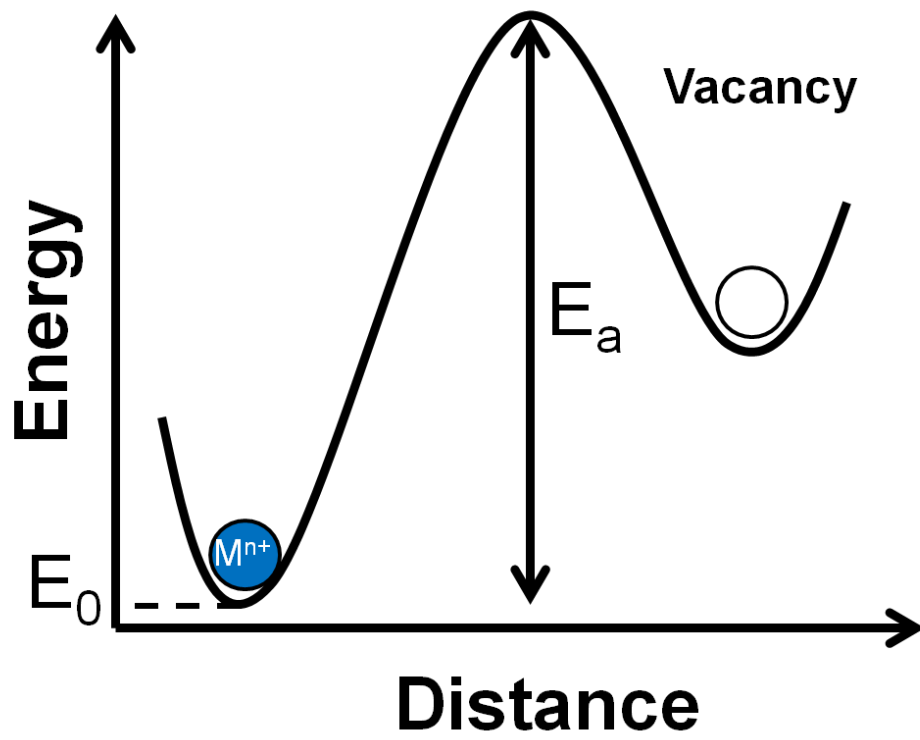


Fig. 1-5. Energy diagrams of the 'hopping process' between the site (energy level of zero, E_0) to the next neighbor vacancy. The activation energy of the hopping is E_a .¹⁷

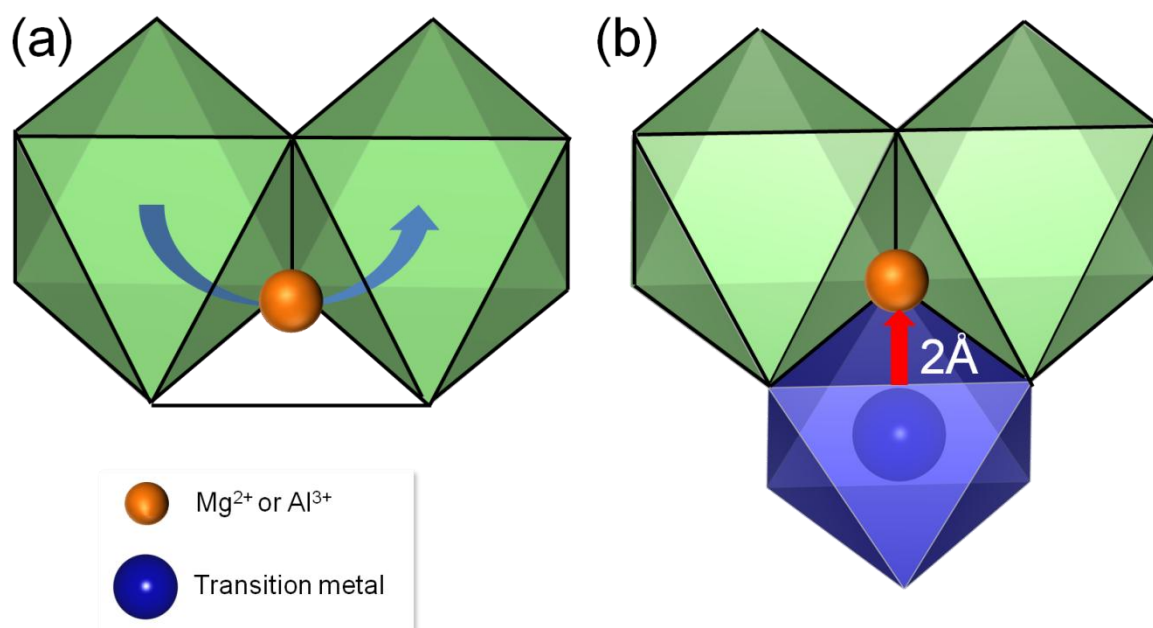


Fig. 1-6. The cation ‘hopping’ in the crystal structure of M_xTMO_2 (M = mobile ions ex. Mg^{2+} and Al^{3+} , TM = transition metals): (a) the cation pathway from one octahedral site to another, and (b) the cation–cation interactions; a short distance of $2\text{ \AA}$ exists between the M (inserted) cation in the transport site and an adjacent TM atom.¹⁷

Table 1-2. List of the cathode materials for the magnesium battery.

Material	Molecular weight	$x_{\max}$ in Mg ₂ MX(M=transition metal, X = anion)		obtained potential (V vs. Mg ²⁺ / Mg)	Ref
		electrochemical insertion x_m	obtained capacity(mAh g ⁻¹)		
RuO ₂	133.07	0.66	265	2.55	21
Co ₃ O ₄	240.79	0.8	222	2.28	21
MgCo ₂ O ₄	206.17	1.53	200	2.9	51
WO ₃	231.85	0.5	116	2.16	21
α -MnO ₂	86.94	0.47	280	2	40
Mn ₂ O ₃	157.88	0.66	224	2.4	21
Mn ₃ O ₄	228.82	0.66	154	2.4	21
Mn _{2.15} Co _{0.37} O ₄	203.93	0.23	60	-	19
MgMn ₂ O ₄	198.19	1	275	2.3	51
MgFe ₂ O ₄	200.01	only CV	-	2.2	51
MgCr ₂ O ₄	192.31	only CV	-	3.4	51
PbO ₂	239.19	0.25	56	3.1	21
Pb ₃ O ₄	685.57	0.25	20	3.1	21
U ₃ O ₈	842.09	0.78	49.6	1.8	20
MoO ₃	143.94	0.5	143	2.28	21
V ₂ O ₅	181.88	0.5	140	3.2	34
V ₂ O ₅ xerogel	181.88	1	300	2.5	36
MgMnSiO ₄	171.34	0.8	253.8	1.8	59
MgFeSiO ₄	172.25	1	300	2.4	64
olivine-MgFeSiO ₄	172.25	0.4	125.1	1.8	57
MgCoSiO ₄	175.33	0.98	299.59	1.8	62
Mo ₆ S ₈	112.01	1.22	75	1~1.3	32
TiS ₂	112.01	0.15	157	1.63	21
ZrS ₂	155.34	0.66	228	2.6	21
VS ₂	115.06	0.34	154	1.71	21
Graphen-like MoS ₂	160.06	0.5	170	1.8	46

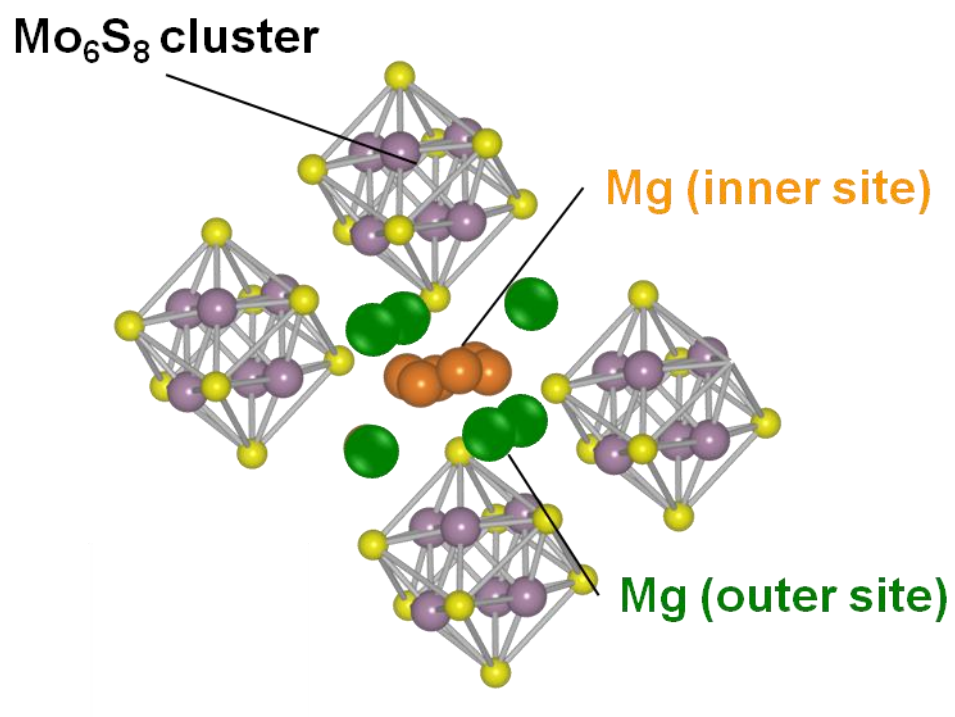


Fig. 1-7. Crystal structure of the chevrel $\text{Mg}_2\text{Mo}_6\text{S}_8$ phase. Green, orange, purple, and yellow spheres represent Mg (outer site), Mg (inner site), Mo, and S atoms, respectively.

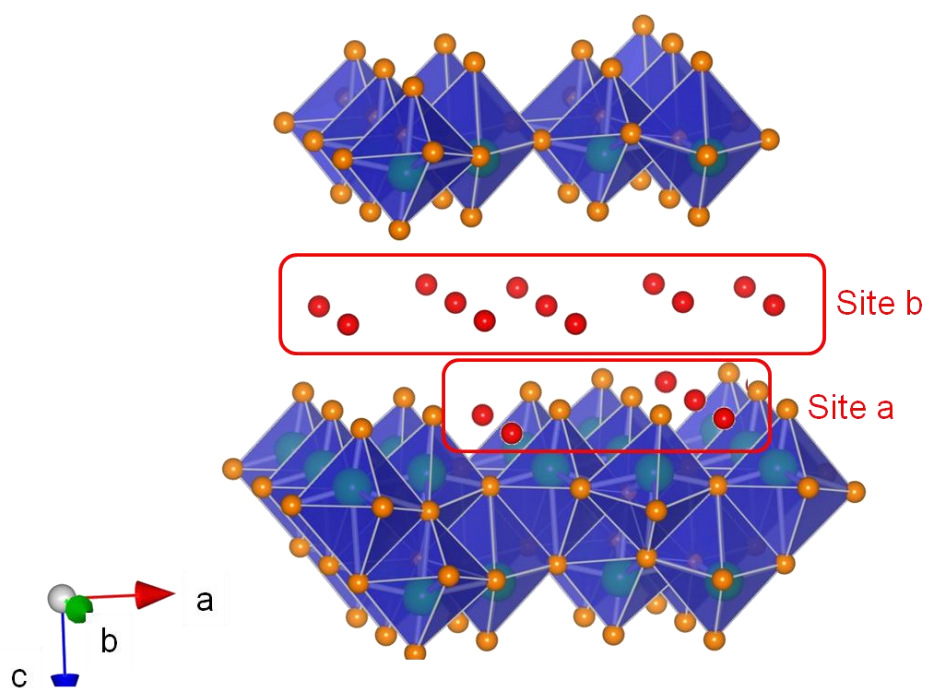


Fig. 1-8. Crystal structure of the V₂O₅ aero-gel. Green, orange, and yellow spheres represent V, O(1), and O(2) atoms, respectively.³⁸

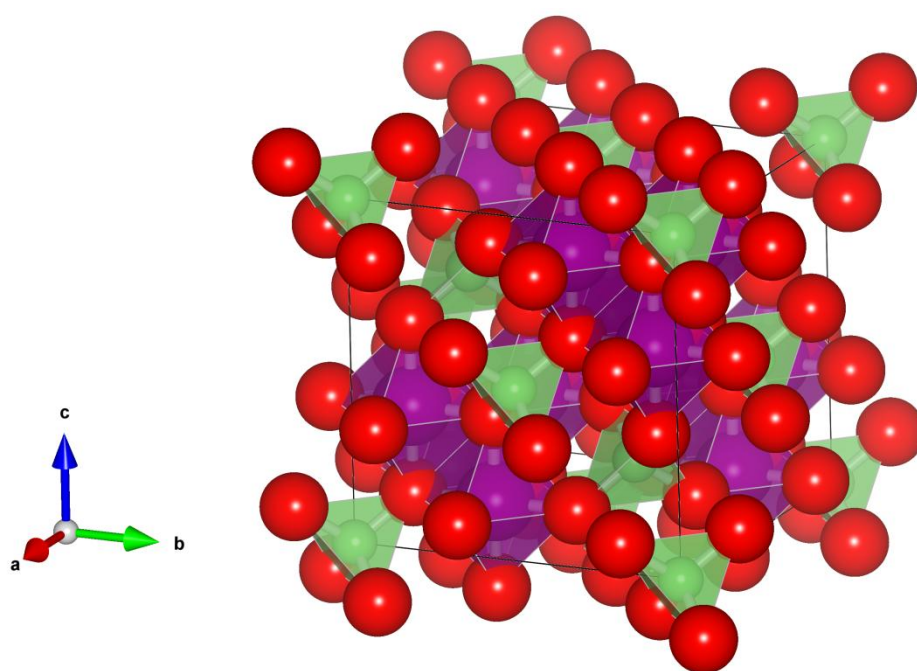


Fig. 1-9. Crystal structure of the Spinel-type LiMn_2O_4 . Green, purple, and red spheres represent Li, Mn, and O, respectively.

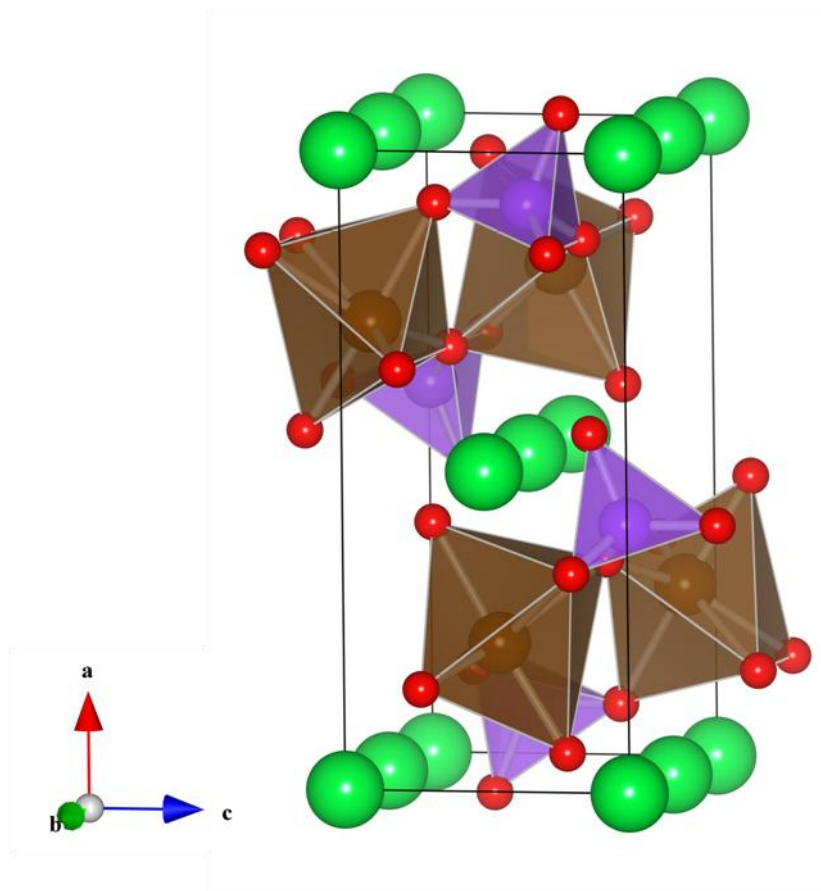


Fig. 1-10. Crystal structure of the olivine-type LiFePO_4 . Green, purple, brown, and red spheres represent Li, P, Fe, and O atoms, respectively.

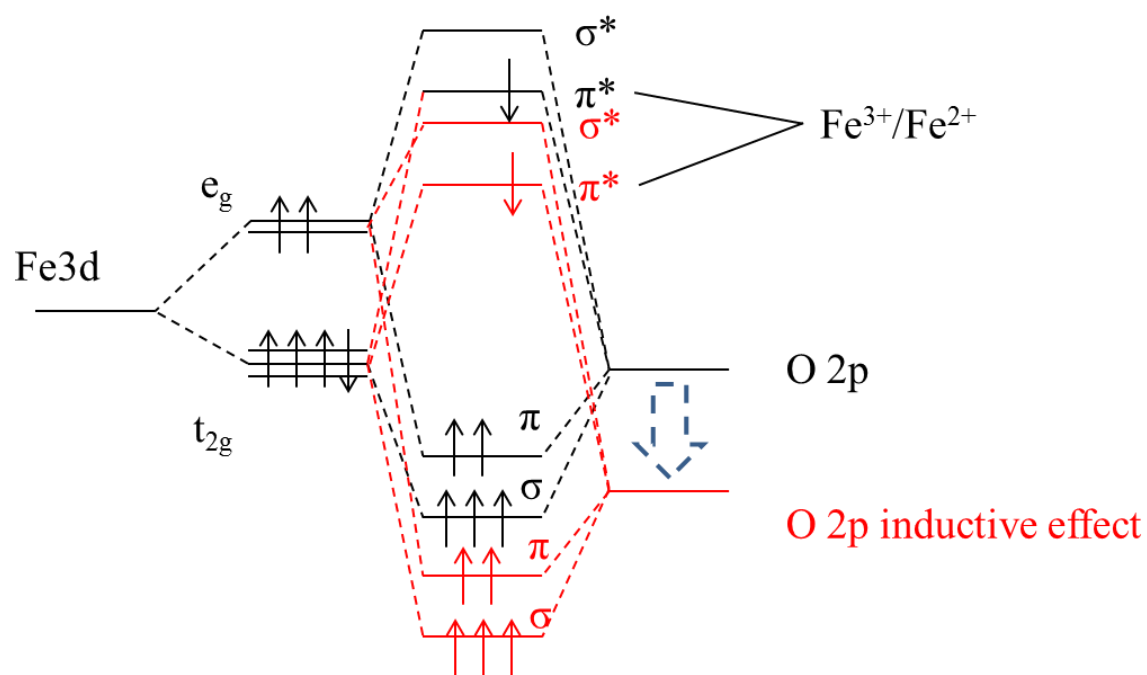


Fig. 1-11. Schematic diagram of the inductive effects for the iron based oxide compound.⁵³

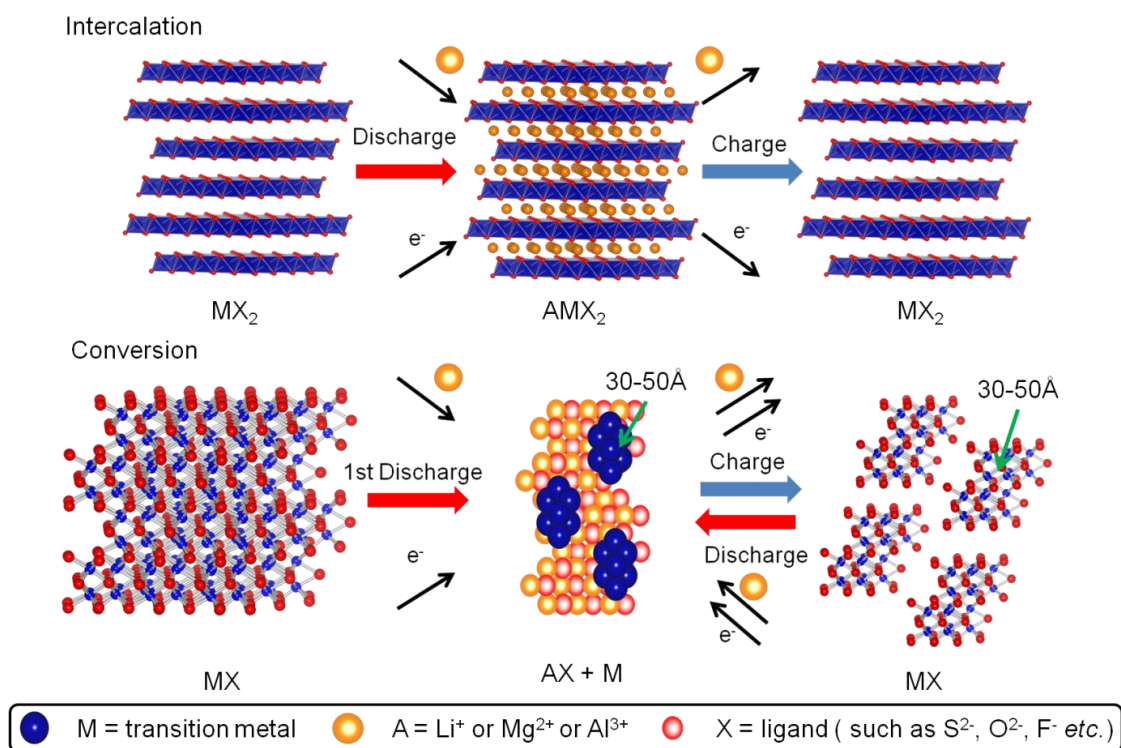


Fig. 1-12. Schematic diagram of the intercalation reaction and conversion reaction.¹

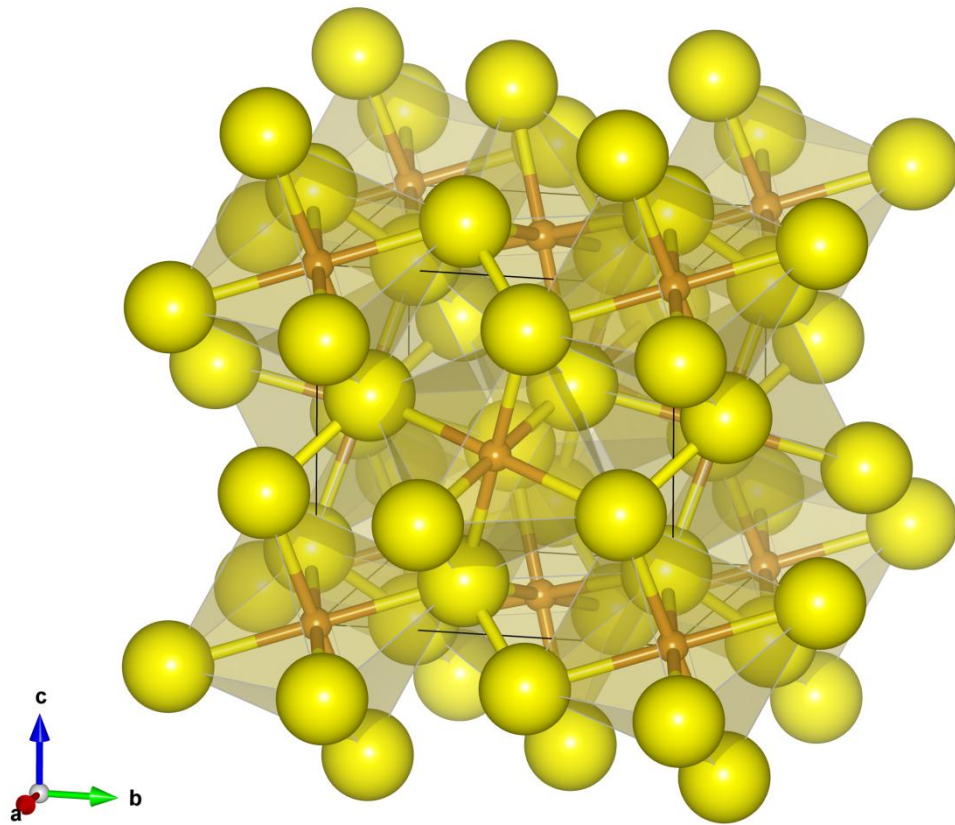


Fig. 1-13. Crystal structure of the pyrite FeS_2 . Yellow and brown spheres represent S and Fe atoms, respectively.

Part 1: Sulfide cathode materials for the multivalent cation batteries

Chapter 2: Discharge/charge reaction mechanisms of FeS₂ cathode material for aluminum rechargeable batteries at 55°C.

2.1. Introduction

Aluminum rechargeable batteries are considered viable alternatives for large-scale energy storage devices, because aluminum metal anodes have a high theoretical capacity (2980 mAh g⁻¹, 8063 mAh cm⁻³), abundance, and are safe ¹. The demonstration of electrolytes that can effectively dissolve/deposit aluminum (such as AlCl₃ mixed with organic chloride salt based ionic liquids, that is, chloroaluminate ionic liquids) ^{2,3} has led to a surge in interest in the search for electrode materials that can reversibly use aluminum ions when coupled with such electrolytes.

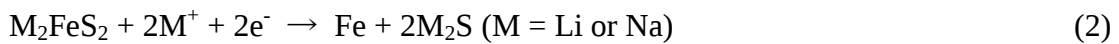
For the cathode materials of aluminum batteries, V₂O₅ ^{4,5}, VO₂ ⁶, and fluorinated graphite ⁷ have been reported as an insertion host for aluminum ions. However, these cathode materials show a relatively low redox voltage, and evidence of the insertion of the aluminum ions has not been obtained. Owing to the high charge density of trivalent aluminum ions, it appears difficult to develop cathode materials using the intercalation reaction.

Therefore, we have focused on the conversion electrodes^{8,9}, such as transition metal sulfides, oxides, and fluorides. Aluminum oxides and fluorides seem to show a lack of reversibility of the conversion reaction owing to the strong ionic bond between aluminum and O²⁻/F⁻. However, aluminum sulfides are expected to be excellent candidates for cathode materials for the conversion reaction in aluminum batteries

because of the relatively weak ionic bond between aluminum and S^{2-} . Among these compounds, iron-based pyrite (FeS_2) is an interesting material, because it exhibits a high theoretical capacity (894 mAh g^{-1} , 4470 mAh cm^{-3}) and is naturally abundant.

The application of FeS_2 as a cathode material for aluminum rechargeable batteries has recently been reported ¹⁰. Koura *et al.* were the first to demonstrate the feasibility of using FeS_2 as a cathode material for aluminum rechargeable battery systems operating at elevated temperatures of approximately 240°C and also investigated the charge-discharge reaction mechanism ¹¹. For the practical application of aluminum rechargeable batteries, the charge-discharge reaction should be observed at relatively low temperatures. While the use of FeS_2 as aluminum rechargeable battery cathodes at 25°C has also been reported by Koura *et al.* ¹², their mechanisms are still not well understood. It is important to understand the reaction mechanisms for the aluminum rechargeable battery cathode because such knowledge is useful for the design principles of the high capacity cathode materials.

FeS_2 can be used as a cathode material for the lithium and sodium ion battery cathodes^{13, 14}. In these cases, under ambient temperature conditions, the first discharge reactions have been proposed as the following equations^{13, 15-17},



In the case of the lithium ion battery, Li_2FeS_2 has a layered structure assigned to the $P3m1$ space group ¹⁸. This phase transition from FeS_2 to Li_2FeS_2 is related to the rate of

lithium diffusion through the bulk (for example, there were two step reactions above 37°C, at C/20 rate)¹³. Li_2FeS_2 phase is transformed to the Fe and Li_2S phases after further lithiation. At the high rate or low-temperature conditions, FeS_2 is directly converted to Fe and Li_2S through a 4 electrons reaction^{13, 15}. Moreover, the charge compensation of FeS_2 during discharge is dominant at sulfur atoms^{16, 19}. Compared with lithium and sodium ions, it is difficult for trivalent aluminum ions to diffuse inside solid electrode materials, which seems to vary the reaction mechanism.

In this study, the capacity of FeS_2 for use as aluminum rechargeable battery cathodes at 55°C was drastically improved by controlling the particle size of FeS_2 . Moreover, the reaction mechanisms of the FeS_2 as an aluminum battery cathode are investigated. Nanoparticles were prepared by ball milling to improve the material usage of the FeS_2 cathode material for an aluminum battery. The reaction mechanism, including the crystal structure and the electronic structure changes, were investigated by X-ray diffraction and X-ray absorption spectroscopy (XAS). We report the reaction mechanism of FeS_2 aluminum battery cathodes operating at 55°C. This information is very important for the further development of aluminum battery cathode materials.

2.2. Experimental

FeS_2 powders (99.9%, Alfa Aesar) were put into a ball mill pot under an argon atmosphere, and the milling was carried out using a planetary ball milling machine (Pulverisette 5, Fritsch) at 500 rotations per minute for 12, 24, and 48 hours with a ball-to-powder weight ratio of 10:1. The prepared samples were characterized by X-ray diffraction (XRD) measurements conducted by Rint UltimaIII (Rigaku), scanning electron microscope (SEM; JEOL, JM-890) observations, and energy dispersive X-ray

spectrometry (EDX; EDAX, Genesis APEX2).

Galvanostatic charge and discharge measurements were conducted with a two-electrode cell. The current density was 8.94 mA g^{-1} (C/50), and the measuring temperature was 55°C . The working electrode was comprised of a composite mixture of the active material, vapor-grown carbon fiber (VGCF), and PTFE binder (70:25:5 weight ratio) pressed on a Mo foil. An aluminum wire was used as the counter electrode. An ionic liquid consisting of AlCl_3 in 1-ethyl-3-methyl imidazolium chloride (EMIC) (2:1 molar ratio) was used as the electrolyte. This liquid was prepared and purified as follows. All subsequent protocols were conducted in an argon-filled glove box. EMIC was dissolved into acetonitrile (super dehydrated) and then precipitated from the solution by the addition of ethyl acetate (super dehydrated) and filtered in a vacuum²⁰. The obtained EMIC was mixed with AlCl_3 at a molar ratio of 1:2. Aluminum foil was soaked in the prepared electrolyte for at least 24 hours to purify it. FeS_2 nanoparticles are easy to dissolve in this electrolyte. The electrolyte with FeS_2 already dissolved was used for galvanostatic measurements, and the concentration of FeS_2 in the electrolyte was 3.6 mol m^{-3} by inductively coupled plasma (ICP) measurements.

XRD and XAS measurements were carried out for each charged and discharged electrode sample. All the samples are washed with super-dehydrated ethanol and dried in vacuum conditions. XRD measurements were performed by Rint UltimaIII (Rigaku). The samples are sealed using Kapton film in an Ar-filled glovebox. S and Al *K*-edge XAS measurements were conducted at BL-10 of the Synchrotron Radiation Center (Ritsumeikan University). The partial fluorescence yield mode (PFY mode) was used for XAS measurements, and the incident X-ray beam was monochromated by a Ge 111 crystal at the S *K*-edge and by a KTP (KTiOPO_4) 111 crystal at the Al *K*-edge. In

addition, the absolute photon energies were calibrated under the assumptions that the strong resonance of K_2SO_4 ($\text{S } 1s \rightarrow t_2$) appears at 2487.1 eV at the S K -edge²¹, and peaks of the Al foil appears at 1559.0 eV at Al K -edge. All samples were sealed in an argon-filled transfer vessel and transferred to the chamber for S and Al K -edge XAS measurements²². Fe K -edge XAS measurements were carried out at the BL14B2 beam line of SPring-8 (JASRI) in transmission mode. The energy scale was calibrated by the Fe foil. The first inflexion point of the Fe foil was 7112 eV. All samples were sealed in a laminated aluminum pocket under argon atmosphere.

2.3. Results & Discussions

Preparation of the FeS_2 nanoparticles

Figure 2-1 shows the particle morphology of FeS_2 after high-energy ball milling. Ball milling of FeS_2 powders decreased their particle size. The crystallite size was calculated using the Bragg diffraction peaks from the XRD pattern based on the Scherrer equation. The obtained values of the crystallite sizes were 127 (pristine), 89 (12 hours milling), 41 (24 hours milling), and 72 nm (48 hours milling). The crystallite size is smallest after 24 hours of ball milling, and there are no impurity phases, as apparent from Fig. 2-2. Ball milling for 12 hours yields trace amounts of the FeS phase arising from thermal decomposition of FeS_2 ²³. This FeS phase clearly reacts again to form the FeS_2 phase upon ball milling for 24 hours. The crystallite sizes depend on the milling time. However, after 48 hours of milling, the crystallite sizes of FeS_2 are increased. After longer milling time, the surface of the particle is more activated and particles are recombined. The secondary particle size distributions of milling samples are provided in Fig. 2-3, which also show the smallest particle size of the 24 hour milled sample. The

chemical composition of ball-milled FeS₂ powders does not depend on ball-milling time from the results of the EDX measurements (Table 2-1).

The discharge profile is shown in Fig. 2-4. Figure 2-5 shows the effect of the crystallite size on the discharge capacity of FeS₂. A strong correlation exists between the attainable discharge capacity and the crystallite size of FeS₂. The nanoparticles prepared by mechanical milling for 24 hours exhibit a capacity of approximately 600 mAh g⁻¹. A milling time of 24 hours of the FeS₂ nanoparticles showed the best performance among the prepared samples. We then used these particles for the analysis of the discharge/charge mechanisms for FeS₂ as cathode material in an aluminum rechargeable battery.

Discharge/charge reaction mechanisms of FeS₂ in chloroaluminate ionic liquids

We conducted XRD and XAS measurements to elucidate the reaction mechanism of FeS₂ in an aluminum ion cell. Charge-discharge curves are shown in Fig. 2-6, in which measurement points for XRD and XAS are also indicated as A-I. Figure 2-7 shows the *ex situ* XRD patterns of the charging and discharging electrodes. After discharging, the initial FeS₂ phase was maintained, and a low-crystallinity FeS phase was also formed. When the discharge reaction:



is proceeded, the theoretical capacity is 447 mAh g⁻¹. The weight of FeS₂ in the electrode was 2.8 mg and that in the electrolyte was 1.6 mg. The total amount of FeS₂ in the electrochemical cell was 4.4 mg. Therefore, in our electrochemical cell, the total capacity is 2.0 mAh if the all FeS₂ in the electrode and electrolyte is contributed. The

observed capacity of the first discharge reaction was 1.7 mAh which corresponds to 85% of the theoretical capacity. Because there is the unreacted FeS₂ in the electrochemical cell even in the end of discharge, the diffraction peaks of FeS₂ are observed. The generated FeS phase converted to the initial FeS₂ phase during the charging process. Although we also performed TEM experiments, we were unable to confirm the obtained phases because the phases were affected by the electron beam.

The absorption edges of the S *K*-edge XANES spectra taken in the PFY mode for various charged/discharged samples are shown in Fig. 2-8. The spectra measured in the PFY mode indicate the bulk characteristics of the particles. There is a strong peak at 2472 eV. FeS₂ has dumbbell-shaped S₂²⁻ in its crystal structure²⁴, whose molecular orbital leads to a higher antibonding π^* state. The strong peak at 2472 eV shows a transition from the S 1s to the antibonding S 3p band²⁵. After discharging, the peak maximum is decreased, and the absorption edges are shifted to lower energies. These changes are reversible upon charging. During discharge, the sulfur is reduced and the S₂ dimer bond in the FeS₂ structure is broken. In this structure, the antibonding π^* state of the sulfur dimer has an energy corresponding to the Fermi level²⁵.

The absorption edges of the Fe *K*-edge XANES spectra were also analyzed to confirm the oxidation state of the iron atoms, as shown in Fig. 2-9. No peak shifts are observed at 7115 eV during discharging and charging. Therefore, the Fe 3d orbital hardly takes part in the redox reaction, which is in contrast with the results of the S *K*-edge XANES, while the Fe *K*-edge XANES spectra show an isosbestic point at ~7130 eV. The existence of the isosbestic point in the spectra indicates that two Fe compounds co-exist in the electrodes. In the conversion reaction, metallic iron is expected to be a product of the discharge reaction. If metallic iron are generated during discharging, the absorption

edges of the Fe *K*-edge XANES at 7110 eV is change to resemble those of iron foil. However, there is no tendency for the pre-edge peaks at 7110 eV during discharging/charging, which indicates no iron phases in our experiment.

We discuss the discharge/charge reaction mechanisms of the FeS₂ in chloroaluminate ionic liquids. From the results of Fe and S *K*-edge XANES, S *K*-edge XANES spectra show a decrease in the peak intensity and lower energy shift, and Fe *K*-edge XANES spectra show no energy shift. These results indicate that the sulfur atoms play a significant role in the redox reaction. This is the same redox mechanism of the monovalent ion systems (such as Li and Na ion batteries)^{16, 19}. From the results of the XRD, low crystalline FeS is confirmed after discharging. The appearance of two Fe species in the electrodes are also confirmed by the isosbestic points in Fe *K*-edge XANES spectra. Moreover, this low crystalline nature is also explained by the Fe *K*-edge EXAFS (Fig. 2-10). The first main peak at 2.0 Å corresponds to the contribution of the Fe-S shell, while the second peak appearing at 3.5 Å corresponds to the contribution of the Fe-Fe shell. The peak intensity decreases / increases upon discharging / charging, reversibly. The change of the peak intensity influences the coordination number or Debye–Waller factor (signature of distortion). This change indicates an increase in the Debye–Waller factor with discharging, since Fe atoms in FeS₂ and FeS show similar coordination states. Therefore, the changes observed in the FT from EXAFS oscillations show the disordering of the Fe-S mean bond length, indicating the formation of a low crystalline phase during discharging. Then, the reaction (3) is expected during discharging.

Therefore, the absorption edges of the S *K*-edge XANES peaks are fitted with the linear combination of the standard FeS₂, FeS, and Al₂S₃. Fitting results of the linear

combination for the S *K*-edge XANES spectra of the certain state D in Fig. 2-6 are shown in Fig. 2-11. The FeS and Al₂S₃ are confirmed by S *K*-edge XANES. It has been reported that the Al₂S₃ are easily dissolved into the chloroaluminate ionic liquids²⁶. The aluminum reacting with the FeS₂ phase is also checked by the difference of the quantities of the aluminum after discharging (E in Fig. 2-6.) and charging (I in Fig. 2-6.) from the results of the Al *K*-edge XANES (Fig. 2-12.). The aluminum content in FeS₂ is calculated from the electric charge. The main peaks contain the residual of the ionic liquids after washing. These peaks do not correspond to the Al₂S₃ peaks. We checked the aluminum content of these electrodes. The washing process is performed in the same conditions. The aluminum content is reflected in the jump of the Al *K*-edge XANES spectra. The spectrum of E shows higher contents of the aluminum compounds. The aluminum ions are related to the galvanostatic discharge reactions of the FeS₂ particles. The existence of the amorphous Al₂S₃ phase is indicated by the S *K*- and Al *K*-edge XANES. These obtained phases are reversed to the original FeS₂ phase from the results of the XRD and S and Fe *K*-edge XAS measurements.

Finally, we propose schematic reaction models in Fig. 2-13. The FeS₂ pyrite structure contains dumbbell-shaped disulfide ions, which tend to react with aluminum ions. This reaction dominantly occurs in the vicinity of the surface through the reduction of sulfur (that is, $S_2^{2-} \rightleftharpoons 2S^{2-}$). This redox mechanism is the same phenomenon as the case of the monovalent ion carrier^{16, 19}. As sulfur is reduced, the original FeS₂ phase transforms into FeS, in conjunction with the formation of amorphous Al₂S₃ phases. FeS and Al₂S₃ phases revert to FeS₂ after charging, which indicates that the reaction is reversible. At 55°C, the dissolving nature of the sulfide is the main problem to improve their performance as a cathode material for an aluminum rechargeable battery.

In the monovalent ion battery system, initially, the FeS_2 phase is transformed to M_2FeS_2 ($\text{M} = \text{Li}$ or Na) through reaction Equation (1). Although this layered phase can be obtained at low rate conditions in the lithium ion battery case, no layered phase is observed in the aluminum battery case. Transformations for the layered phase need diffusion of the guest ion into the bulk FeS_2 ¹³. The aluminum ion exhibits a high charge density and strong electronic interactions in the host structure. These properties do not only effect the slow diffusivity of the ions into the bulk structure, but also the instability of the layered phase inserted by the aluminum ion. As a result of the reaction with the aluminum ion, FeS_2 transforms to the FeS phase and Al_2S_3 phase, as in a conversion reaction.

2.4. Conclusions

We investigated the discharge/charge reaction mechanisms of the FeS_2 as a cathode material for aluminum rechargeable battery systems incorporating ionic liquids. XRD and XAS measurements were conducted to determine the reaction mechanism of the FeS_2 pyrite phase reacting with aluminum ion. XRD and S, Fe, and Al K-edge XANES spectra show that the pristine FeS_2 transforms into low crystalline FeS and amorphous Al_2S_3 , and the S 3p orbitals dominantly contribute to the charge compensation process during discharging/charging. Transformed phases are reversed to FeS_2 during the charging process. The products of the reaction are different from the monovalent ion battery case.

For practical application of Al/FeS_2 battery, this battery was suffer from the low cell voltage, and the poor cycle stability due to the dissolution of sulfides. The voltage differences between Al/FeS_2 and Li/FeS_2 batteries are corresponded with the difference

of the potentials of anode metals. The theoretical energy density of Al/FeS₂ battery (462.7 Wh kg⁻¹, and 1939.0 Wh L⁻¹) was smaller than Li/FeS₂ battery (1337.0 Wh kg⁻¹, and 2602.7Wh L⁻¹)²⁷. However, we believe that Al/FeS₂ battery has the merit for the low cost, and safety because of abundance, and high melting points of aluminum anode. The poor cycle stability in FeS₂ cathodes is caused by the dissolution of sulfides, which also becomes a problem in a lithium sulfur battery. In order to overcome the problem of sulfur compounds, several methods have been proposed²⁸⁻³⁶. For examples, the complex with carbon material is one of the interesting methods for the practical application of sulfide compounds cathode materials³⁴⁻³⁶. Therefore, we believe the improvement of the cycle stability of Al/FeS₂ battery can be possible.

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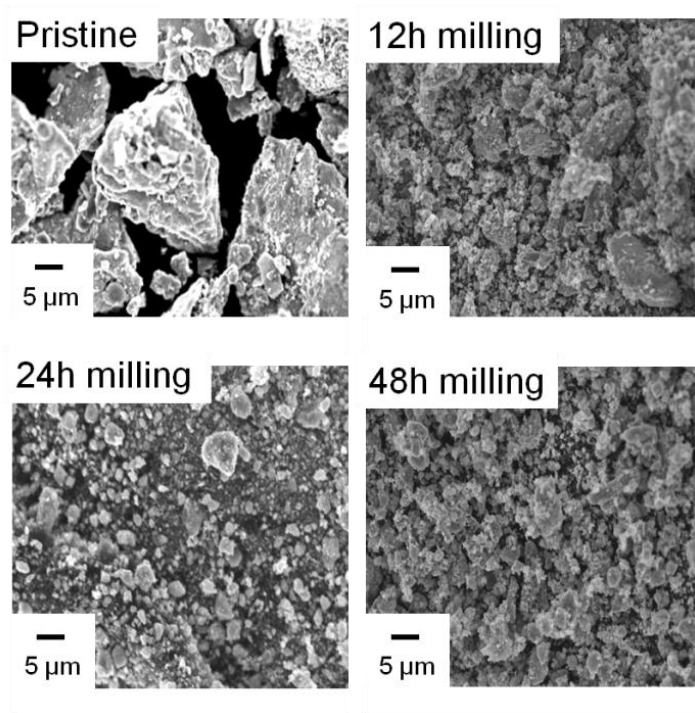


Fig. 2-1. SEM images of FeS₂ particles: pristine, ball milled for 12 hours, ball milled for 24 hours, and ball milled for 48 hours.

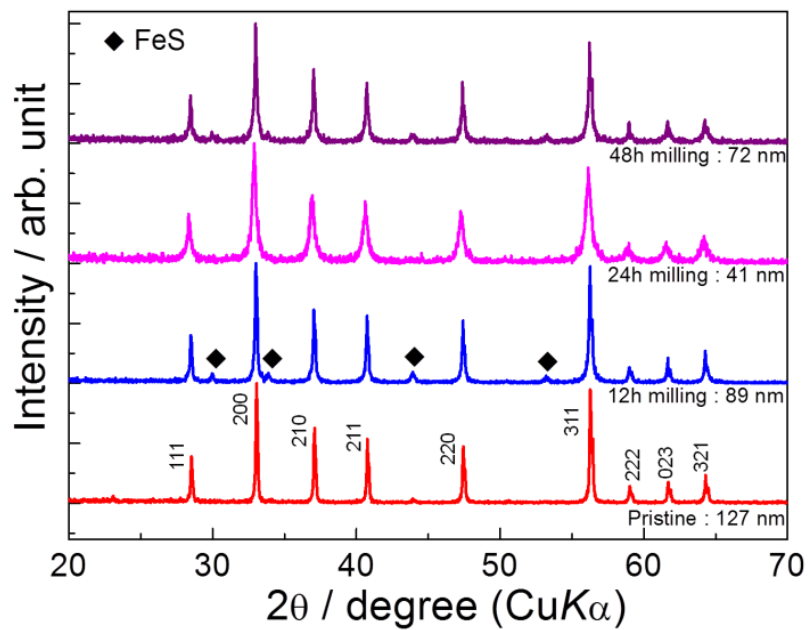


Fig. 2-2. XRD patterns for FeS₂ powders: pristine, ball milled for 12 hours, ball milled for 24 hours, and ball milled for 48 hours. The inset diameters are the crystallite sizes calculated from the Scheerer equation from the results of the XRD.

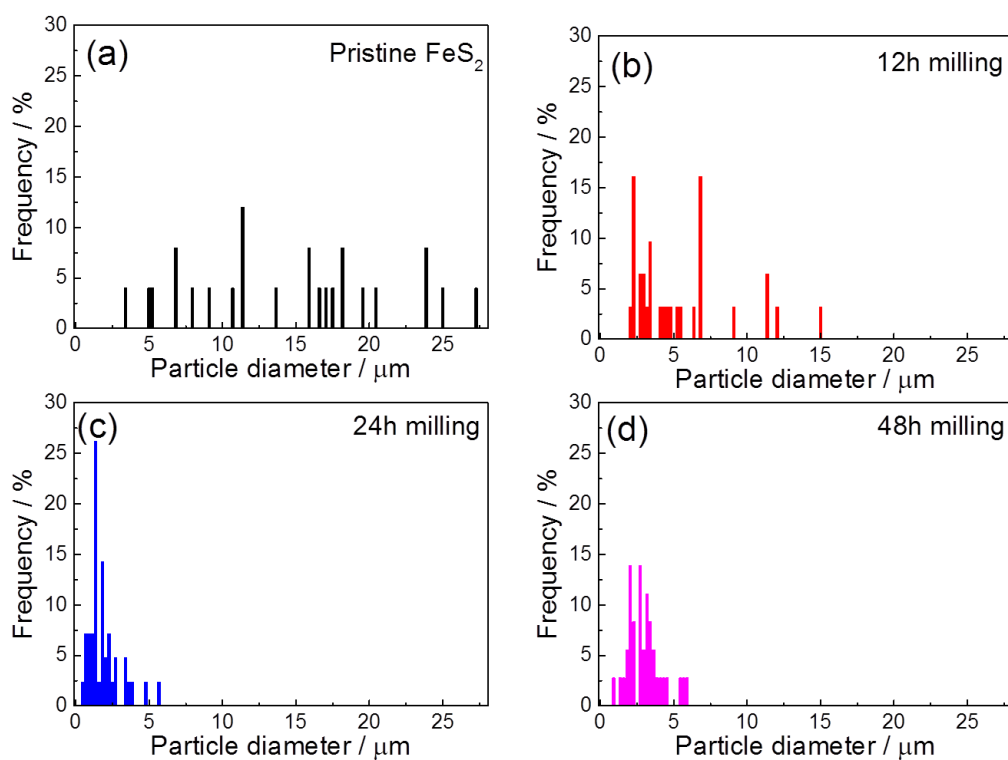


Fig. 2-3. Particle size distributions of (a) pristine FeS₂, (b) 12 hours milled sample, (c) 24 hours milled sample, and (d) 48 hours milled sample.

Table 2-1. Chemical composition of FeS₂ powder for the charge-discharge measurements.

Sample	Fe (at%)	S (at%)
Pristine	65	35
12 hours milling	64	36
24 hours milling	65	35
48 hours milling	65	35

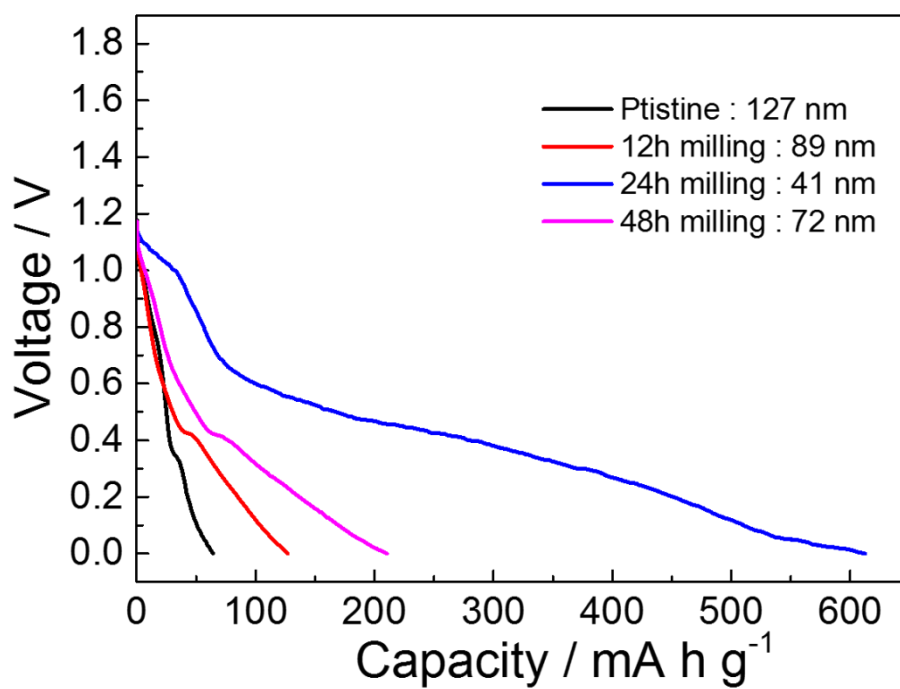


Fig. 2-4. Discharge behavior of the FeS₂ powders milled by various times. Their crystallite sizes are calculated from the results of the XRD by Scherrer equations.

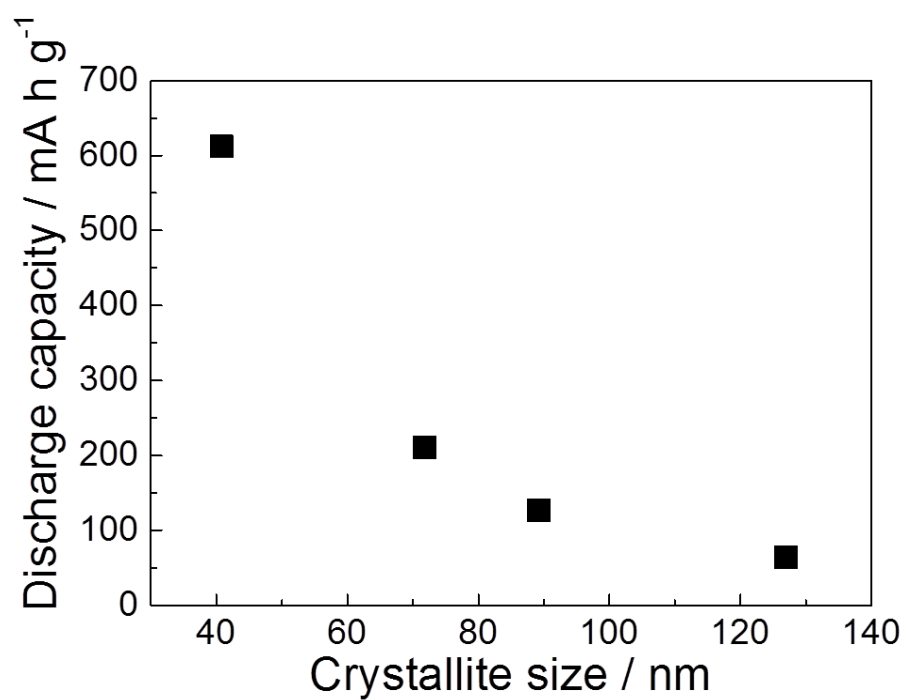


Fig. 2-5. Dependence of the initial discharge capacity on crystallite size. Galvanostatic measurements were performed at 55°C and 8.94 mA g⁻¹.

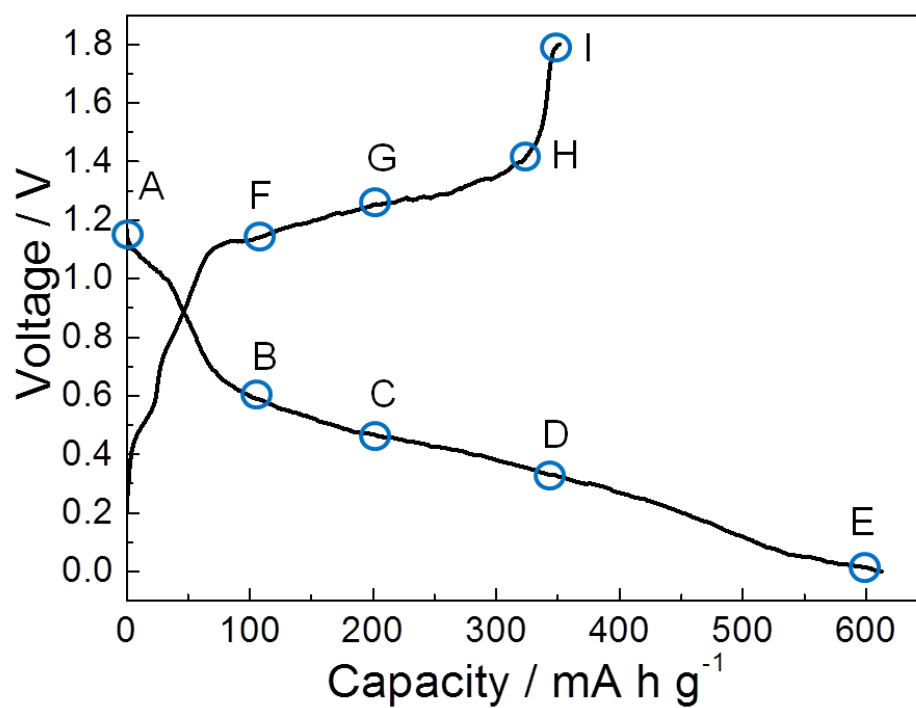


Fig. 2-6. Discharge-charge curves of the FeS₂ milled for 24 hours. Galvanostatic measurements were performed at 55°C and 8.94 mA g⁻¹. The circles show the measurement points for the XRD and XAS measurements.

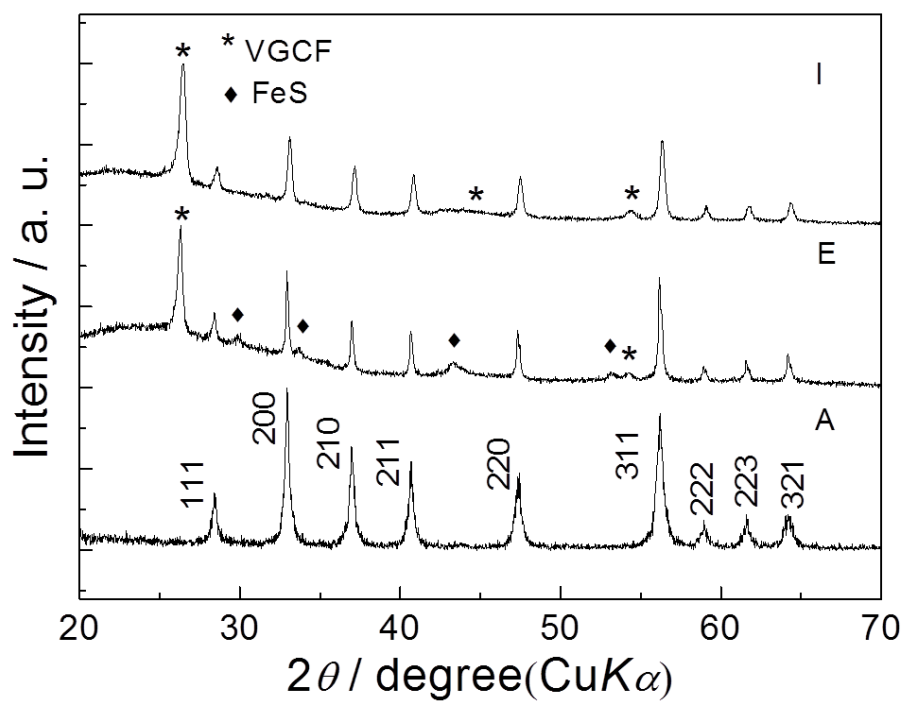


Fig. 2-7. *ex situ* XRD patterns of the ball-milled FeS_2 powder (A) and the electrodes charged to 350 mAh g^{-1} (I) and discharged to 600 mAh g^{-1} (E).

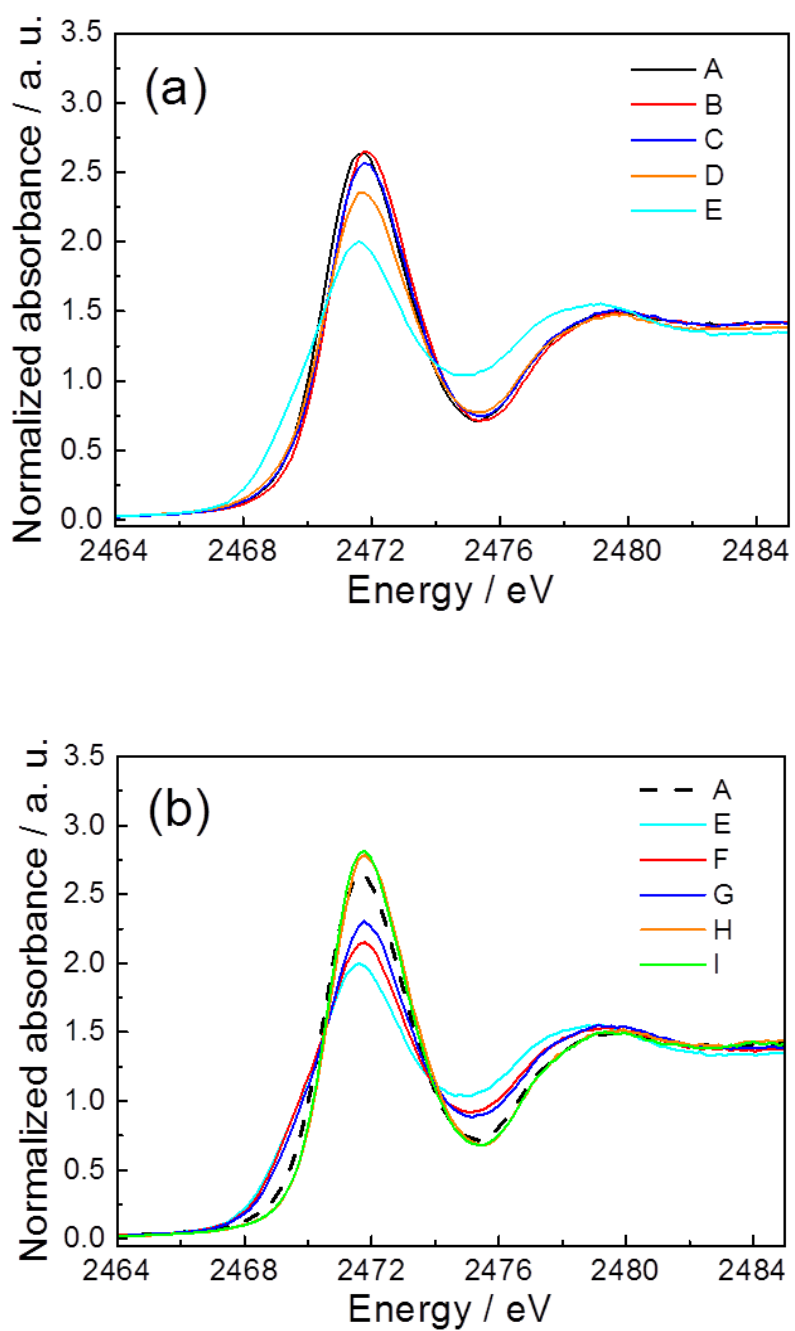


Fig. 2-8. S K-edge XANES spectra measured in the PFY mode for (a) discharged FeS_2 electrodes and (b) charged FeS_2 electrodes. The measurement points indicate in Fig. 2-6.

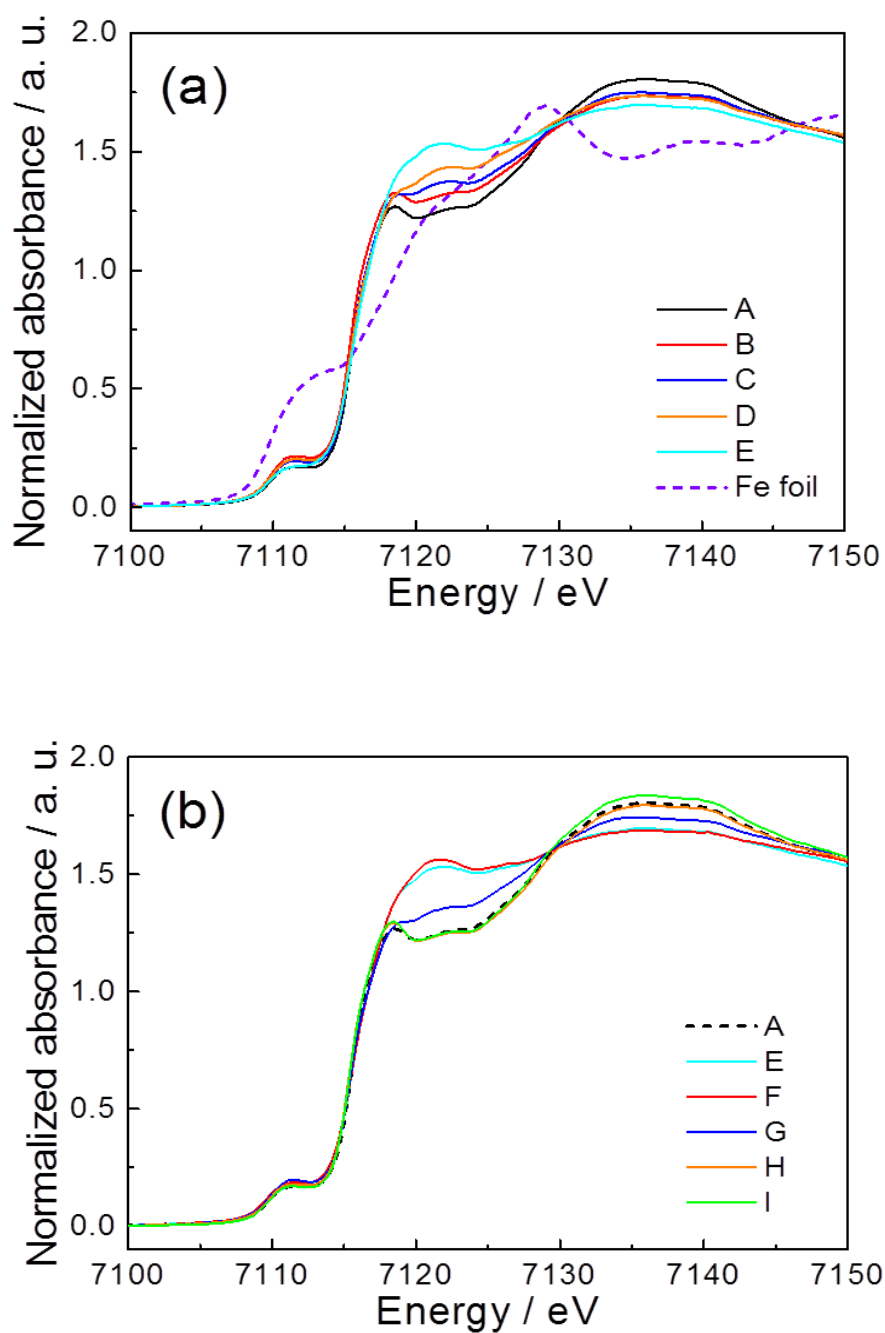


Fig. 2-9. Fe K-edge XANES spectra of (a) discharged FeS₂ electrodes, and (b) charged FeS₂ electrodes. The measurement points indicate in Fig. 2-6.

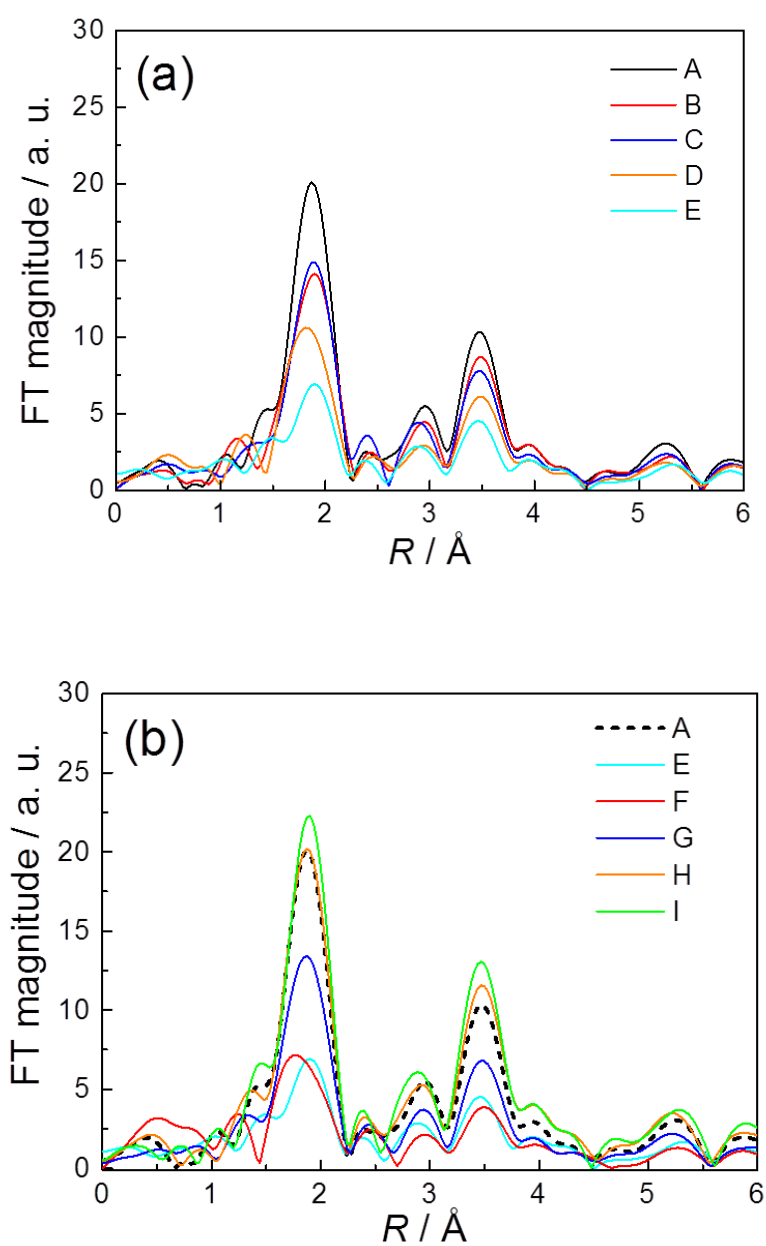


Fig. 2-10. Fourier transformation of the Fe K-edge EXAFS spectra for a FeS₂ positive electrode during (a) discharging and (b) charging. Local structural changes around Fe atoms were investigated by extended X-ray absorption fine structure (EXAFS).

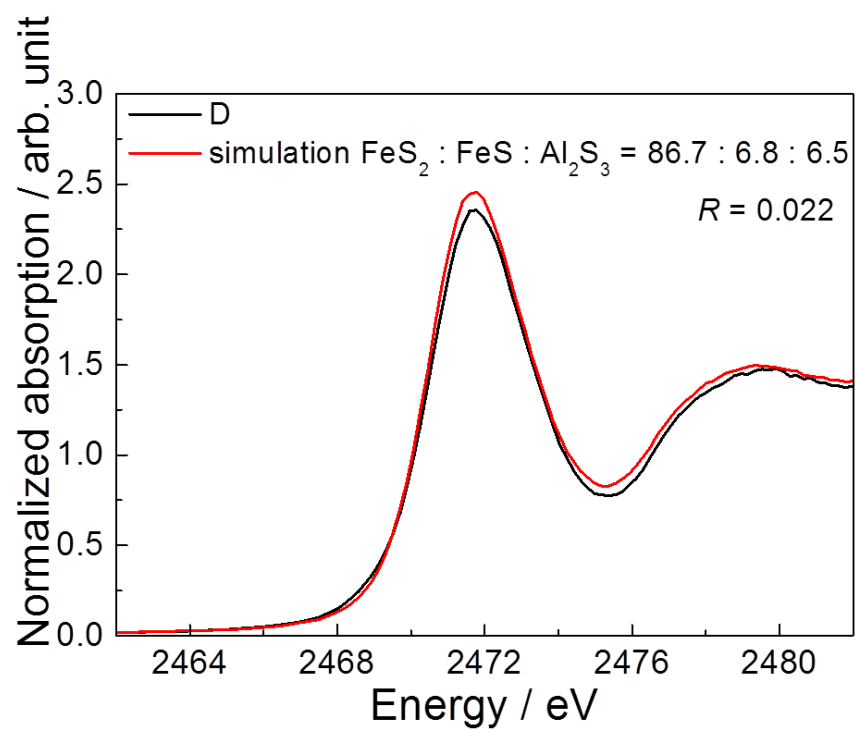


Fig. 2-11. S *K*-edge XANES spectra of the D in Fig.4 and fitting of the linear combination of standard spectra of FeS_2 , FeS, and Al_2S_3 .

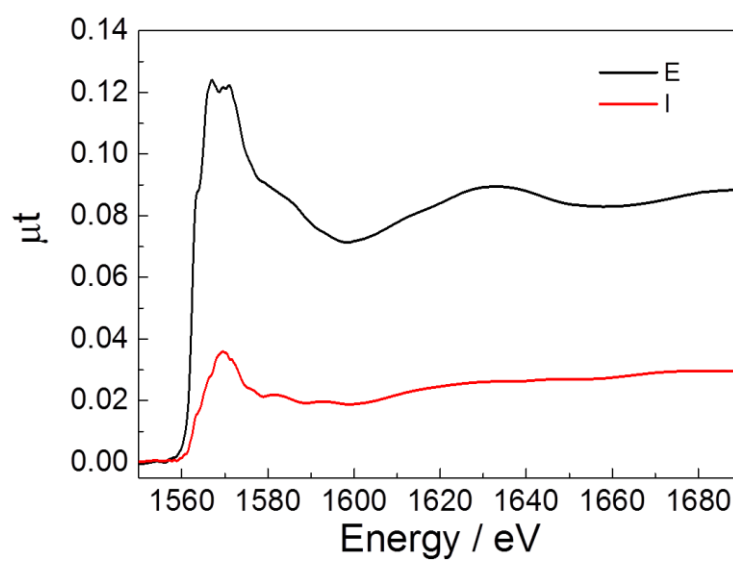


Fig. 2-12. Al *K*-edge XANES spectra of the discharging electrodes (E in Fig.2-6) and the charging electrodes (I in Fig. 2-6).

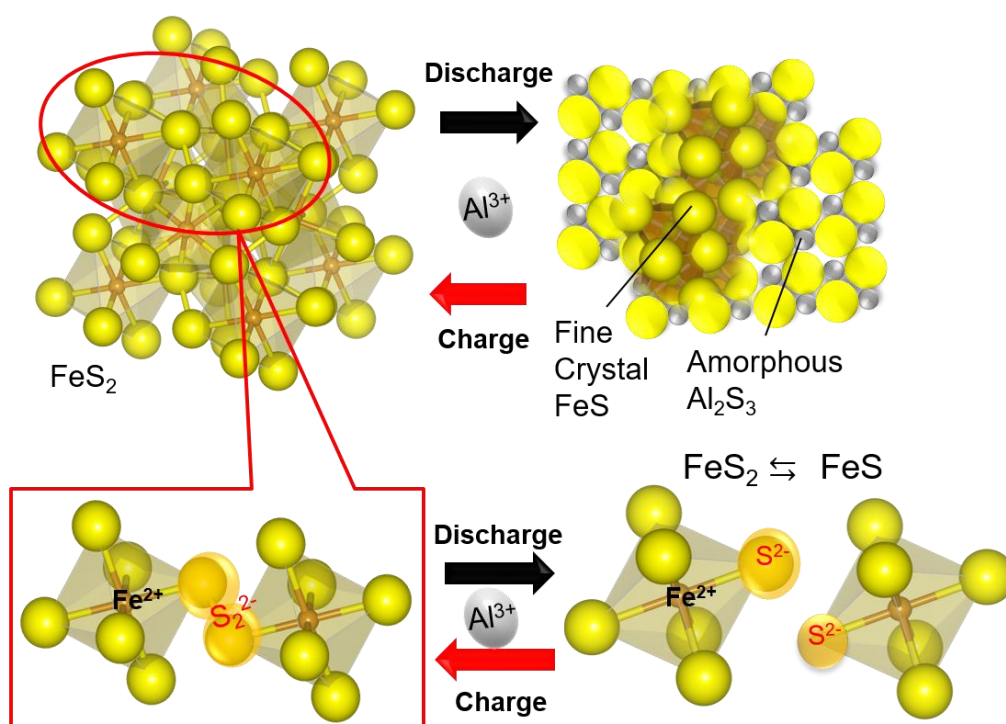


Fig. 2-13. Charge-discharge reaction model of FeS_2 with aluminum ions in an AlCl_3 -EMIC ionic liquid at 55°C .

Chapter 3: Mg^{2+} insertion mechanism of the Mo_6S_8 Chevrel phase investigated by Hard and Soft X-ray absorption spectroscopy

3.1. Introduction

Magnesium rechargeable battery has deemed as the next generation battery, because of the nature of the magnesium metal anode, *i.e.* high capacity, low cost, and safety.¹ Then development of the cathode materials has been desired for high performance magnesium rechargeable battery. The prototype magnesium rechargeable battery cathode was chevrel phase (Mo_6S_8).² This material shows low voltage (ca. 1.1V vs. Mg^{2+}/Mg) and low capacity (ca. 130 mAh g^{-1}). Then so many researchers have developed high energy density cathode materials.³⁻¹¹ However, the cycle stability and rate performances were not better than the performances of chevrel phase.

We refocused on the Mo_6S_8 chevrel phase as a model material of the insertion host for the magnesium battery, and investigated the insertion mechanisms which led to the design principles of the cathode materials for the magnesium rechargeable battery. This material is available to insert the two magnesium ions into the host structure. The below two step reactions have been reported,¹²⁻¹⁵



The insertion sites of the magnesium ions are able to insert into two different sites, which are called inner site and outer site, respectively in Fig.3-1. Inner site is energetically favorable site from the results of the first principle calculation by Kganyago *et al.*¹⁶ They proposed that the both ions were occupied in the same inner ring after fully magnesiation. However, Levi *et al.* proposed another reaction model. During the electrochemically insertion reaction of magnesium, these reactions are progressed two phase co-existence states. At the 1st step, Mo_6S_8 and MgMo_6S_8 are co-existence, and MgMo_6S_8 and $\text{Mg}_2\text{Mo}_6\text{S}_8$ are co-existence at 2nd step.¹⁷ They performed X-ray diffraction (XRD) and Neutron powder diffraction (NPD) applied for the powders which is chemically magnesiated chevrel phase of MgMo_6S_8 , and $\text{Mg}_2\text{Mo}_6\text{S}_8$. They reported that the MgMo_6S_8 phase has the magnesium ion into the inner site, and the $\text{Mg}_2\text{Mo}_6\text{S}_8$ phase has them into outer site and inner site, respectively.¹⁷ Moreover, they reported the kinetic difference between reactions (1) and (2). The reaction (2) is kinetically favorable reaction than reaction (1). At the reaction (1), magnesium ion is inserted into the inner site of the chevrel phase. The inner site magnesium was trapped at this site because the distance between inner site and outer site was longer than that between inner site inner site.¹⁷

Until now, the structural insight for the magnesiated Mo_6S_8 chevrel phase has been studied. There was no knowledge of the interactions between magnesium ion and host structure. The strong interaction between magnesium and host structure are expected to hinder the diffusion into the bulk structure. Then the more detailed reaction mechanisms are obtained by the analysis of the electronic and local structural change during magnesiation of the chevrel phase. Then we performed X-ray absorption spectroscopy (XAS) which has atomic selectivity to investigate electronic and local structural change

at each atoms.

In this study, we investigated the electronic and local structural change of the Mo_6S_8 chevrel phase during discharging by Mo K -edge, Mo L_{III} -edge, and S K -edge X-ray absorption fine structure (XAFS) measurements, and investigated the insertion mechanisms of the magnesium ions into the Mo_6S_8 chevrel phase. The charge compensation mechanisms are investigated from the X-ray absorption near edge structure (XANES) and local structure of the absorbing atoms are also investigated from the Extended X-ray absorption fine structure (EXAFS).

3.2. Experimental

Material synthesis, and electrochemical characterization

Mo_6S_8 chevrel phase was synthesized by chemical reaching of Cu from $\text{Cu}_2\text{Mo}_6\text{S}_8$ (Nippon Inorganic Coluor & Chemical Co., ltd).¹⁸ The purchased $\text{Cu}_2\text{Mo}_6\text{S}_8$ were soaked into the 6 mol dm^{-3} HCl saturated by O_2 gas for 3days. After soaking, the powders were washed with distilled water and filtered. The materials were thereafter dried in an oven at 80°C for 8 hours. Crystal structures of the as-prepared powders were characterised on a Rigaku Rint-ULTIMA III/G diffractometer using Cu $K\alpha$ radiation at room temperature. The diffraction data were collected in a 2θ range of 10° to 60° with a step size of 0.02° . The exposure time was 1.0s at each step. Particle size was measured by scanning electron microscopy using (JEOL, JSM-890).

Magnesium insertion / desertion properties were investigated by cyclic voltammetry. Composite electrodes were composed mixture of the prepared Mo_6S_8 , carbon (VGCF: Vapor Grown Carbon Fiber, Showa Denko) and

polyvinylidene difluoride (PVdF) binder with a weight ratio of 80:10:10. The dried active electrodes were pressed on SUS304 foil as the working electrode. Electrochemical measurements were performed using three electrodes cell. 0.4M $(\text{PhMgCl})_2 - \text{AlCl}_3 / \text{THF}$ ¹⁹ was used as electrolyte. (Ph = phenyl groups) Mg rods were used as the counter and reference electrodes, respectively. The cell assembly was carried out in a glove box under argon atmosphere. Cyclic voltammetry measurements were conducted HZ-5000 systems (Hokuto Denko). Scanning range were between 0.5V and 1.8V vs. $\text{Mg}^{2+} / \text{Mg}$, and scanning rate was set 0.01 mV s^{-1} at 40°C .

Sample preparation for X-ray measurements

The magnesium contents x in the $\text{Mg}_x\text{Mo}_6\text{S}_8$ were controlled by galvanostatic charge discharge measurements. The current density was set 5.0 mA g^{-1} . The composite electrodes composed mixture of the prepared Mo_6S_8 , VGCF and polytetrafluoroethylene (PTFE) binder with a weight ratio of 69:30:1 were used due to obtain the enough amount for the X-ray measurements. These types of electrodes are easy to control the thickness. The measurement samples have several composition x into $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) were rinsed several times with THF. The numbers of x are calculated by the electrical charge from the results of the galvanostatic charge measurements. .

XRD measurements for electrodes samples

In order to avoid the exposure from the air, all the samples are sealed into the liquid paraffin. XRD measurements are performed by Rigaku Rint-ULTIMA

III/G diffractometer. The diffraction data were collected in a 2θ range of 30° to 50° with a step size of 0.01° . The exposure time is 5.0s at each step.

Hard and Soft XAFS measurement for electrodes samples

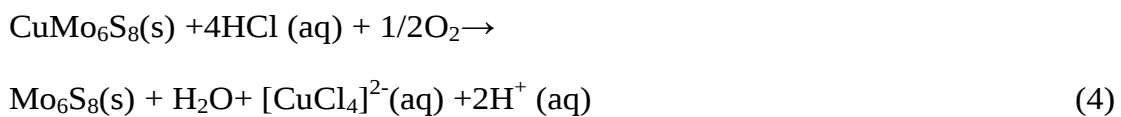
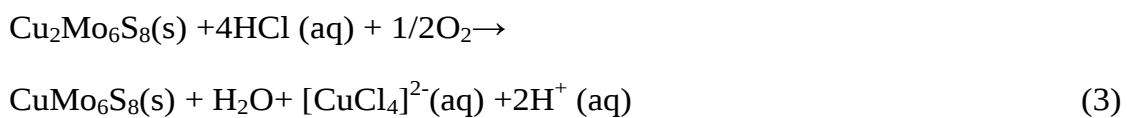
For Hard X-ray XAS, $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) electrodes were intimately mixed with boron nitride powders and pressed into pellets. The pellets were sealed in laminated packets in an argon-filled glove box. XAS measurements were performed on the beamline BL01B1 at SPring-8 (Hyogo, Japan). The synchrotron radiation X-ray from the storage ring was monochromated by a Si 111 crystal. Mo K -edge XAS measurements were performed at room temperature in transmission mode using two ion-chambers. The local structural parameters were obtained from the curve fitting procedure against k^3 weighed EXAFS spectra by using REX2000 XAFS analysis software (Rigaku Co., Inc.). k -range is between $3 \text{ \AA}^{-1}$ and $14.8 \text{ \AA}^{-1}$. The effective back scattering, phase correction, and total central atom phase shift were calculated with the multiple-scattering theoretical calculation program, FEFF8.20.^{20, 21} For calculation of FEFF8.20, the model structure was determined by the structure of the obtained Mo_6S_8 powders.

For Soft X-ray XAS, same charging and discharging state electrodes were applied to carbon tape onto SUS304 sample holder and they are into Ar filled transfer vessel.²² S K -edge and Mo L_{III} -edge XAS measurements were conducted at BL-10 of the Synchrotron Radiation Center (Ritsumeikan University). The incident X-ray beam was monochromated by a Ge 111 crystal. In addition, the absolute photon energy was calibrated under the assumption that the strong resonance of K_2SO_4 ($\text{S } 1s \rightarrow t_2$) appears at 2487.1 eV.

3.3. Results & Discussions

Characterizations of the obtained Mo₆S₈ phase.

We prepared the Mo₆S₈ chevrel phase by reported chemical reaching methods.¹⁸ Fig.3-2. shows the XRD patterns of the pristine Cu₂Mo₆S₈ powders (pristine powders: black line in Fig.2) and prepared Mo₆S₈ powders (3days of leaching: red one in Fig.2). The pristine powders are fully indexed by *R*-3 space groups and their lattice constants are below; $a = 9.6061(4) \text{ \AA}$, and $c = 10.2163(3) \text{ \AA}$. Their values are corresponded with the reported one, and initial pristine powders are single phase of the Cu₂Mo₆S₈.²³ After chemical leaching all peaks differ from the pristine one, and they are indexed by *R*-3 space groups, and also determined lattice parameters are below; $a = 9.183(1) \text{ \AA}$, and $c = 10.874(1) \text{ \AA}$. These values are also corresponded with reported Mo₆S₈ values.²⁴ The chemical reaction of the Cu₂Mo₆S₈ are progressed below two step equations¹⁸



We obtained single phase Mo₆S₈ powders for 3days of chemical leaching in the 6M HCl solutions bubbled by oxygen. In order to confirm the particle size of the

obtained Mo_6S_8 powders, SEM images are shown in Fig.3-3. The particle sizes are about 100nm.

We obtained single phase of the Mo_6S_8 chevrel phase. Then we investigated the electrochemical insertion / desertion process by cyclic voltammetry. Fig.3-4. shows the results of the cyclic voltammograms of the Mo_6S_8 in 0.4M $(\text{PhMgCl})_2\text{-AlCl}_3$ in THF electrolyte. At the 1st cycle, the over voltage of the cathodic peaks are large. This large over potential was reported for the reaching materials. After cathodic sweep, there is clearly appeared two step reactions, which is indexed by a-a' and b-b'. Indexed reactions are scheme (1) and (2), respectively. Levi *et al* shows the reaction mechanisms of (1) are inserted into the inner site of the Mo_6S_8 chevrel phase, and (2) are inserted outer site of it. Fig.3-5 shows the *ex situ* XRD results of the $\text{Mg}_x\text{Mo}_6\text{S}_8$ electrodes. At $0 < x < 1$, the reflection peaks derived from the Mo_6S_8 phase(CP) and that done from the $\text{MgMo}_6\text{S}_8(\text{MgCP})$ phase were confirmed. These two phase which are Mo_6S_8 and MgMo_6S_8 were co-existence. At $1 < x < 2$, the reflection peaks derived from the MgMo_6S_8 phase and that done from the $\text{Mg}_2\text{Mo}_6\text{S}_8(\text{Mg}_2\text{CP})$ phase were confirmed. These two phases which are MgMo_6S_8 and $\text{Mg}_2\text{Mo}_6\text{S}_8$ were also co-existence. Then the Mo_6S_8 shows the two step reactions which are two phase co-existence reactions, respectively. This two phase behavior was corresponded with the reported one.¹⁷ These reactions are two phase co-existence reaction and we also confirmed them. The peak separation of a-a' couples are larger than b-b' couples. (Fig.3-4) The reaction rate of a-a' redox couples are more slowly process than b-b'.¹²⁻¹⁵ We confirmed the reported two step behaviour of the Mo_6S_8 .

XAFS analysis of the $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($x = 0, 0.5, 1.0, 1.5, 2.0$)

To investigate electronic and local structural change of the chevrel phase during discharging, we performed Mo L_{III} -edge, Mo K -edge, and S K -edge XAFS measurements for several magnesiated electrodes. Fig.3-6 shows the results of the Mo L_{III} -edge XANES spectra for several composition x in $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($x = 0, 0.5, 1.0, 1.5$, and 2.0). The peak at $\sim 2525\text{eV}$ is revealed the transition between $2p$ and $4d$. The peak top positions are continuously shifted to lower energy against increasing x . This result indicated that the Mo atoms play a role of charge compensation process during discharging.

Fig.3-7 shows the results of the S K -edge XANES spectra for several composition x in $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($x = 0, 0.5, 1.0, 1.5$, and 2.0). The peak at $\sim 2472\text{eV}$ are appeared the transition between $1s$ and $3p$. Intensities of these peaks are continuously changed against increasing x in $\text{Mg}_x\text{Mo}_6\text{S}_8$. S atoms are also compensated the charge of the chevrel phase after magnesiation. Especially, the regions of $0 < x < 1$, S K -edge XANES spectra are drastically changed than them in the regions of $1 < x < 2$.

Mo K -edge XANES also shows the compensation mechanisms of the Mo_6S_8 . Mo K -edge XANES are shown in Fig.3-8. The absorption edges are shifted lower energies during discharging. (shown in left figure of inset one) The lowering energy shift indicated the reduction of the Mo atoms during discharging. Moreover, the peak top at 20020eV was decreasing during discharging. (shown left figure of inset one) This peak top indicate that the transitions between Mo $1s \rightarrow 5p$. This orbital hybridized with the sulfur atoms. Therefore the hybridized orbital between Mo and S are affected for the charge compensations during

discharging. Then the S K-edge XANES spectra are also changed during discharging.

From the results of XANES spectra of Mo L_{III} -edge, K-edge and S K-edge, each atom compensated the charge of the chevrel phase during discharging. Inner site magnesium ions exist near the S atoms of the Mo_6S_8 cluster. If the magnesium ions are inserted into the inner site of the chevrel structure, S atoms are more strongly affected than Mo atoms. Our results also indicate the magnesium ions inserted into inner site in the Mo_6S_8 crystal structures at $0 < x < 1$. At the $1 < x < 2$, the change are smaller than that at $0 < x < 1$. If all of the magnesium is inserted into inner site of the chevrel phase, the S K-edge XANES show the continuously change during discharging. Then this change support that the outer site insertion reaction was occurred at $1 < x < 2$.

This result also indicates the effect of the electronic interaction between Mg and S are one of the hindering issue for the diffusion process of the magnesium ions. Effect of the anions for the rate properties of the chevrel phase are reported.¹² Mo_6Se_8 chevrel phase shows the excellent rate property at each site insertion reactions.¹² For addition of the structural insight, we also performed Mo K-edge XAFS, and local structural change are determined by Mo K-edge EXAFS spectra.

Mo K-edge XAFS spectra are shown in Fig.3-9, and the Fourier transformation of Mo K-edge EXAFS spectra for $\text{Mg}_x\text{Mo}_6\text{S}_8$ electrodes are shown in Fig.3-10. The peaks at near $2\text{\AA}$ are revealed contributions of the Mo-S shells, and the ones at $2.5\text{\AA}$ are revealed contributions of the Mo-Mo shells. To investigate the effects of inner site and outer site, we obtained the two types of the Mo - S

distances from the fitting results of the Mo *K*-edge EXAFS. The Mo - S (*N* = 4) (which indicate black arrow of the inset figure of Fig.3-10) is a bond inside the cluster, and Mo - S (*N* = 1) (which indicate red arrow of the inset figure of Fig.3-10) is a bond between clusters. Mo - S (*N* = 1) distance is affected by outer site insertion reaction of the chevrel phase. Fig.3-11. shows the plots of the atomic distances and Debye Waller factors of Mo - S (*N* = 4), Mo - S (*N* = 1), and Mo-Mo against *x* in Mg_{*x*}Mo₆S₈. The fittings of the Mo *K*-edge EXAFS spectra are good fitting because their residues are below 0.2%. The fitting results are listed in Table 3-1. Atomic distances of the Mo - S (*N* = 1) are drastically increased between at $0 < x < 1$ and $1 < x < 2$. Moreover the atomic distances of the Mo - S (*N*=4) is also decreased at $1 < x < 2$. However atomic distances of the Mo - Mo are almost same at all regions.

These structural change affected by the insertion sites of the chevrel phase. From the results of XANES analysis, the insertion sites are indicated that inner site insertion reaction are occurred at the regions of $0 < x < 1$, and outer site insertion reaction are occurred at $1 < x < 2$. The atomic distances of the Mo - S (*N* = 1) are increased at $1 < x < 2$. If the magnesium ions are inserted into the outer site, the distances between Mo₆S₈ clusters are increased because of the repulsion between Mg and Mo. This strong repulsion increase the distances of the Mo - S (*N* = 1) (The schematic diagrams are shown in Fig.3-12). Then the local structural change also indicate the outer site insertion are occurred at $1 < x < 2$. The insertion models reported by Levi *et al* are also confirmed by the analysis based on the XAS. Moreover, at $1 < x < 2$, the local structure of the inner site are also changed. The distances of the Mo - S (*N* = 4) are decreased and the one of

the Mo – Mo are almost unchanged. When the outer site insertion was occurred, the Mo₆S₈ clusters are separate by the repulsion between Mg and Mo. Hence, the bond distances of the Mo – S (N = 4) are decreased after separation of the Mo₆S₈ clusters. The decreasing of the atomic distances Mo – S (N =4) indicate the lowering of the strong attraction between inner site Mg and S. Then the interactions of the inner site Mg and S are controlled by the outer site atoms, which leads inhibit the trapping effect of the magnesium ions into the inner sites.

Finally, the schematic diagrams of the insertion mechanisms of the magnesium ions into the chevrel phase are shown in Fig.3-12. At $0 < x < 1$, the first magnesium ions are inserted into the inner site from the results of the S K-edge and Mo L_{III}-edge XANES. The strong interactions between Mg and S are confirmed. At $1 < x < 2$, the second magnesium ions are inserted into the outer site from the results of the Mo K-edge EXAFS. This reaction models are corresponded with the reported models by Levi *et al* from the results of the XRD, and NPD. Moreover we turn up the structural change at the inner site between outer site insertion reaction ($1 < x < 2$). Outer site insertion causes the strong repulsions between Mg and Mo. This results leads the lowering the attractions between Mg and S. The control of the interactions between clusters leads the lowering the interactions between inner site Mg and S which leads the highly diffusivity of the inner site magnesium ions, and high rate reactions of the chevrel phase. Then the interactions between Mg and host structures are inhibited factors for the high rate performances of the cathode materials for magnesium rechargeable battery.

3.4. Conclusions

We prepared Mo_6S_8 chevrel phase by chemical leaching of Cu from the $\text{Cu}_2\text{Mo}_6\text{S}_8$. Chevrel phase reveals two step intercalation reactions, which indicate inner site insertion and outer site insertion, in the 0.4M $(\text{PhMgCl})_2\text{-AlCl}_3$ by cyclic voltammetry. Then we performed soft and hard X-ray absorption spectroscopy for discharged electrodes of $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($x = 0, 0.5, 1.0, 1.5, 2.0$). The change of the S K-edge XANES spectra at $0 < x < 1$ are larger than them at $1 < x < 2$. This change indicate that the inner site reactions are occurred at $0 < x < 1$. At $1 < x < 2$, the outer site insertion reaction are expected to progress. This outer site insertion also are confirmed by the Mo K-edge EXAFS. The bond distances of the Mo - S ($N = 1$) are increased at $1 < x < 2$. This change derived from the repulsions between outer site magnesium and Mo_6S_8 clusters. Moreover, at $1 < x < 2$, the Mo - S ($N = 4$) are decreased. Then the cluster is contracted, and the interactions between inner site magnesium and clusters are decreased. The local structural change affected by the outer site magnesium is expected to lead the high diffusivity of the inner site magnesium.

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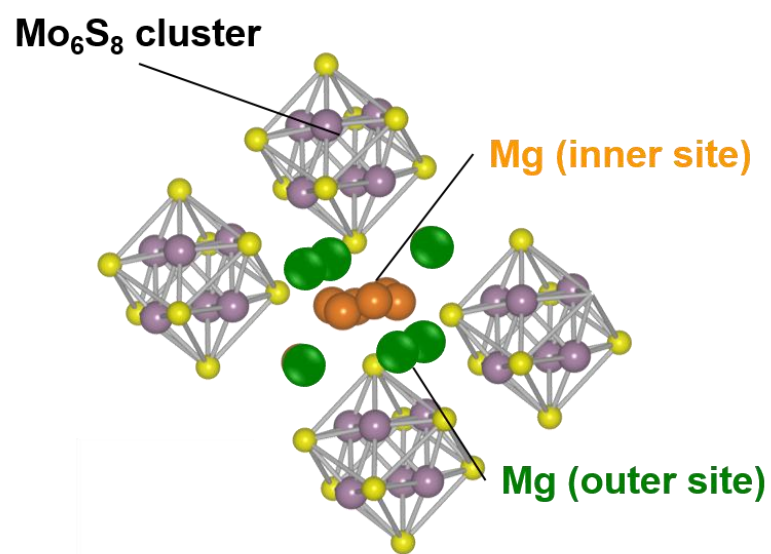


Fig. 3-1. Schematic diagrams of the insertion sites of the Chevrel phase. The crystal structure are viewed by VESTA programs.²⁵

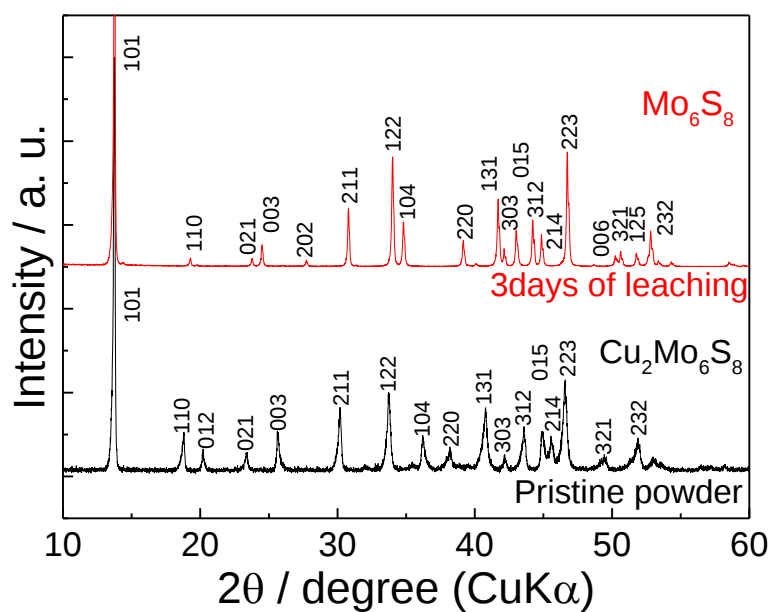


Fig. 3-2. XRD patterns of the pristine CuMo_6S_8 powders (black line, all the peaks are indexed by CuMo_6S_8) and CuMo_6S_8 powders after chemical leaching in 6mol dm^{-3} HCl solutions bubbled by O_2 (Red line, all the peaks are indexed by Mo_6S_8).

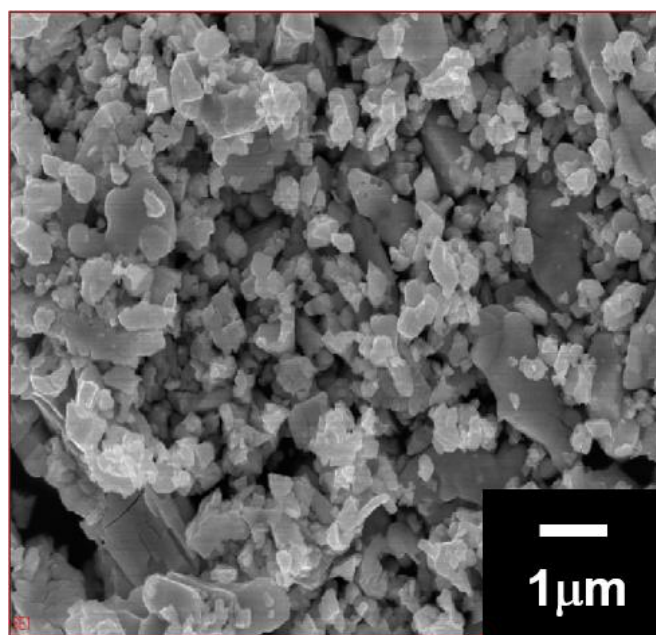


Fig. 3-3. SEM image of the powders after chemical leaching in the O₂ bubbling 6mol dm⁻³ HCl solutions.

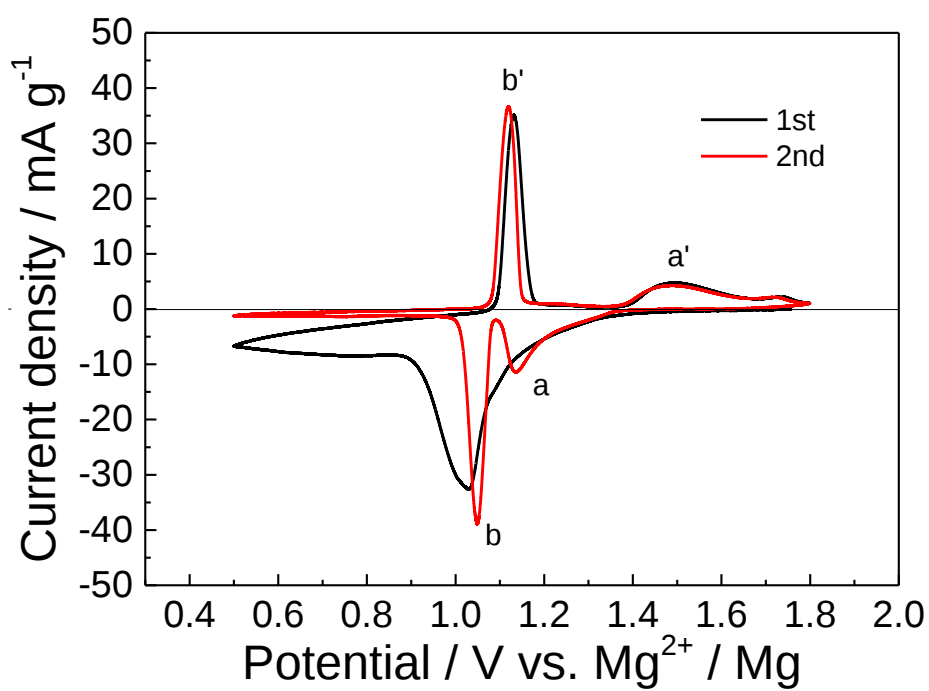


Fig. 3-4. Cyclic Voltammograms of the Mo_6S_8 in the 0.4M $(\text{PhMgCl})_2\text{-AlCl}_3$ /THF solutions at 313K. The scan rate is 0.01 mV s^{-1} .

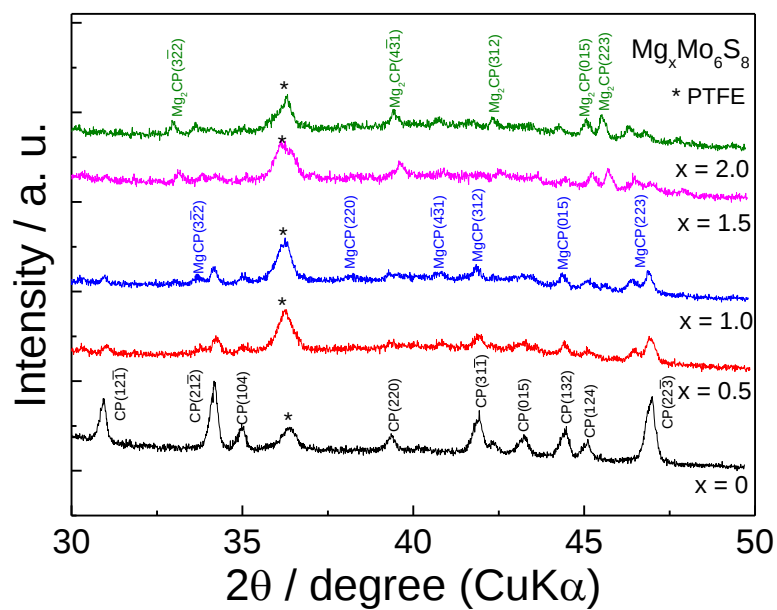


Fig. 3-5. XRD patterns of the $\text{Mg}_x\text{Mo}_6\text{S}_8$ electrodes ($x = 0, 0.5, 1.0, 1.5, 2.0$). CP, MgCP and Mg_2CP mean Mo_6S_8 phase, MgMo_6S_8 phase and $\text{Mg}_2\text{Mo}_6\text{S}_8$ phase, respectively.

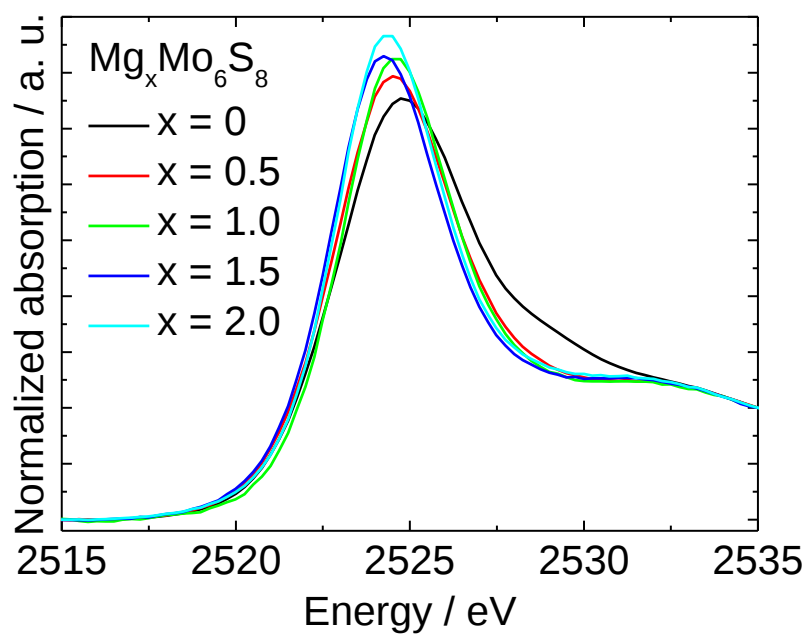


Fig. 3-6. Mo L_{III} -edge XANES spectra measured in the Total Electron Yield for $Mg_xMo_6S_8$ electrodes ($x = 0, 0.5, 1.0, 1.5, 2.0$).

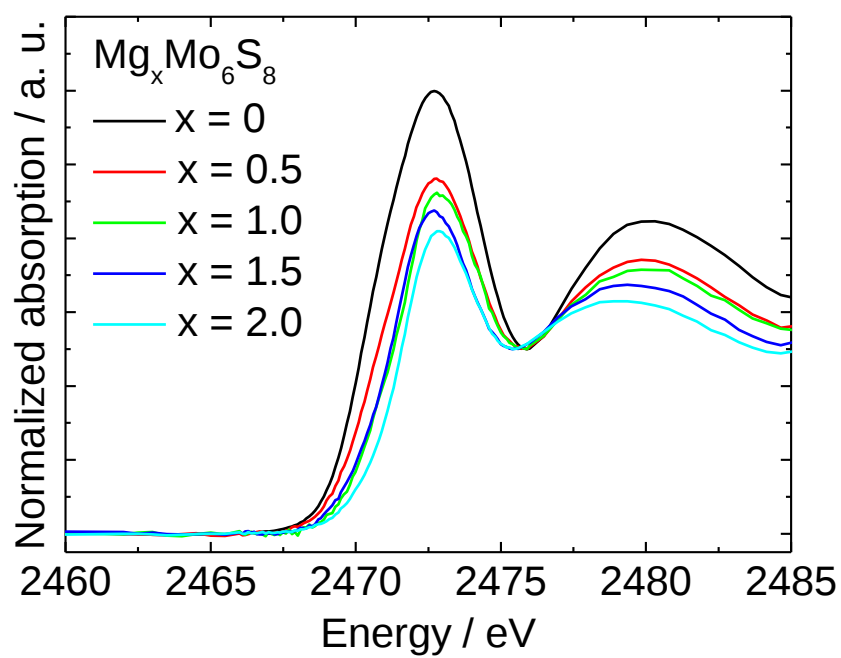


Fig. 3-7. S K-edge XANES spectra measured in the Total Electron Yield for $\text{Mg}_x\text{Mo}_6\text{S}_8$ electrodes ($x = 0, 0.5, 1.0, 1.5, 2.0$).

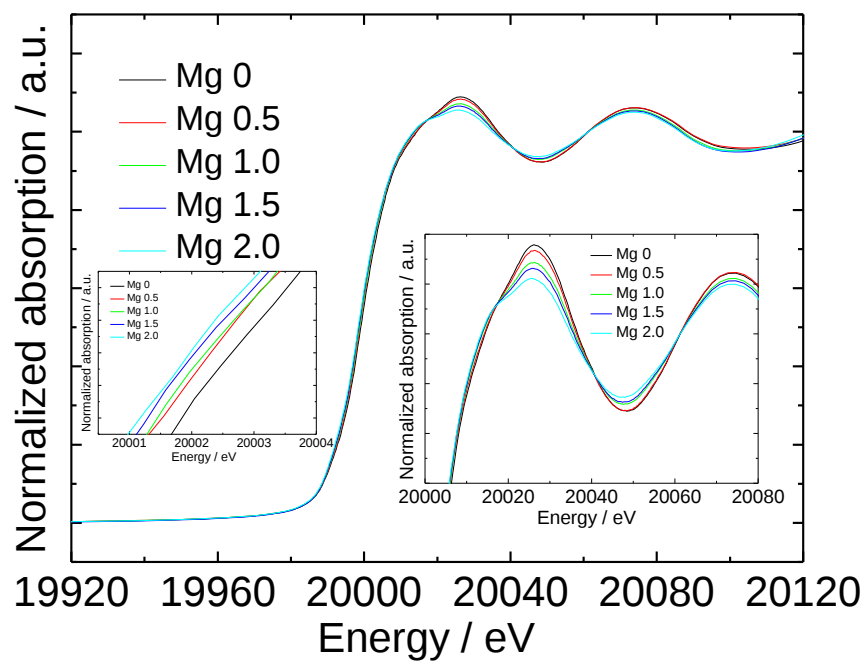


Fig. 3-8. Mo K-edge XANES spectra for $\text{Mg}_x\text{Mo}_6\text{S}_8$ electrodes ($x = 0, 0.5, 1.0, 1.5, 2.0$).

Inset figures are enlarged ones.

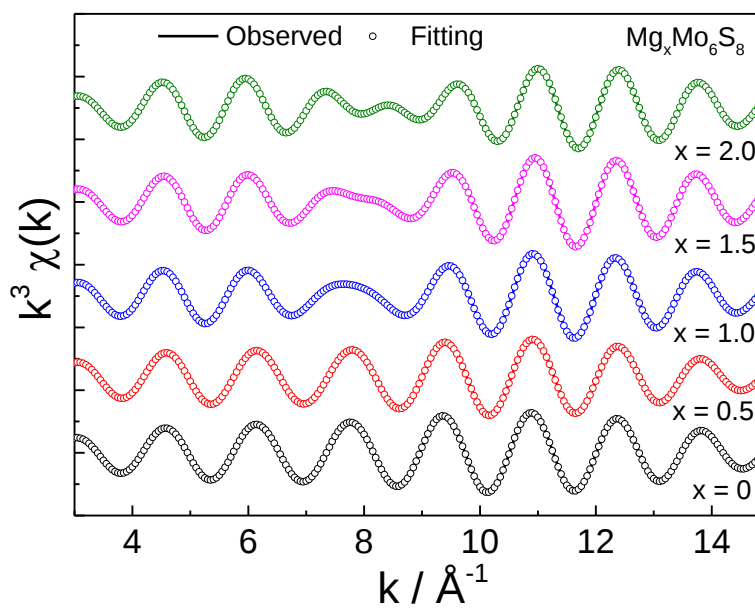


Fig. 3-9. Results of curve-fitting procedure for inverse FT spectra of Radial structure function for Mo *K*-edge EXAFS for $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($x = 0, 0.5, 1.0, 1.5, 2.0$). *K* range is between $3 \text{ \AA}^{-1}$ and $14.8 \text{ \AA}^{-1}$.

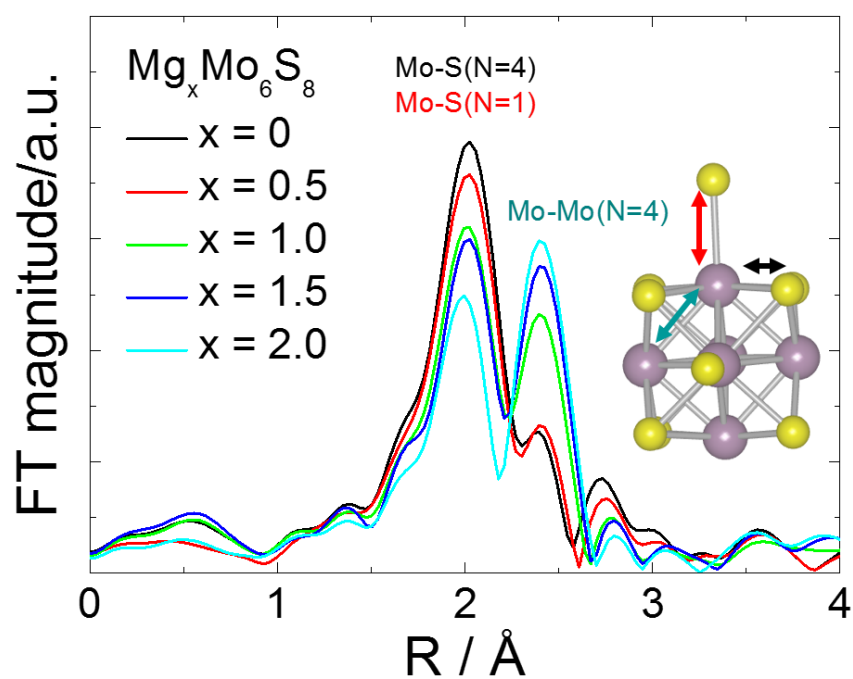


Fig. 3-10. Fourier Transformation of Mo *K*-edge EXAFS spectra for $\text{Mg}_x\text{Mo}_6\text{S}_8$ electrodes ($x = 0, 0.5, 1.0, 1.5, 2.0$). Inset figures reveal the bonds of Mo – S ($N = 1$), Mo – S ($N = 4$), and Mo – Mo, respectively.

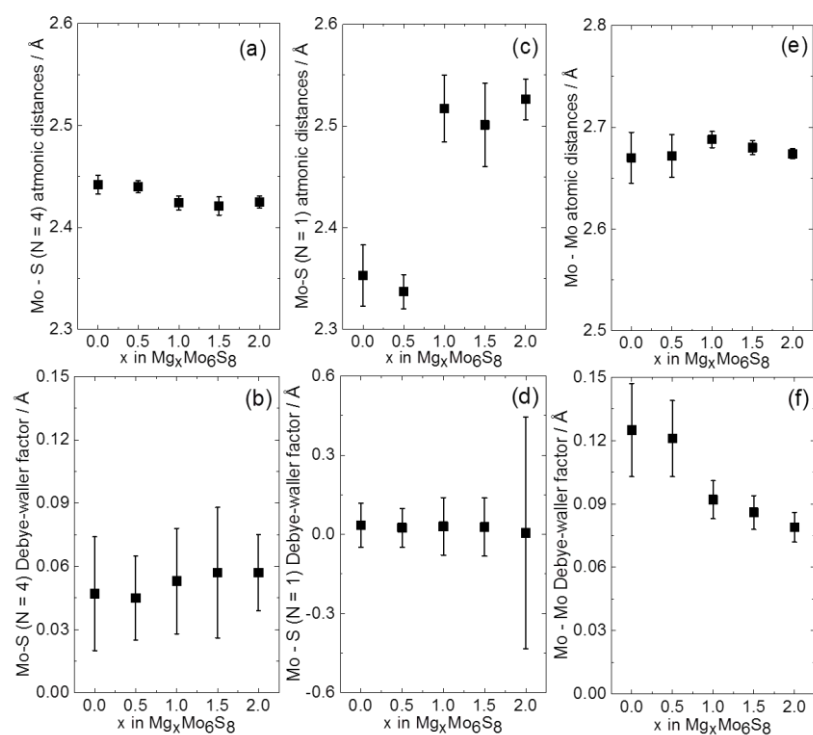


Fig. 3-11. The atomic distances and the Debye-Waller factor of the (a)(b) the nearest Mo-S, (c)(d) the next nearest neighbor Mo-S, and (e)(f) Mo-Mo determined from Mo K-edge EXAFS spectroscopy as a function of the concentration of the Mg in Mo_6S_8 .

Table 3-1. Structure parameters which are coordination number (N), inter atomic distances (R), and DW factor (σ) for $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) determined by Mo *K*-edge EXAFS spectroscopy.

x	Shell	N	R/Å	$\sigma/\text{\AA}$	Residue/%
0	Mo-S	4	2.442	0.047	0.035
	Mo-S	1	2.353	0.034	
	Mo-Mo	4	2.67	0.125	
0.5	Mo-S	4	2.44	0.045	0.03
	Mo-S	1	2.337	0.025	
	Mo-Mo	4	2.672	0.121	
1	Mo-S	4	2.424	0.053	0.038
	Mo-S	1	2.517	0.03	
	Mo-Mo	4	2.688	0.092	
1.5	Mo-S	4	2.421	0.057	0.08
	Mo-S	1	2.501	0.027	
	Mo-Mo	4	2.68	0.086	
2	Mo-S	4	2.425	0.061	0.118
	Mo-S	1	2.514	0.033	
	Mo-Mo	4	2.674	0.081	

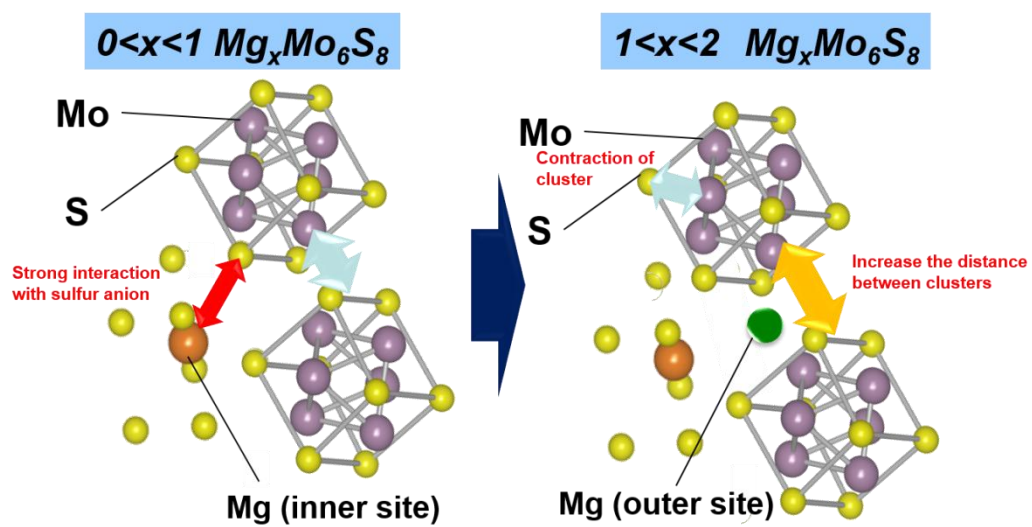


Fig. 3-12. Schematic diagrams Mg insertion model of $\text{Mg}_x\text{Mo}_6\text{S}_8$ ($0 < x < 1$, and $1 < x < 2$).

Part 2: Oxide cathode materials for the multivalent cation batteries

Chapter 4: Local structural change during charge transfer reaction of the cathode materials for magnesium battery using nano-sheet structured model electrodes

4.1. Introduction

Magnesium rechargeable battery is expected as high energy density, safe and low cost battery because of its divalent features, relatively low redox potential (Mg^{2+}/Mg (-2.37 V vs. NHE)), abundance, and stable characteristics.¹ For high energy density battery systems, one of the serious problem is lack of excellent the cathode materials.

The Chevrel phase (Mo_6S_8) has been reported as a cathode material for the prototype magnesium rechargeable battery due to their many insertion sites in the structures and electric charge are easy to redistribution of cluster structures.² This material shows the good reversibility and realatively high rate properties for the magnesium ion (de)insertion reaction. However, the redox potential (*ca.* 1.1V vs. Mg^{2+}/Mg), and the theoretical capacity was (*ca.* 130 mAh g⁻¹) lowcompared with them of the lithium ion batteries. Untill now, several cathode materials, which based on the oxide materials, have been explored for the decade.³⁻¹¹

To developpe the oxide based materials, the diffusivity of the Mg^{2+} into the inorganic host materials and the charge compensation during (de)magnesiumation were serious problem due to high electronic charge of the Mg^{2+} . The enhancement of the diffusivity of divalent ions achieved by the crystal structure of the host materials. Theoretical calculations indicate that the spinel host materials was suitable host for the diffusion of

the Mg^{2+} into the crystal structure. However, the reaction kinetics cannot be determined by only diffusivity. The crystal structures were changed by during magnesiation reactions. Then the knowledge of the charge compensation mechanisms entailed the local structural deformations were important to make the better cathode materials for the magnesium batteries.

We focused on the nano-sheet structure composed of the transition metal oxide to investigate the local structural change during charge transfer reactions. Analysis of the structural change of the magnesiated nano-sheet is directly reflected by the local structural change during the charge compensations. These nanostructure materials, such as nanostructured graphene-like MoS_2 ¹²⁻¹⁶, have been reported as cathode materials for the magnesium rechargeable battery. We chose the MnO_2 nano-sheets as a model electrode. MnO_2 nano sheet has two-dimensional sheet-like materials with a thickness about 1 nm.¹⁷ Application of MnO_2 nano sheet as a cathode material for lithium ion batteries have been already reported.¹⁸ Previously reports suggested that MnO_2 nano sheet exhibited reversible absorption / desorption reaction of the lithium ion during charging/discharging. Then this material is potentially available to apply the cathode materials for the magnesium rechargeable batteries. Therefore, this system is suitable for the analysis of the local structural change of the oxide type cathode materials during magnesiation / demagnesiation.

In this study, we investigated the structural change of the MnO_2 nano sheet reacted with magnesium ions by X-ray Absorption Spectroscopy (XAS). Extended X-ray absorption fine structure (EXAFS) spectra are suitable tool to investigate the local structural change and their bond length and distortions. Moreover, local structural change after absorption of the magnesium ions are compared with that of the lithium

ions, and discuss the effect of the divalent ions for the local structural distortions. This knowledge leads to the design principles for the oxide based cathode materials of the magnesium rechargeable batteries.

5.2. Experimental

Preparing materials and electrochemical characterizations

Nano sheet structured MnO_2 (MnO_2 nano sheet) was prepared by the one-pot process reported by Kai *et al.*¹⁹ The nano sheet was prepared *via* electrostatic absorption of MnO_2 nano sheet on surface of acetylene black (AB). Then we obtained MnO_2 nano sheet / AB composite.²⁰ The composition of the prepared MnO_2 nano sheet was $(\text{TMA})_{0.2}\text{MnO}_2$ (TMA = tetra methyl ammonium).¹⁹

Electrochemical measurements were carried out using a three-electrode cell with an Ag^+/Ag double junction reference electrode. The working electrode was made by mixing 90 wt% the obtained MnO_2 / AB composite (weight ration of MnO_2 nano sheet/AB is 1/10), and 10 wt% polyvinilidenedifluoride and the resulting mixture was coated onto the stainless steel foil. The counter electrode was a magnesium rod, and the electrolyte was 0.2 M magnesium trifluoromethanesulfonate ($\text{Mg}(\text{CF}_3\text{SO}_3)_2$)(Tokyo Chemical Industry Co., ltd., purity is 98.0%) in *N,N* - dimethylacetamide (DMA) (purchased from Sigma Aldrich). Galvanostatic discharge and charge measurements were performed with 61.76 mA g^{-1} (C/5 rate of the theoretical capacity based on the one electron per MnO_2 , *i.e.* Mn^{4+} reduce to Mn^{3+} . (*ca.* 308.8 mAh g^{-1})), 154.4 mA g^{-1} (C/2 rate), 308.8 mA g^{-1} (1C rate), and 1.54 A g^{-1} (5C rate) in the potential range of -1.0 V to 0.2 V vs. Ag^+/Ag at 25°C .

ex situ XAS measurements

XAS measurements of the discharged/charged electrodes was conducted in the energy region of the Mn *K*-edge at room temperature in transmission mode at beam lines BL01B1 and BL14B2 of the SPring-8 synchrotron radiation facility in Hyogo, Japan. After the electrochemical measurements, the samples were rinsed several times with DMA and dried. The dried sample was mixed with boron nitride and pelletized, then sealed in laminated packets in an argon-filled globe box.

The local structural parameters were obtained from the curve fitting procedure against k^3 weighed EXAFS spectra by using REX2000 XAFS analysis software (Rigaku Co., Inc.).²¹ k -range is between 2.8 Å⁻¹ and 11.8 Å⁻¹. The effective back scattering, phase correction, and total central atom phase shift were calculated with the multiple-scattering theoretical calculation program, FEFF8.20.^{22, 23} For calculation of FEFF8.20, the model structure was determined by the reported structure of the MnO₂ nano sheet.^{19, 24}

5.3. Results & Discussions

Charge-discharge Properties of the MnO₂ nano sheets

Fig. 4-1 shows the initial discharge curves of the MnO₂ nano sheet dependence on the current densities. Results obtained by using Ag⁺/Ag reference electrode were converted to the potential versus Mg²⁺ / Mg on the basis on the reported values (-2.5V vs. Ag⁺/Ag).²⁵ We also confirmed the only AB composite electrode in this electrolyte.(in Fig.4-2.) There is 50 mAh g⁻¹ at 1st discharge, and few capacities at subsequent cycles. Then this discharge capacity is obtained by the reaction of the MnO₂ nano sheet with magnesium ions. The obtained initial discharged capacity at C/5 rate is about the theoretical capacity (*ca.* 308.8 mAh g⁻¹) of the



The redox potential value is near the reported one of the MnO_2 as a cathode in the magnesium battery electrolyte.^{26, 27} Moreover we also performed galvanostatic cycling at C/5 rate at 25°C. Fig. 4-3 shows the discharge/charge curves of the MnO_2 nano sheet in 0.2M $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ / DMA at 25°C. The current density is C/5 rate. MnO_2 nano sheet / AB composite show the excellent reversibility at C/5 rate at 25°C.

Another types of the MnO_2 cathode material for magnesium battery has been already reported.²⁶⁻³⁰ The hollandite type $\text{K}\alpha\text{-MnO}_2$ shows relatively poor rate performances (0.015C) and less cycle performances.²⁷ This phenomena originated from the reaction mechanisms because the reaction progressed only surface and MnO_2 convert to amorphous Mn_2O_3 and MgO , like a conversion reaction, and these phase change to the amorphous mixture of the (Mg, Mn)O phase only surface after cycling.³¹ Comparably, the rate properties of the MnO_2 nano sheets are high, and cycle properties are also good. Then the charge-discharge mechanism of the MnO_2 nano sheet indicates reversible adsorption/desorption reaction of the magnesium ions. We can use this material for the model electrodes to investigate the local structural change during charge transfer reaction.

X-ray absorption spectroscopy during discharging /charging

To clarify the structural change during discharging/charging, we performed Mn K-edge XAS measurements for the discharged and charged electrodes. The charge compensation mechanism was confirmed by XANES spectra, and local structural change was discussed by using EXAFS spectra.

Fig.4-4. shows the Mn K-edge XANES spectra of the Mg_xMnO_2 during charging/discharging. The dotted lines are reference compounds which have various valence state of the manganese. The position of the absorption edge energy reflect the information of the valence state of the Mn. MnO_2 , Mn_2O_3 , MnO correspond with Mn^{4+} , Mn^{3+} , and Mn^{2+} , respectively. For example, the absorption edge of the initial state of the MnO_2 nanosheet (show black line in Fig.4-4 (a)) is between MnO_2 one (show purple dotted line in Fig.4-4 (a)) and Mn_2O_3 one (show orange dotted line in Fig.4-4 (a)). The prepared MnO_2 nano sheet has TMA cation and their initial composition is $(\text{TMA})_{0.2}\text{MnO}_2$.¹⁹ Therefore, the valence state of the Mn is expected to +3.8. This is agreement with the results of the Mn K-edge XANES spectra. Then we used the absorption edge energies for the index of the valence state of the Mn ion.

During discharging/charging (adsorption/desorption of the magnesium ion), absorption edge of the Mn K-edge XANES are shifted to the lower/higher energies. This results indicated that the manganese ion compensate the charge during discharging/charging. This result corresponds with the galvanostatic experiments, and redox reactions are progressed during discharging/charging. Then the local structural change during charge transfer reaction can be discussed by the Mn K-edge EXAFS.

The local structural change of the MnO_2 nano sheets are investigated by the Mn K-edge EXAFS spectra. Fig.4-5 shows the Fourier transform (FT) magnitudes of k^3 -weighted Mn K-edge EXAFS oscillations during discharge and charge processes. The peak position of the FT magnitude spectrum represents the distance between absorbance atoms and the neighboring scattering atoms, in which the phase shift results in the deviation from the actual bond length. The peak intensity reflects the number of the coordination ions as well as the degree of the local distortion (Debye-waller (DW))

factor). The first main peak at 1.5 Å corresponds to the contribution of the Mn-O shell, and second peak at 2.5 Å corresponds to the contribution of the Mn-Mn shell. During discharging process (Fig.4-5 (a)), the two peaks intensity decrease suggesting an increase in the local structural distortion of Mn-O bonds and Mn-Mn bonds. The increase in the valence state of Mn cation imparts distortion in the MnO_6 owing to the Jahn-Teller effect of reduced Mn^{3+} ions. Therefore, the observed local structural changes are signature of changes in the oxidation state of Mn cations induced by the adsorption of the magnesium ion on to the MnO_2 nano sheets. This structural change is reversibly changed during charging shown in Fig.4-5 (b). More detail of the local structural change (atomic distances and debye-waller factor) of the MnO_2 nano sheets are determined by fitting results of the Mn *K*-edge EXAFS spectra.

The obtained values from the results of fitting of the Mn *K*-edge EXAFS are listed in Table 4-1, 4-2, and EXAFS spectra and fitting curves are shown in Fig.4-6. Fig.4-7. shows the plots of atomic distance and DW factor obtained by EXAFS analysis of Mn *K*-edge spectra dependence on the Mg contents in MnO_2 during discharging/charging. For EXAFS analysis, we assumed that the coordination number of the Mn-O shell and Mn-Mn shell have not changed during discharging/charging. Their coordination number is six. FT magnitude of the EXAFS spectra (especially Mn-Mn shell) is decreased with progression of the discharging. The residue of the fitting results of the $\text{Mg}_{0.5}\text{MnO}_2$ is high and the authenticity of the structural parameter (here, atomic distances and DW factor of Mn-O and Mn-Mn) of the $\text{Mg}_{0.5}\text{MnO}_2$ from the results of the fitting are less. Therefore the results of $\text{Mg}_{0.5}\text{MnO}_2$ are not plotted in Fig.4-7.

During discharging, the atomic distances of Mn-O are decreasing (Fig.4-7. (a)), and Mn-Mn is increasing (Fig.4-7. (b)), and DW factors of the Mn-O and Mn-Mn are

increasing. Then the distortion of their bonds is increased. After reduction of the Mn, Mn^{4+} is reduced to Mn^{3+} which is Jahn-Teller ions. Then the tetragonal distortion is occurred and Mn-O distance of the x and y directions (4direction) are decreased and z directions (2direction) are increased in the ordered octahedral MnO_6 . Then the average atomic distance of Mn-O is decreased during discharging. Moreover this local structural change makes strain in the nano sheet structure. As a result, the atomic distances of the Mn-Mn are increased and the distortion of Mn-O and Mn-Mn are increased. Then the adsorption of the magnesium onto the MnO_2 nano sheet makes large strain in the structure. This phenomenon hindered the high rate performances of the MnO_2 nano sheets. During charging, these parameters are reversibly changed, and their tendency of the local structural change are corresponded with the contents of the magnesium ions in the MnO_2 nano sheets (shown in Fig. 4-7 c, d, g, and h). At low rate conditions, these changes are reversibly.

To compare with the results of the lithium ion battery case, we performed Mn K-edge XAS for the MnO_2 nano-sheet adsorbed lithium ions. These samples have same valence states of manganese ions confirmed by Mn K-edge XANES in Fig.4-8. The absorption edges have same energies in the lithium and magnesium case. We can estimate the difference of the strain effect for the nano-sheet structures between lithium and magnesium. Fig.4-9. shows the FT magnitudes of k^3 -weighted Mn K-edge EXAFS oscillations after discharged in the Li electrolytes, and Mg electrolyte. The original vibration of the Mn K-edge EXAFS and their fitting results are also shown in Table 1, and Fig.6. Note that these spectra include same Jahn-teller effect derived from the Mn^{3+} in the nano-sheet structures. In the magnesium ion case, the peak intensities of the Mn-O and Mn-Mn shells are lower than them of lithium. The coordination number of

the MnO₂ nano-sheet has been expected not to change during adsorption/desorption of the carrier ions. Then this change indicates the increasing of the DW factors. Increasing the DW factor indicate the structural distortion for their bonds are increased. The quantities of the structural parameters are investigated by the curve fitting of the Mn K-edge EXAFS spectra. The obtained intensity of the Mn-Mn shell is low and divided to two different peaks. Then the residue of the fitting results is so large. Then the difference of the Mn-O shell is discussed. The difference of the average bond length of the Mn-O are similar, however, the difference of the DW factors are 15%.

We will discuss the effect of the difference of the carrier ions. From the obtained results, their average atomic distances of Mn-O are similar with each other. The magnesiated samples were decreased the Mn-O distances derived from the Jahn-teller effect. The oxidation state of the Mn is expected 3+. If Mn²⁺ ions are exists in the structure, there are no Jahn-teller effects and magnesiated samples show the tendency of the increasing of the Mn-O distances. Then the bond-length of the Mn-O is determined by the oxidation states of Mn. On the other hand, the DW factors are more difference between lithiated sample and magnesiated sample. Then the polarization effect of the magnesium ions induced local structural distortions for overall structure. This local structural distortion derived from the strong polarization effect of the divalent magnesium ions, not from the local valence of transition metals in the structure.

The schematic diagrams of the difference of the carrier ions are shown in Fig.4-10. When Mn⁴⁺ are reduced to Mn³⁺, Mn³⁺ induced Jahn-teller effects and make large tetragonal distortion in the MnO₆ octahedral units. This local structural change affect for the overall nano sheet structure, and cause large strain effect. These reactions are same even supposing that the difference of the carrier ions. However, in the magnesium ion

battery case, the distortions of the bonds in the structure are large due to their strong polarization characters. Then the main problems for the transition metal oxide based cathode materials of the magnesium ion batteries is the strong interactions between magnesium ions and host structure. This phenomenon indicates the hamper to obtain the high rate capability of the cathode materials based on the transition metal oxide for magnesium rechargeable battery.

5.4. Conclusions

We performed the discharge/charge experiments for the MnO_2 nano-sheets in the magnesium electrolytes. The MnO_2 nano-sheets show the excellent rate and cycle performances due to the adsorption/desorption mechanisms with charge compensation of the manganese ion. Then MnO_2 nano-sheets are used as model electrodes to investigate the local structural change during charge transfer reactions. The Mn *K*-edge EXAFS spectra was suitable tool to analyze the local structural change. During discharging in the magnesium electrolytes, Mn-O distances are decreased, and Mn-Mn distances are increased. This structural change derives from the Mn^{3+} which induces the Jahn-teller effect. Finally, we draw a comparison between lithium and magnesium as carrier ions. The Mn-O distances are similar values each other, however, the DW factor of the magnesium ion case is larger than that of lithium ion case. This result indicates the structural distortions are affected by the interaction between magnesium ion and host structure due to strong polarization characters of the divalent magnesium ions. This charge density effect is the problems to enhance the reaction kinetics and reversibility of the cathode materials based on the transition metal oxide.

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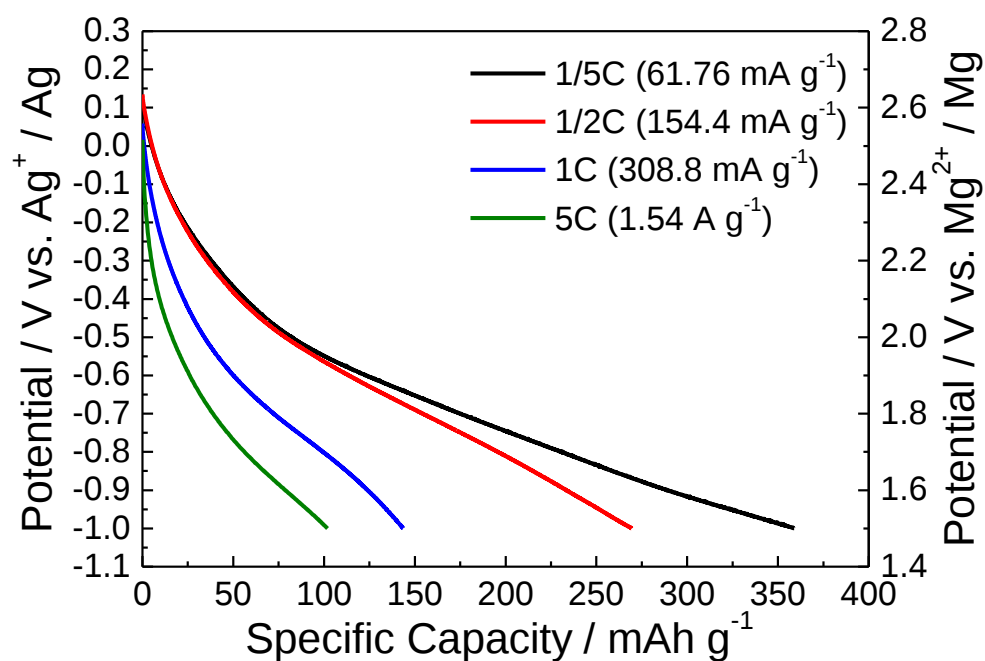


Fig. 4-1. Initial discharge curves of the MnO₂ nano sheets in 0.2M Mg(CF₃SO₃)₂ / DMA at 25°C dependence on the current densities.

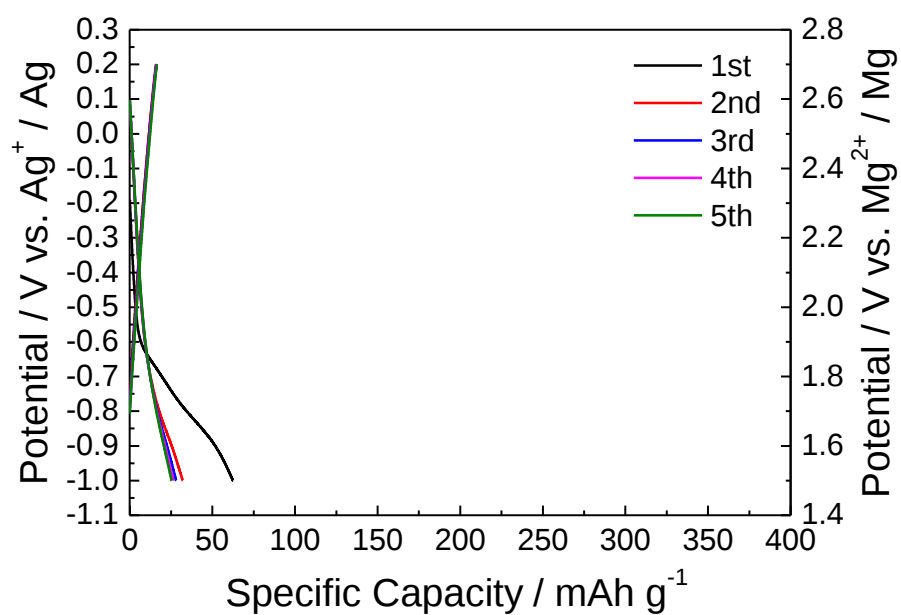


Fig. 4-2. Charge-discharge curves of composite electrode composed with Acetylene black and PTFE binder in 0.2M $\text{Mg}(\text{CF}_3\text{SO}_3)_2$ / DMA at 25°C. The current density is $61.76 \text{ mA g}^{-1}_{\text{-MnO}_2}$.

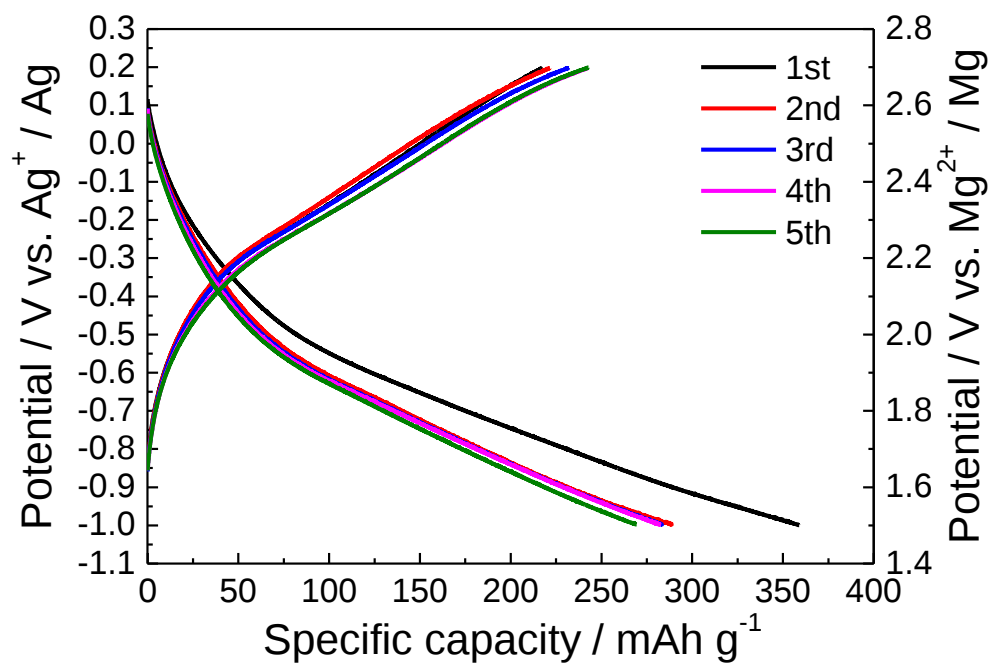


Fig. 4-3. Charge-discharge curves of the MnO_2 nano sheets in $0.2\text{M Mg}(\text{CF}_3\text{SO}_3)_2$ / DMA at 25°C . The current density is $61.76 \text{ mA g}^{-1} (\text{C}/5)$.

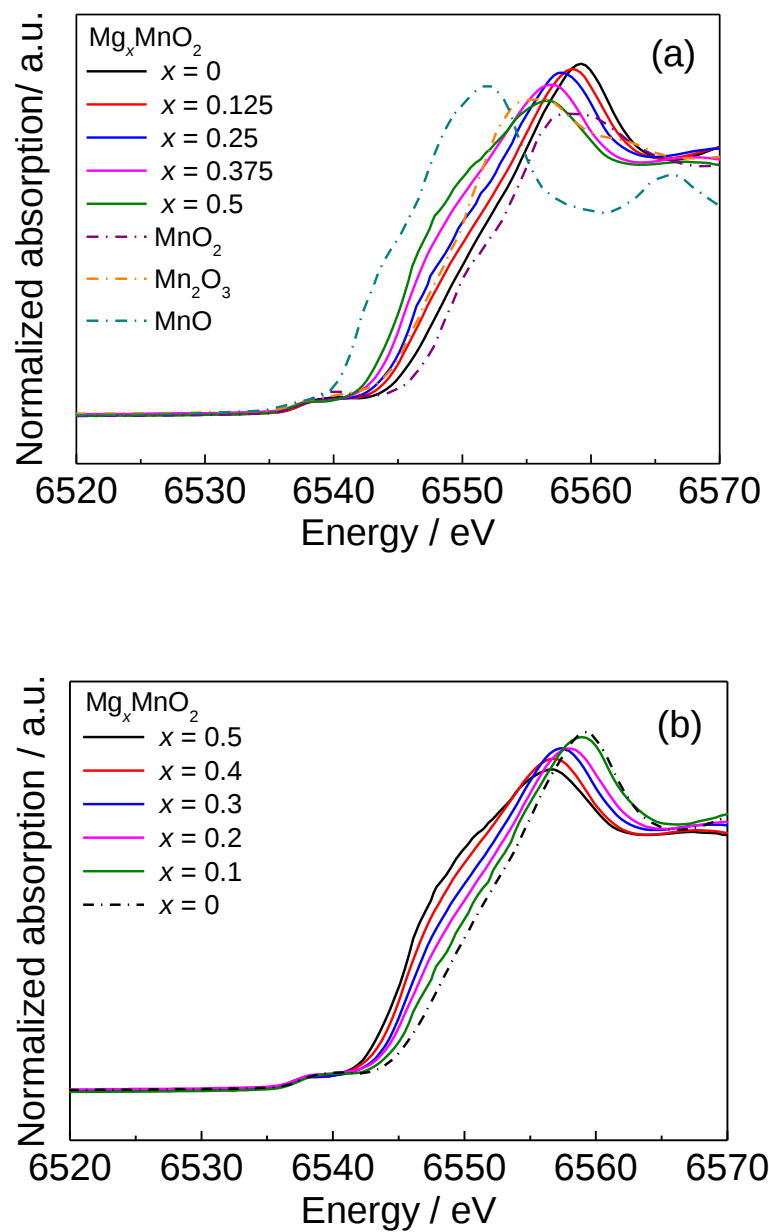


Fig. 4-4. Mn K-edge XANES spectra measured (a) for Mg_xMnO_2 electrodes ($x = 0$, 0.125, 0.25, 0.375, 0.5) during discharging and reference compounds (MnO_2 , Mn_2O_3 , and MnO), (b) for Mg_xMnO_2 electrodes ($x = 0.5$, 0.4, 0.3, 0.2, 0.1) during charging and pristine MnO_2 nano sheets.

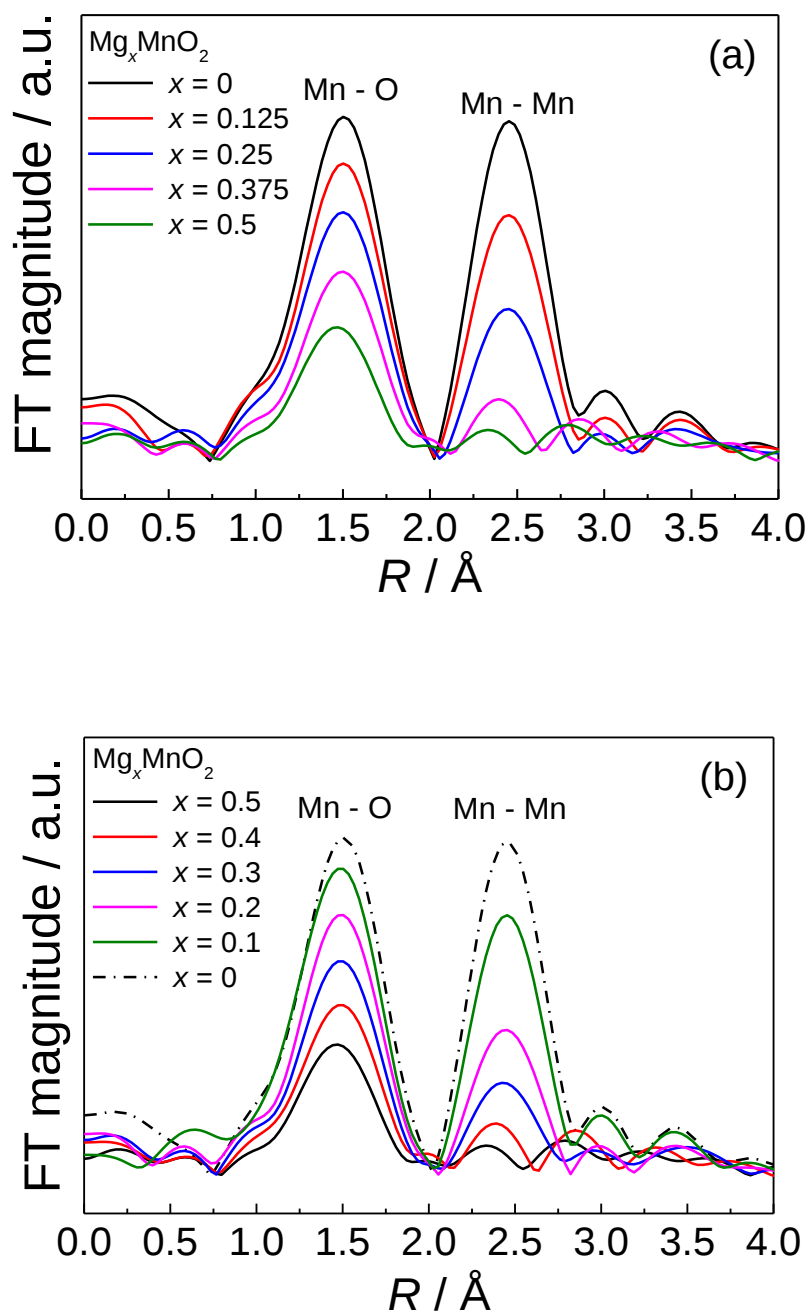


Fig. 4-5. Fourier Transformation of Mn K-edge EXAFS spectra (a) for Mg_xMnO_2 electrodes ($x = 0, 0.125, 0.25, 0.375, 0.5$) during discharging, and (b) for Mg_xMnO_2 electrodes ($x = 0.5, 0.4, 0.3, 0.2, 0.1$) during charging and pristine MnO_2 nano sheet.

Table 4-1. Structure parameters which are coordination number (N), inter atomic distances (R), and DW factor (σ) for Mg_xMnO_2 ($x = 0, 0.125, 0.25, 0.375, 0.5$) during discharging, and Li absorbed MnO_2 nano sheets. The results of the Li has the same valence of $\text{Mg}_{0.5}\text{MnO}_2$ from the results of the Mn *K*-edge XANES.

x	Shell	N	R/ Å	σ / Å	Residue/ %
0	Mn-O	6	1.896	0.093	4.07
	Mn-Mn	6	2.888	0.103	
0.125	Mn-O	6	1.893	0.101	6.71
	Mn-Mn	6	2.9	0.117	
0.25	Mn-O	6	1.889	0.112	9.22
	Mn-Mn	6	2.911	0.14	
0.375	Mn-O	6	1.871	0.129	17.5
	Mn-Mn	6	2.918	0.188	
0.5	Mn-O	6	1.842	0.151	26.8
	Mn-Mn	6	2.879	0.2	
Li	Mn-O	6	1.848	0.131	22.4
	Mn-Mn	6	2.809	0.174	

Table 4-2. Structure parameters which are coordination number (N), inter atomic distances (R), and DW factor (σ) for Mg_xMnO_2 ($x = 0.5, 0.4, 0.3, 0.2, 0.1$) during charging determined by Mn K-edge EXAFS spectroscopy

X	Shell	N	R/ Å	σ / Å	Residue/ %
0.5	Mn-O	6	1.842	0.151	26.8
	Mn-Mn	6	2.879	0.2	
0.4	Mn-O	6	1.863	0.134	21.3
	Mn-Mn	6	2.909	0.198	
0.3	Mn-O	6	1.881	0.121	12.5
	Mn-Mn	6	2.922	0.163	
0.2	Mn-O	6	1.886	0.109	8.78
	Mn-Mn	6	2.901	0.142	
0.1	Mn-O	6	1.893	0.1	7.61
	Mn-Mn	6	2.891	0.115	

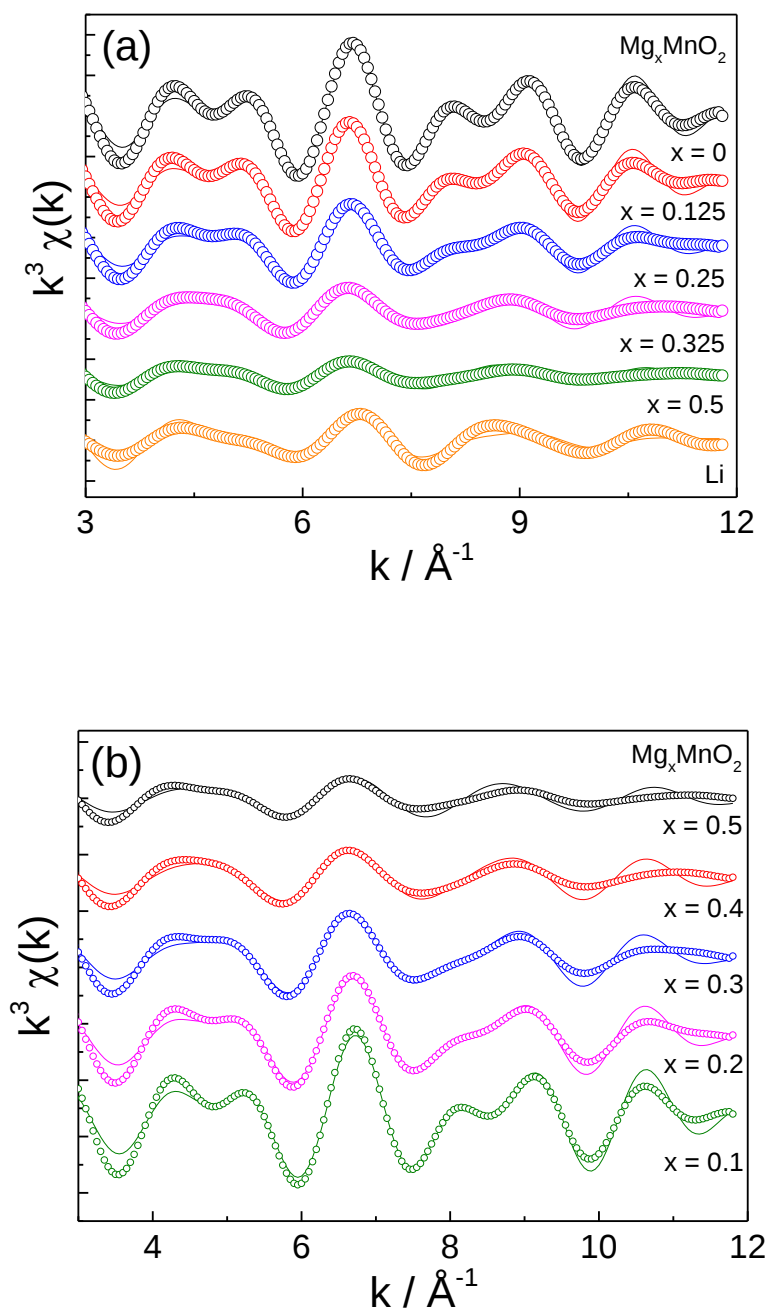


Fig. 4-6. Results of curve-fitting procedure for inverse FT spectra of Radial structure function for Mn *K*-edge EXAFS for (a) Mg_xMnO_2 ($x = 0, 0.125, 0.25, 0.375, 0.5$) during discharging, and Li adsorbed MnO_2 nano sheets, and (b) Mg_xMnO_2 ($x = 0.5, 0.4, 0.3, 0.2, 0.1$) during charging. *K* range is between $2.8 \text{ \AA}^{-1}$ and $11.8 \text{ \AA}^{-1}$.

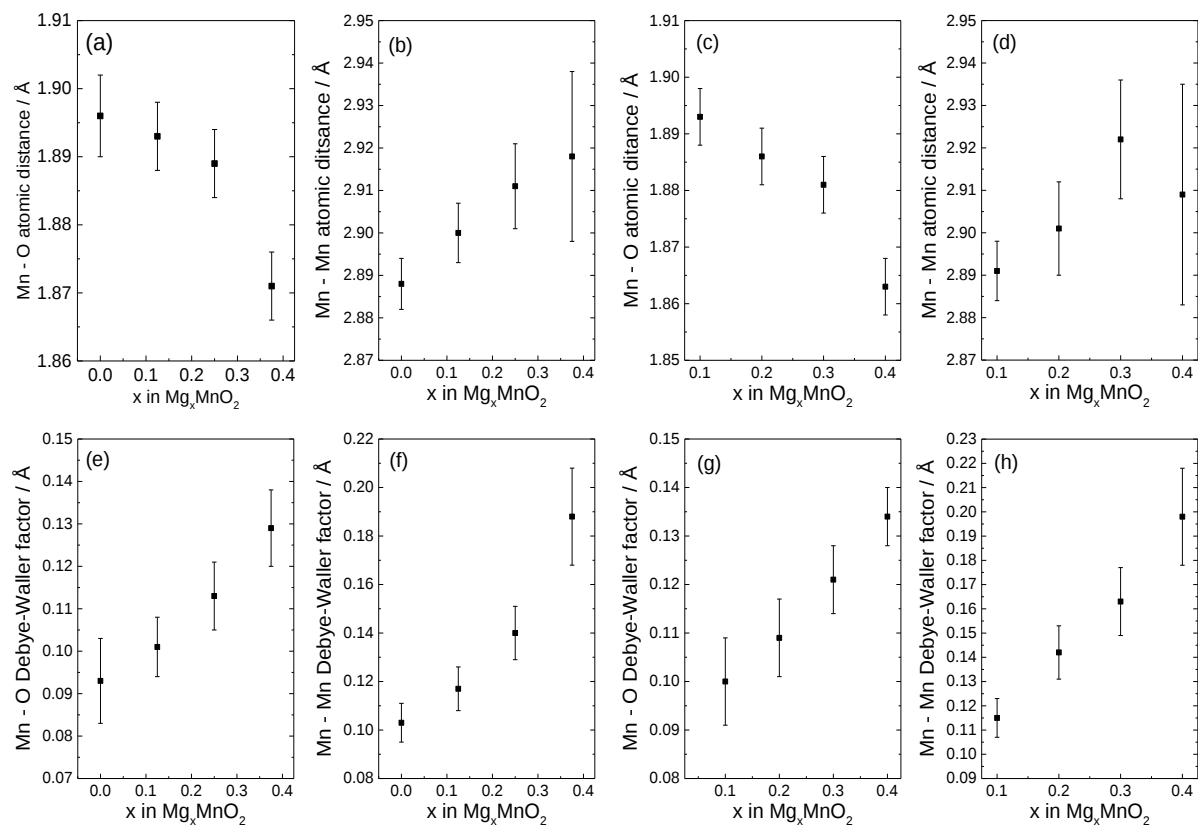


Fig. 4-7. Plots of atomic distance(a,b : discharging, c,d : charging) and Debye-Waller (DW) factor (e,f : discharging, g,h : charging)obtained by EXAFS analysis of Mn *K*-edge spectra for Mg_xMnO₂ (*x* = 0, 0.125, 0.25, 0.375) during discharging and Mg_xMnO₂ (*x* = 0.1, 0.2, 0.3, 0.4) during charging.

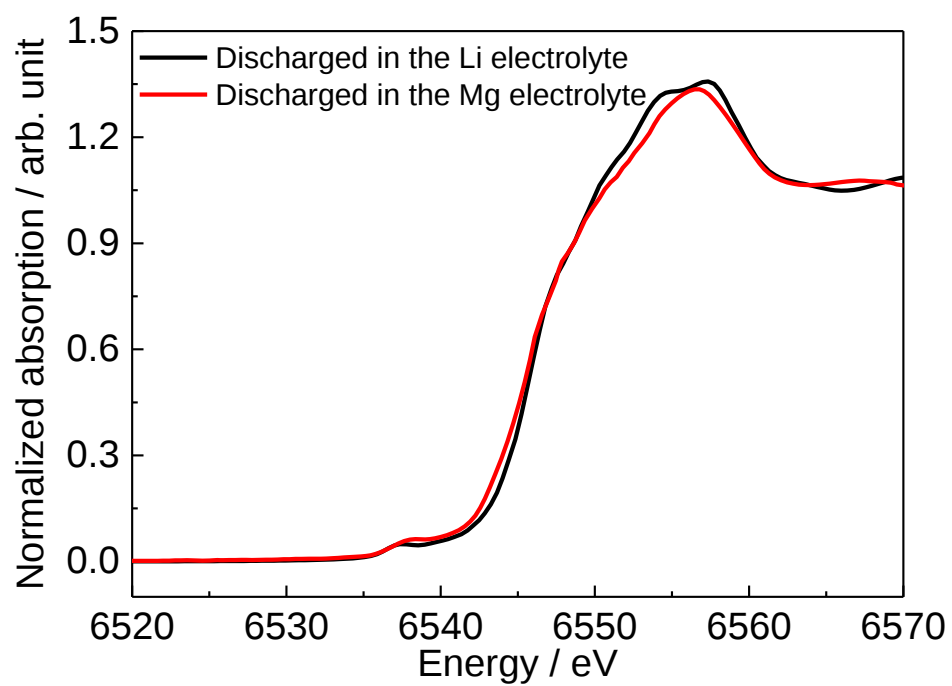


Fig. 4-8. Mn *K*-edge XANES spectra measured for discharged MnO₂ electrodes in the various electrolytes.

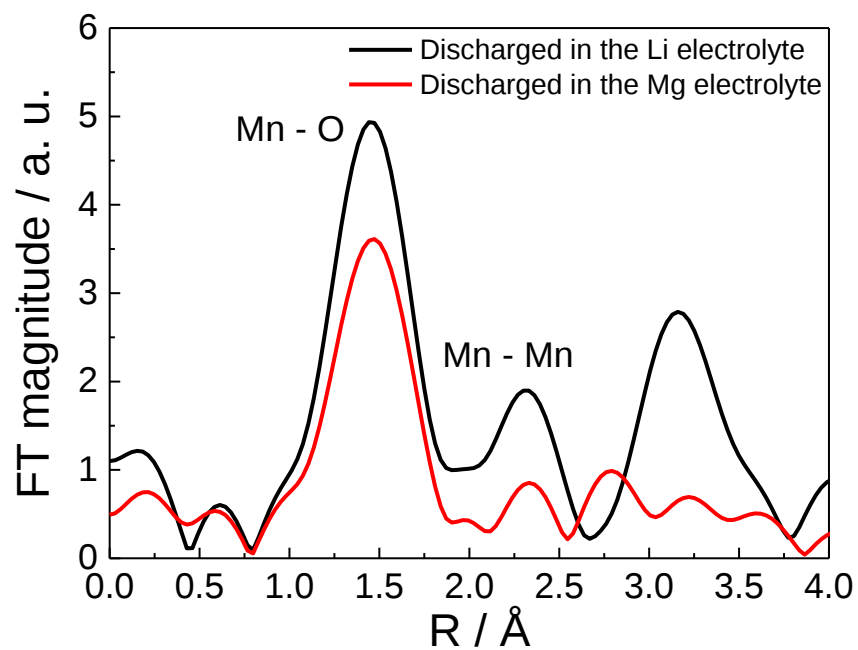


Fig. 4-9. Fourier Transformation of Mn *K*-edge EXAFS spectra of the MnO₂ nano-sheet discharged in the various electrolytes.

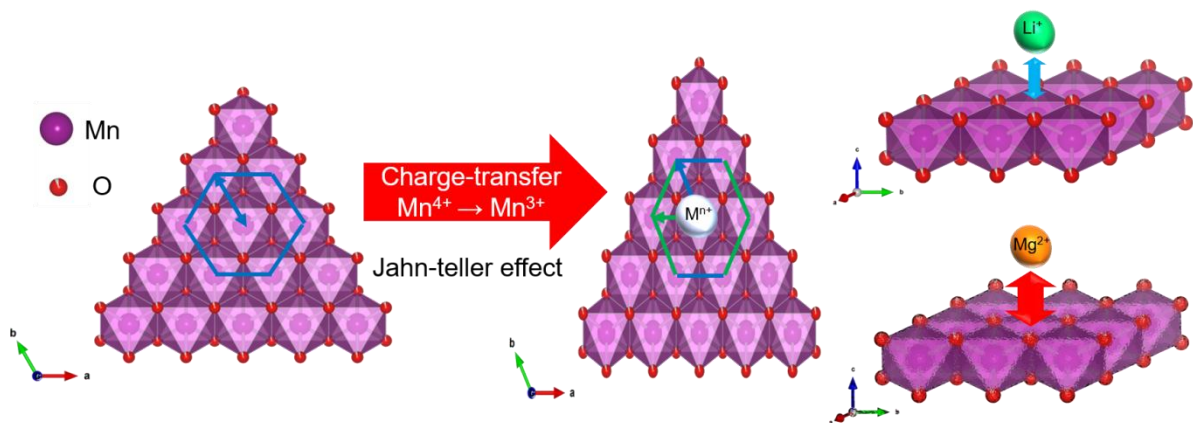


Fig. 4-10. Schematic diagrams of local structural change during charge transfer reaction of the MnO_2 nano-sheets. The magnesium ions have strong interactions between it and MnO_2 nano-sheets structures.

Chapter 5: Anti-site Mixing Governs Electrochemical Performances of Olivine-type MgMnSiO_4 Cathode for Rechargeable Magnesium Battery

5.1. Introduction

Rechargeable magnesium battery is a viable candidate for next-generation battery systems,¹ because magnesium, which is used as the anode in these batteries, has a theoretically high energy density, low cost, and stability.^{2, 3} Although magnesium battery technology has been a subject of intensive research over the decades, the performance of magnesium batteries has still not reached the level of lithium ion batteries that are currently used.^{1, 2, 4-11}

Magnesium battery suffers from a low cell voltage, low capacity, and low diffusivity of the magnesium ion, due to the limitations of the choice of the cathode materials. A number of cathode materials for magnesium batteries have been reported, such as Chevrel phases,^{1, 12, 13} V_2O_5 ,^{5, 14} and nanomaterials.^{6, 9} However, the intrinsically low diffusion of the divalent magnesium ion in the solid electrode structure^{15, 16} has hampered the improvement of the performance of magnesium cathodes.

We have recently reported that a polyanion compound, MgFeSiO_4 , is a promising cathode material for magnesium batteries.¹⁷ However, the crystal structure of MgFeSiO_4 exhibits anti-site mixing between Mg and Fe, which might disturb the diffusion of the magnesium ion in the host structure. In order to maintain the diffusion path in the host structure, we herein investigated olivine-type MgMSiO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{or Ni}$). Because the olivine-type structure in LiFePO_4 , which has a one-dimensional (1D)

path,^{18, 19} exhibits high diffusivity of the lithium ion,²⁰ it is expected that the magnesium ion in the olivine structure will exhibit high diffusivity. Moreover, olivine-type MgMSiO_4 shows high theoretical capacity that exceeds 300 mAh g^{-1} and high theoretical redox potential (4.1V for $\text{Mn}^{4+}/\text{Mn}^{3+}$ and 3.0V for $\text{Mn}^{3+}/\text{Mn}^{2+}$).²¹ The synthesis and electrochemical performance of MgMSiO_4 have been reported by NuLi *et al.*^{7, 22-27} However, its innate electrochemical properties have not been examined because the electrochemical reaction from the copper current collector with the electrolyte also affects its performance, as reported recently.²⁸

We try to measure the electrochemical properties of MgMnSiO_4 synthesized by the flux method at 1000°C ²² on a Cu foil in 0.25 M $\text{Mg}(\text{AlCl}_2\text{EtBu})_2/\text{THF}$ electrolyte. The observed results are shown in Fig. 5-1. The charge–discharge behavior of MgMnSiO_4 resembles the reported one.²² However, the redox potential of MgMnSiO_4 are lower than the theoretical values.²¹ We measured the Mn K-edge X-Ray absorption spectroscopy (XAS) for both charged and discharged electrodes. The Mn K-edge X-Ray absorption near edge structure (XANES) spectra are shown in Fig. 5-2. If the Mn atoms take part in the reduction/oxidation along with magnesium insertion/deinsertion, the Mn K-edge XANES spectra would be shifted to lower/higher energies after discharging/charging. However, Mn K-edge XANES spectra do not shift with charging/discharging. This behavior indicates that the Mn atoms in MgMnSiO_4 do not contribute to the redox reaction. For the reported measurements, it is expected that the capacity of MgMnSiO_4 includes subreactions from the components of the composite electrodes. We tested the electrochemical window of the only Cu current collector in the 0.25 M $\text{Mg}(\text{AlCl}_2\text{EtBu})_2/\text{THF}$ solution. Figure 5-3 shows the charge–discharge curves of the Cu foil in 0.25 M $\text{Mg}(\text{AlCl}_2\text{EtBu})_2/\text{THF}$ solution. The results show that the

charge–discharge of the Cu current collector resembles the behavior of Fig. 5-1. The Cu current collector is not stable in this electrolyte.²⁸ Hence, it is desirable to understand the determinant factor affecting the electrochemical properties of MgMSiO₄.

The rate performance of olivine-type LiFePO₄ is significantly affected by anti-site mixing that occurs between Li and Fe.^{29, 30} We speculate anti-site mixing to also occur in the olivine framework of MgMSiO₄ during magnesium ion diffusion. For intercalation materials with 1D frameworks, a smooth path through which ions transit would be more favorable. We conjecture this aspect to be enhanced the diffusivity of magnesium ions, especially in magnesium battery cathodes, considering the intrinsically sluggish diffusion of magnesium ions within the host structures.

Olivine-type MgMSiO₄ comprises SiO₄⁴⁻ tetrahedra, with M²⁺ and Mg²⁺ occupying corner-shared octahedral positions (M2 site) or chains of edge-sharing octahedral positions (M1 site), as shown in Fig. 1. The M2 site is larger than the M1 site. The cations occupying the M1 site diffuse into the host structure. Site occupancies of these two different sites change, depending on the transition metal cation.³¹⁻³⁵ Among the several transition metal cations, the manganese ion preferentially occupies the M2 site because its ionic radius is larger than that of the magnesium ion.^{31, 33} Therefore, we investigated MgMnSiO₄ as a cathode material for the magnesium battery. The temperature dependence of the degree of anti-site mixing between Mg and Mn was reported.³³ We investigated the effect of the anti-site mixing ratio on the electrochemical properties of olivine-type MgMnSiO₄ by changing the synthesis temperature. In addition, the mechanism for charge-discharge reaction in MgMnSiO₄ magnesium battery cathode is analyzed by X-ray diffraction and X-ray absorption spectroscopy.

5.2. Experimental

Material synthesis.

MgMnSiO₄ was prepared by the flux method. In brief, MgO (Wako pure chemical Industries, >99.9%), MnCO₃ (Kojundo chemical laboratory, >99.9%), and SiO₂ (Kanto Kagaku, >99.9%) were weighed in a molar ratio of 1:1:1, followed by ball-milling in ethanol with a rotation speed of 300 rotations per minute. The mixed powder was combined with flux powders in the molar ratio of 1:4 in an Ar-filled glove box. The resulting materials were used as a precursor that was calcined at various temperatures under a 3% H₂ (Ar balance) gas flux. The products were washed with distilled water and filtered. The materials were thereafter dried in a vacuum oven at 120 °C for 2 h. To change the synthesis temperature, we used KCl for synthesis at 900 °C and 1000 °C, NaCl-KCl at 700 °C, and LiCl-KCl at 450 °C and 500 °C as fluxes. The crystal structures of the as-prepared powders were characterized on a Rigaku Rint-2200 diffractometer using Cu K α radiation at room temperature. The diffraction data were collected in the 2 θ range 10°–80° with a step size of 0.02°. Rietveld analyses were performed using high-resolution synchrotron X-ray diffraction (SXRD) (BL02B2 beam line, SPring-8, Japan). The synchrotron XRD data were collected at room temperature using a large Debye–Scherrer camera with an imaging plate. The diffraction patterns were recorded in the 2 θ range of 3°–75° with a step size of 0.01°. The X-ray wavelength was $\lambda = 0.49995$ Å, calculated by using CeO₂ as a standard. The crystal structure was refined by the Rietveld method with the RIETAN-FP program.³⁶ Particle size was measured by scanning electron microscopy (S-5500, Hitachi).

Electrochemical test

Electrodes were prepared by using the MgMnSiO_4 -active material, carbon (acetylene black), and polytetrafluoroethylene (PTFE) binder, with a weight ratio of 55:40:5. The dried active electrodes were pressed on a Pt mesh as the working electrode, and the typical mass loading of the active powder was ca. 15 mg/cm^2 . Thereafter, the electrode was dried in vacuum at room temperature. Electrochemical measurements were performed using sealed three-electrode glass cells. The electrolyte used was 0.5 M magnesium (trifluoromethanesulfonyl) amide ($\text{Mg}(\text{TFSA})_2$) in acetonitrile (Kishida Chemicals). A Mg ribbon and Pt mesh were used as the anode and the current collector, respectively. As a reference electrode, a Ag wire was inserted into a solution of 0.01 M AgNO_3 and 0.5 M $\text{Mg}(\text{TFSA})_2$ in acetonitrile. This solution, contained in an additional glass tube, was brought into contact with the $\text{Mg}(\text{TFSA})_2$ /acetonitrile solution *via* a micro porous glass membrane. To minimize the effect of the IR drop associated with electrolyte resistance, the tip of the capillary was placed as close as possible to the working electrode. The cell assembly was carried out in a glove box under argon atmosphere. Galvanostatic charge and discharge measurements in the electrolytic window range varying from -1.2 to 1.5 V vs. Ag^+/Ag were carried out at 55 °C. The obtained potential vs. Ag^+/Ag was converted vs. Mg^{2+}/Mg under 2.5 V.³⁷ We confirmed that the Pt current collectors and the electrolyte were stable in these experiments. Based on theoretical calculation, it is estimated that the potential of MgMnSiO_4 will exceed the electrochemical window of the conventional electrolyte such as a Grignard reagent.²¹ To measure the charge–discharge experiment of MgMnSiO_4 , we need a highly stable electrolyte. We selected $\text{Mg}(\text{TFSI})_2$ /acetonitrile (AN) as the electrolyte, and measures the electrochemical window of various current collectors. Figure 5-4 shows the electrochemical window of the aluminum, stainless steel (SUS), and platinum

current collectors. Our results show that platinum is the most stable current collector. Finally, we investigated the electrochemical window of the composite electrode without any active material, i.e., the electrode comprising acetylene black, a PTFE binder, and a Pt mesh current collector. Figure 5-5 shows the charge–discharge curves of the composite electrode without any active material. The electrochemical window is observed at -1.2 to 1.5 V vs. Ag^+/Ag (which translates to about 1.3–4.0 V vs. magnesium³⁷) without active materials. Hence, we were able to determine the performance of the MgMnSiO_4 cathode.

XAS and XRD measurements

After the electrochemical measurements, the electrodes were rinsed several times with acetonitrile, and thereafter characterized with X-ray absorption spectroscopy (XAS) and XRD without air exposure. Both charged and discharged $\text{Mg}_{1-x}\text{MnSiO}_4$ electrodes were intimately mixed with boron nitride powders and pressed into pellets with a diameter of 10mm. The pellets were sealed in aluminum-laminated packets in an argon-filled glove box. XAS measurements were performed on the beamline BL01B1 at SPring-8 (Hyogo, Japan). The synchrotron radiation X-ray from the storage ring was monochromated by a Si 111 crystal. Mn K-edge XAS measurements were performed at room temperature in the transmission mode using two ion chambers. The energy scale was calibrated using Cu and Mn foils. The XRD patterns of $\text{Mg}_{1-x}\text{MnSiO}_4$ electrodes were collected at the beamline BL02B2, SPring-8, equipped with a large Debye–Scherrer camera. The wavelength of the incident X-ray beam was set to 0.49862 Å.

5.3. Results & Discussions

The XRD patterns of phase-pure MgMnSiO_4 prepared at various temperatures and the schematic projection of the olivine-type structure are shown in Fig. 5-6. Olivine-type MgMnSiO_4 comprises SiO_4^{4-} tetrahedra, with the Mn^{2+} and Mg^{2+} occupying the M2 and M1 sites, respectively (Fig. 5-6). No impurity peaks were detected and all the peaks were fully indexed to the *Pnma* orthorhombic space group. The diffraction peaks become broader on decreasing the synthesis temperature, indicating a decrease in the crystallite size of MgMnSiO_4 with synthesis temperature. The estimated crystallite sizes based on the diffraction peak indexed as 311 are provided in Fig. 5-7. The crystallite size for the sample prepared at 1000 °C is about 100 nm, while the samples synthesized at 700 °C, 500 °C, and 450 °C are about 30 nm. A similar estimate of the crystallite size with less deviation was obtained using other Bragg diffraction peaks. It is therefore clear that high-temperature synthesis leads to crystallite growth. Moreover, a change in the intensity ratio of some diffraction peaks owing to the increase in the synthesis temperatures is also apparent. At the Bragg peak position of $2\theta = 35^\circ$, the intensity of the 311 diffraction peak is higher than that of the 121 peak for MgMnSiO_4 prepared at 450 °C. The intensity ratio of diffraction peak 311 to that of 121 is almost similar for the samples synthesized at both 900 °C and 1000 °C. In the MgMnSiO_4 system, anti-site mixing between Mg and Mn is more pronounced, especially when synthesized at high temperatures.^{31, 33}

The anti-site mixing changes the intensity of the diffraction peaks, and thus, the intensity ratio of peaks 311/121 derived from the XRD pattern can be a straightforward descriptor of the extent of cationic anti-site mixing. The simulated diffraction patterns based on the anti-site cationic mixing are also shown in Fig. 5-6 using reported lattice

parameters.³⁸ While the intensity of the 311 diffraction peak is higher than that of the 121 peak when there is hardly any anti-site mixing, the intensity of the 121 diffraction peak becomes higher than of 311 with anti-site mixing. The observed change in the peak intensity is caused by the change in the cationic mixing ratio. For a quantitative analysis, Rietveld analysis was also performed (Figs. A5-1–A5-5 and Tables A5-1–A5-6 in the Supporting Information). The mixing ratio can be calculated based on the occupancy value of the M1 site. A low occupancy value reflects a higher concentration of anti-site mixing between Mg and Mn ions. The occupancy of the Mg ion on the M1 site is plotted as a function of the synthesis temperature in Fig. 5-7. Synthesis at high temperatures increases the cationic anti-site mixing; this mixing can be suppressed by decreasing the synthesis temperature. These results are in good accord with the reported observations based on temperature-dependent neutron diffraction measurement of MgMnSiO_4 .^{31, 33} Our results show that anti-site mixing is more pronounced in samples synthesized at high temperatures.

Further, SEM images for MgMnSiO_4 prepared under various temperatures (Fig. 5-8), indicate that the particle size is highly influenced by the synthesis temperature. A diminution in the particle size from 180 nm (for the sample synthesized at 1000 °C) to 55 nm (for the sample synthesized at 450 °C) is observed. This leads us to conclude that low-temperature synthesis suppresses the increase in the particle size, which is consistent with the lower crystallite size estimate based on XRD analysis.

Importantly, the (dis)charge capacity in MgMnSiO_4 is influenced by the synthesis temperature. (Dis)charge-capacity profiles measured at 55 °C are shown in Fig. 5-9. A large polarization is observed between the charge and discharge curves, which we ascribe to the sluggish kinetics of Mg^{2+} within the olivine framework of MgMnSiO_4 . An

initial discharge capacity of 111 mAh g⁻¹ at the C/20 rate is observed for samples synthesized at 450 °C. The average voltage is ca. 2.9 V vs. Mg²⁺/Mg, which is a high voltage experimentally reported in the cathode materials of magnesium batteries. This value is similar to the calculated redox potential of the Mn²⁺/Mn³⁺ redox couple.²¹

The improvement factor of the capacity are related with the decreased anti-site mixing ratio coupled with the reduced particle size. As olivine-structured materials are deemed to possess the 1D diffusion path akin to that of LiFePO₄, anti-site mixing between Mg and Mn in the M1 site might obstruct the diffusion of Mg²⁺ during Mg (de)insertion. In contrast, a decrease in the particle size can circumvent the slow diffusivity of carrier ions. The particle size for MgMnSiO₄ samples synthesized at 450 °C is similar to that at 700 °C; however, the size of MgMnSiO₄ particles is much smaller than that for the samples synthesized at 1000 °C. If the particle size is the dominant factor underlying the improved electrochemical performance, a remarkable improvement in the capacity should be observed for the samples synthesized at 700 °C and 1000 °C. Nonetheless, the present results prove otherwise. Anti-site mixing is 20% for the samples synthesized at 450 °C, while it is 30% and 33% for those synthesized at 700 °C and 1000 °C, respectively. The obtained capacity shows a similar trend, with a significant improvement on decreasing the temperature from 700 °C to 450 °C. Therefore, the dominant factor underlying the improved capacity is anti-site mixing between Mg and Mn ions.

To investigate the Mg (de)insertion mechanism of MgMnSiO₄, XRD and XAS measurements were performed. The XRD patterns at various charge and discharge states are shown in Fig. 5-10. No extra diffraction peaks were observed during both charge and discharge processes, and the peak slightly shifted to higher or lower position with

charging or discharging, respectively. The lattice constants also decrease or increase with charging or discharging, respectively (Table 5-1 in the Supporting Information). These observations suggest that Mg^{2+} extraction/insertion from/into MgMnSiO_4 proceeds *via* a single-phase mechanism.

The X-ray absorption near edge structure (XANES) spectra of $\text{Mg}_x\text{MnSiO}_4$ electrodes during the charge processes are shown in Fig. 5-11. The oxidation state of Mn can be estimated from the XANES spectra at the Mn *K*-edge. Increase in the oxidation state of Mn shifts the absorption edge toward higher energy. This observation indicates that charge neutrality during Mg^{2+} extraction is maintained by the oxidation of the Mn ion. Local structural changes around the Mn ion during Mg^{2+} extraction were also probed by extended x-ray absorption fine structure (EXAFS) analysis. Fourier transforms (FT) magnitudes of k^3 -weighted EXAFS oscillations during charge-discharge processes are shown in Fig. 5-12. The peak position of the FT magnitude spectrum represents the distance between the absorbance atoms and the neighboring scattering atoms, in which the phase shift results in the deviation from the actual bond length. The peak intensity reflects the number of the coordination ions as well as the degree of local distortion. The first main peak at 1.5 Å corresponds to the contribution of the Mn-O shell. During the charging process, the peak intensity decreases, suggesting an increase in the local structural distortion of Mn-O bonds. During charging, the increase in the valency state of the Mn cation imparts distortion to MnO_6 owing to the Jahn-Teller effect of oxidized Mn^{3+} ions. Therefore, changes in the observed local structure imply changes in the oxidation state of Mn cations induced by the extraction of Mg^{2+} in MgMnSiO_4 . The Fourier transform of the extended X-ray absorption fine structure reflects increase in the local structural distortion of Mn-O

bonds. During charging, the increase in the valency state of Mn ions causes distortion in MnO_6 owing to the Jahn-Teller effect of oxidized Mn^{3+} ions.

5.4. Conclusions

The degree of cationic anti-site mixing impacts the electrochemical performance of MgMnSiO_4 . Our study reveals that low synthesizing temperatures of MgMnSiO_4 suppress the anti-site mixing between magnesium and manganese ion. The charge–discharge reaction in MgMnSiO_4 is performed in a single-phase reaction, and the charge is compensated by change in the valence state of the Mn ion. This study reveals that the performance of rechargeable magnesium battery cathodes is mainly influenced by the diffusion of magnesium ion in solid electrodes. It also demonstrates that the diffusion path is a decisive factor for designing high-performance olivine-type cathode materials for magnesium batteries.

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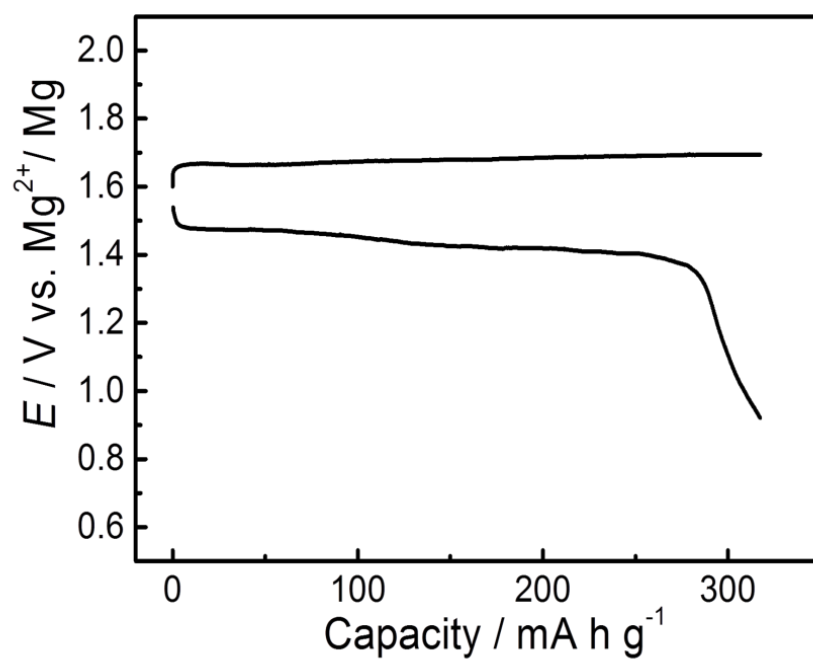


Fig.5-1 Charge-Discharge Curves of the MgMnSiO_4 on Cu foil current collector in 0.25M $\text{Mg}(\text{AlCl}_2\text{EtBu})_2$ / THF electrolyte at 25°C.

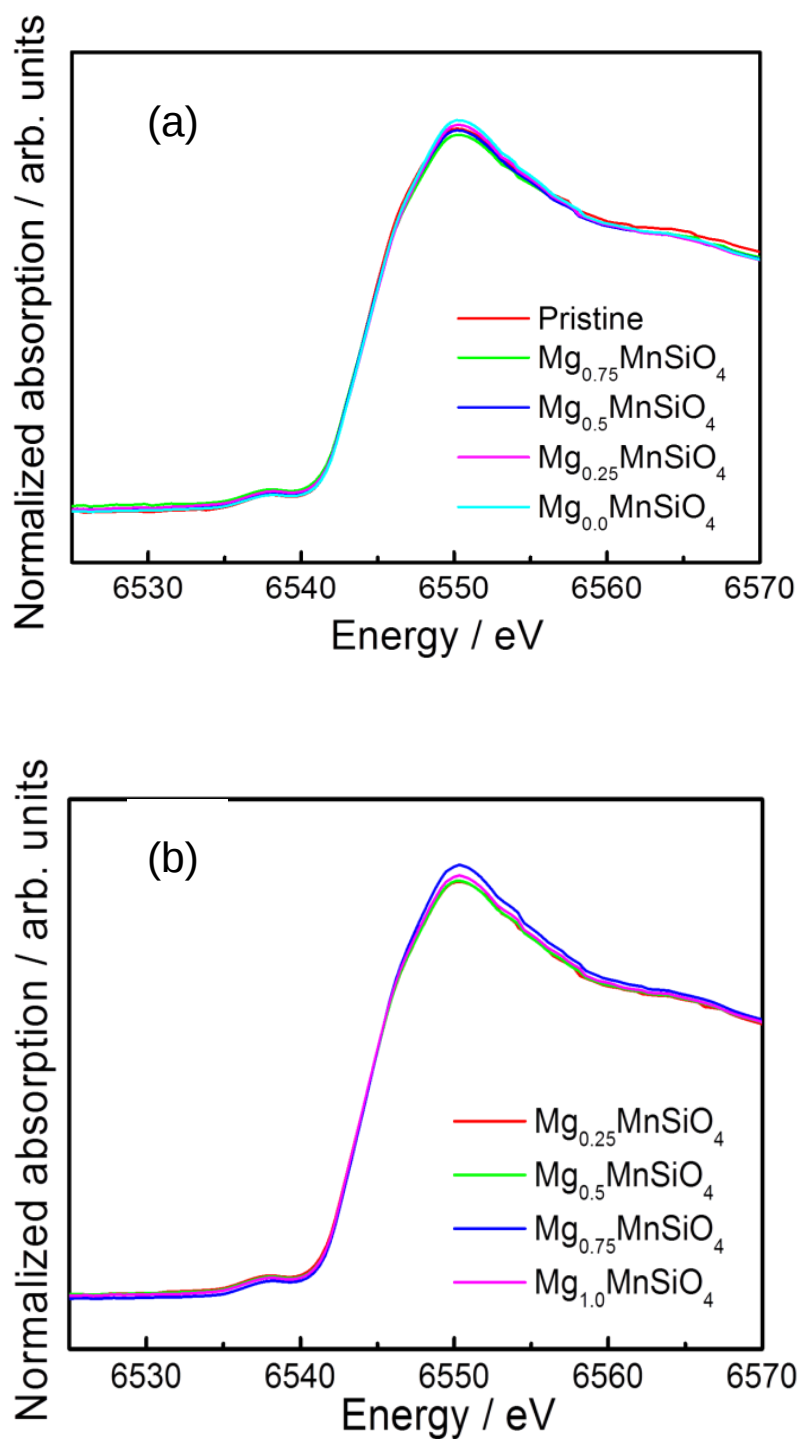


Fig.5-2 Mn K-edge XANES spectra of the $\text{Mg}_x\text{MnSiO}_4$ ($x = 1.0, 0.75, 0.5, 0.25, 0.0$) for (a) charging, and (b) discharging.

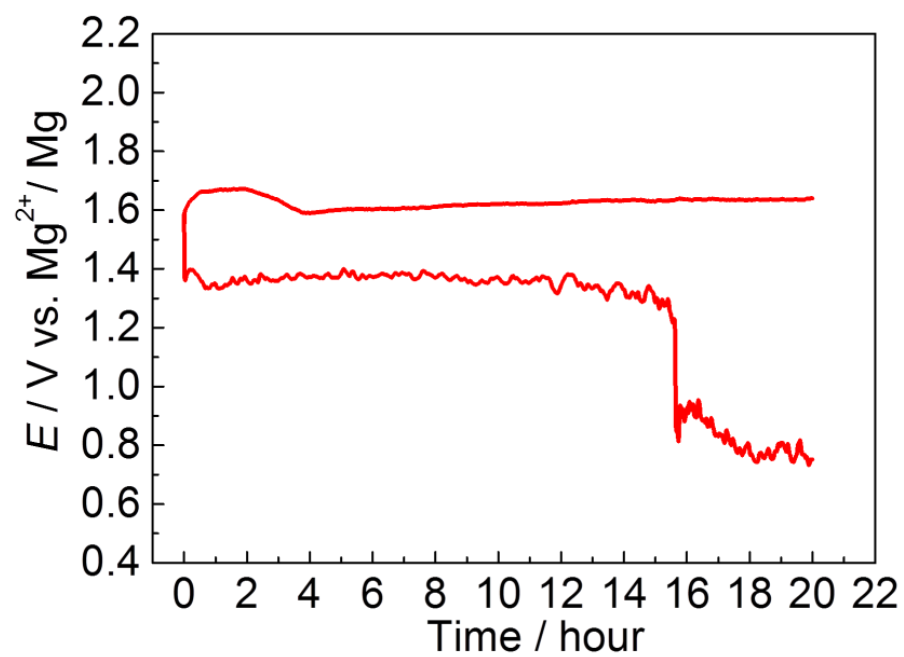


Fig.5-3 Charge-discharge behavior of the Cu current collector in 0.25M $\text{Mg}(\text{AlCl}_2\text{EtBu})_2$ / THF solution at $14 \mu\text{A cm}^{-2}$.

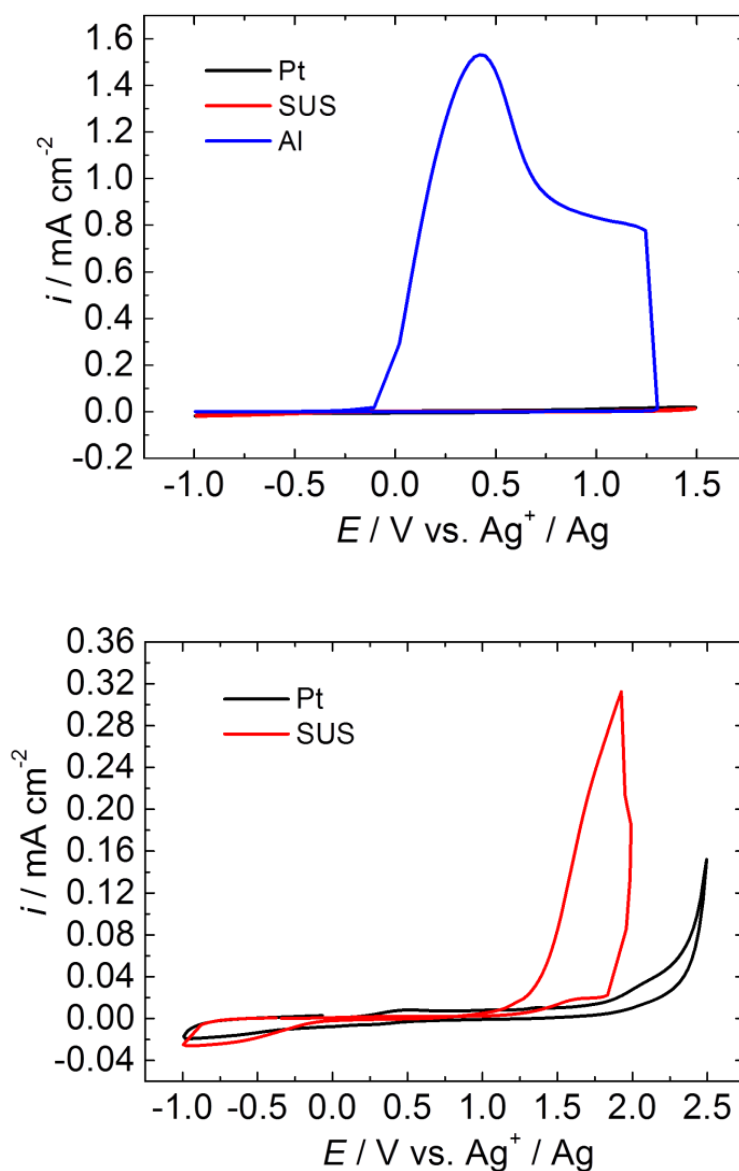


Fig.5-4 Cyclic voltammograms of the various metal electrode in 0.5M Mg(TFSI)₂ / AN solution at 25mV s⁻¹; (a) results of aluminum, SUS, and platinum plate ranging from -1.0V to 1.5V vs. Ag⁺ / Ag, and (b) results of SUS, and platinum plate ranging from -1.0V to 2.5V vs. Ag⁺ / Ag.

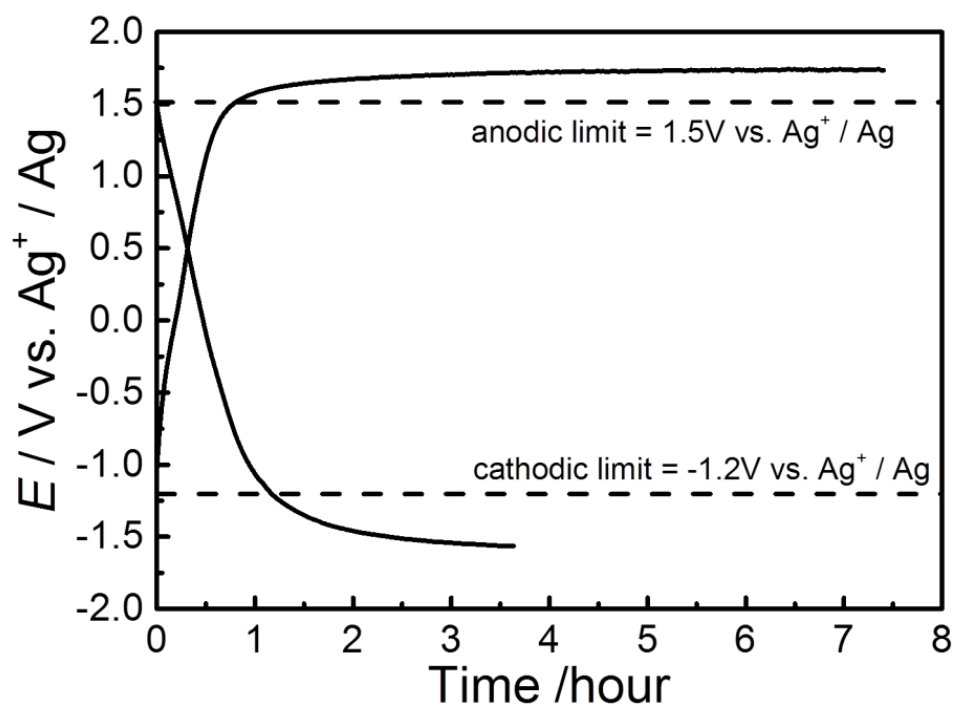


Fig.5-5 Charge - discharge curves of the composite electrode without active materials in 0.5M $\text{Mg}(\text{TFSA})_2 / \text{AN}$ solutions at 55°C. The current density is $20 \mu\text{A cm}^{-2}$.

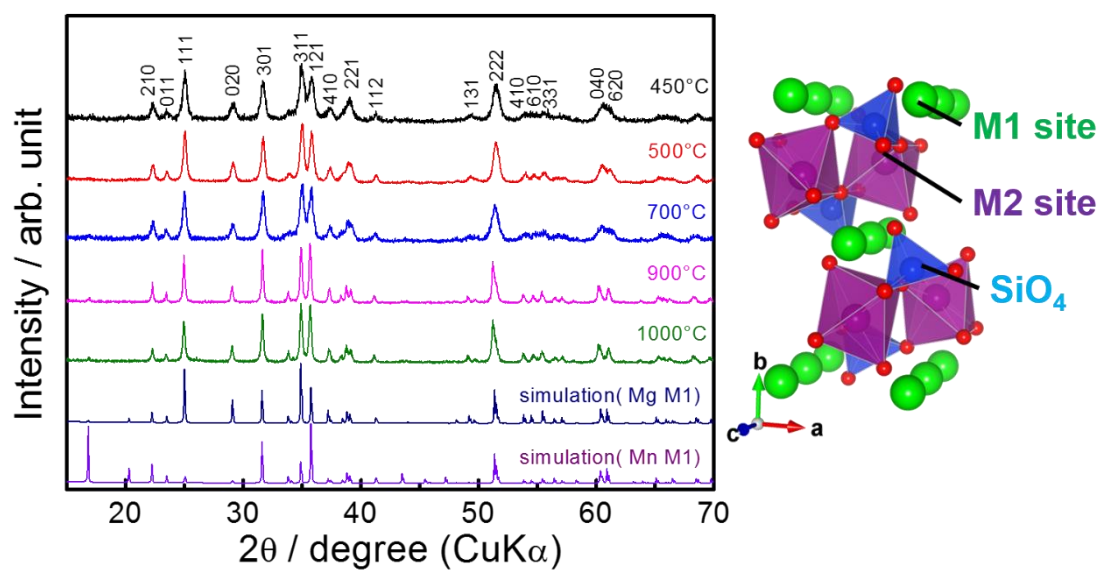


Fig.5-6 Powder XRD patterns of MgMnSiO_4 synthesized at various temperatures, and schematic projection of the olivine-type MgMnSiO_4 visualized by VESTA.³⁹

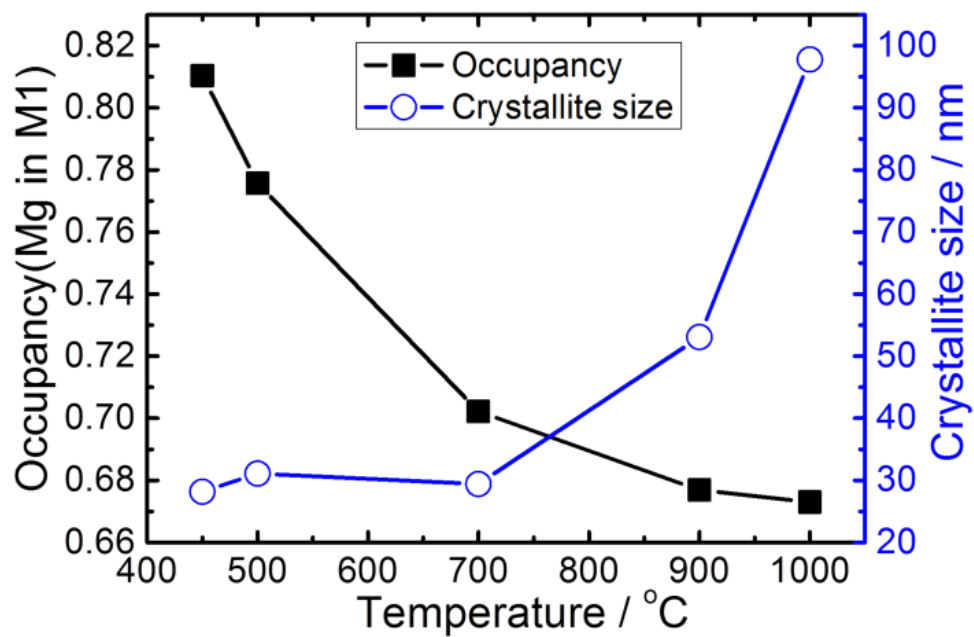


Fig.5-7. The partitioning of Mn and Mg in M1 and M2 octahedralsites of olivine MgMnSiO_4 as a function of annealing temperature (indicated in black), and the dependency of the crystallite size on the synthesis temperature (indicated in blue)

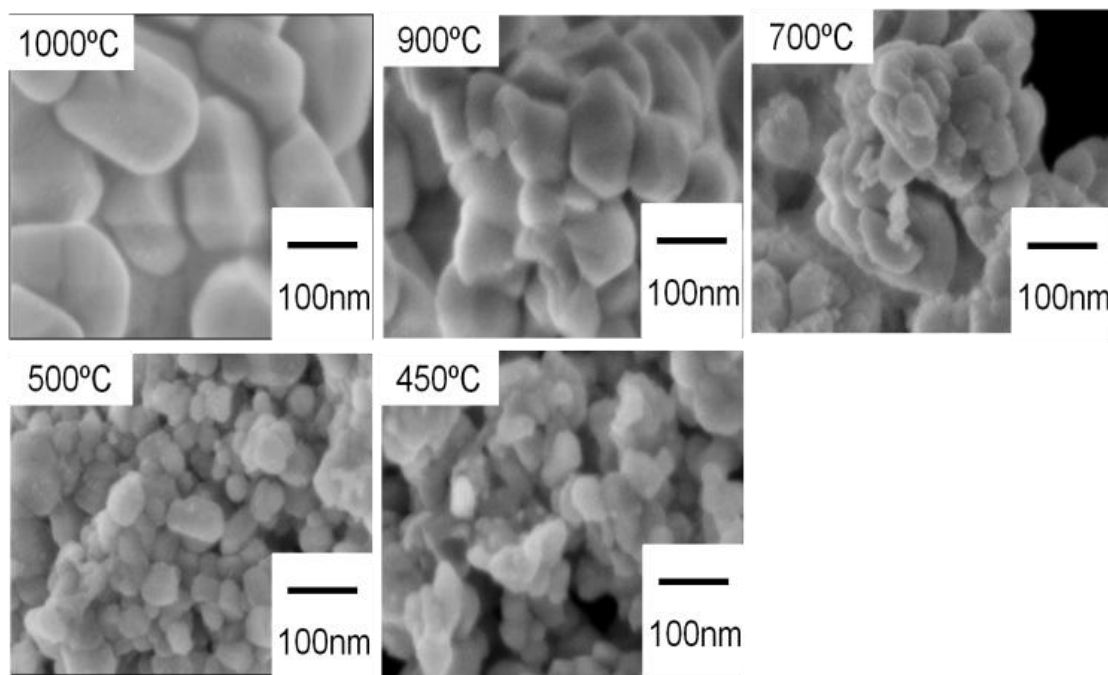


Fig.5-8. High resolution SEM images of MgMnSiO_4 synthesized at various temperatures.

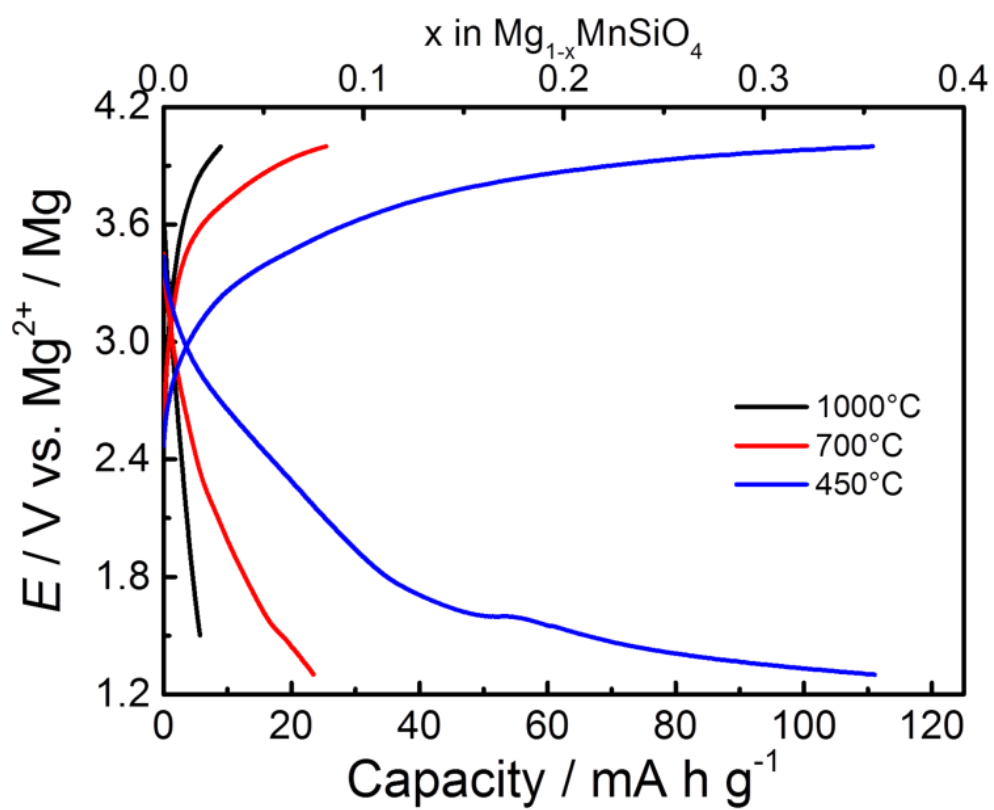


Fig.5-9. Galvanostatic charge and discharge voltage curves of MgMnSiO_4 synthesized at various temperatures at 55°C.

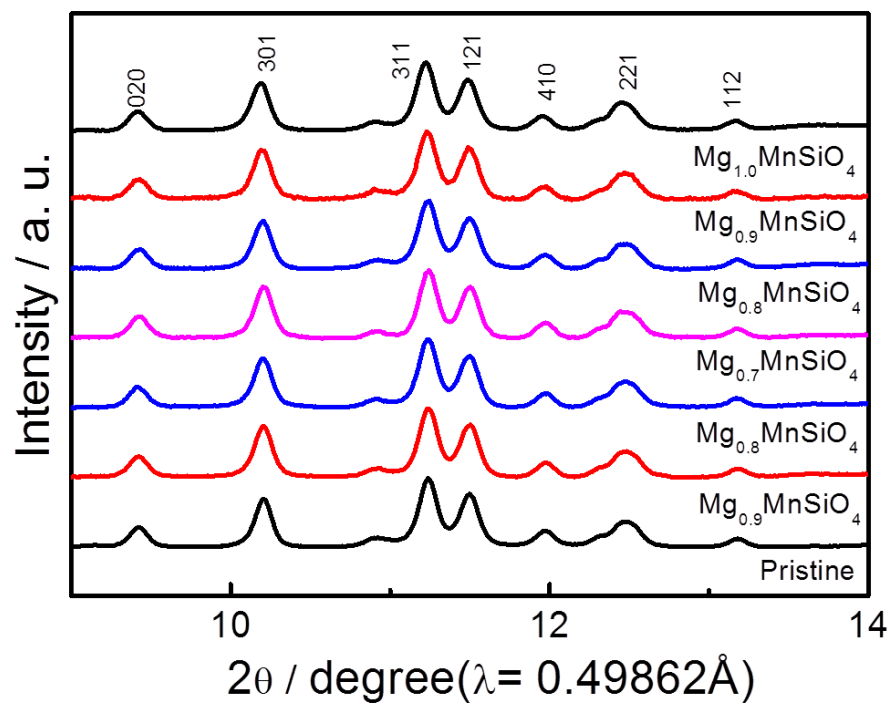


Fig.5-10. XRD patterns of $\text{Mg}_x\text{MnSiO}_4$ ($x = 1.0, 0.9, 0.8, 0.7$) during charging/discharging process.

Table 5-1. Structural parameters obtained from Leval profile fitting of $\text{Mg}_x\text{MnSiO}_4$ ($x = 1.0, 0.9, 0.8, 0.7$) .

composition	Space group	a (Å)	b (Å)	c (Å)	$\alpha = \beta = \gamma$ (°)	V (Å ³)
MgMnSiO₄	<i>Pnma</i>	10.4623(4)	6.1159(2)	4.7977(2)	90	306.77(3)
Mg_{0.9}MnSiO₄	<i>Pnma</i>	10.4514(6)	6.1064(4)	4.7933(3)	90	305.91(4)
Mg_{0.8}MnSiO₄	<i>Pnma</i>	10.4505(6)	6.1050(3)	4.7930(2)	90	305.79(4)
Mg_{0.7}MnSiO₄	<i>Pnma</i>	10.4380(3)	6.1030(3)	4.7880(1)	90	305.00(3)
Mg_{0.8}MnSiO₄	<i>Pnma</i>	10.4642(5)	6.1077(3)	4.7976(2)	90	306.63(4)
Mg_{0.9}MnSiO₄	<i>Pnma</i>	10.4709(8)	6.1089(5)	4.7983(4)	90	306.92(6)
MgMnSiO₄	<i>Pnma</i>	10.4782(6)	6.1104(4)	4.8031(3)	90	307.52(4)

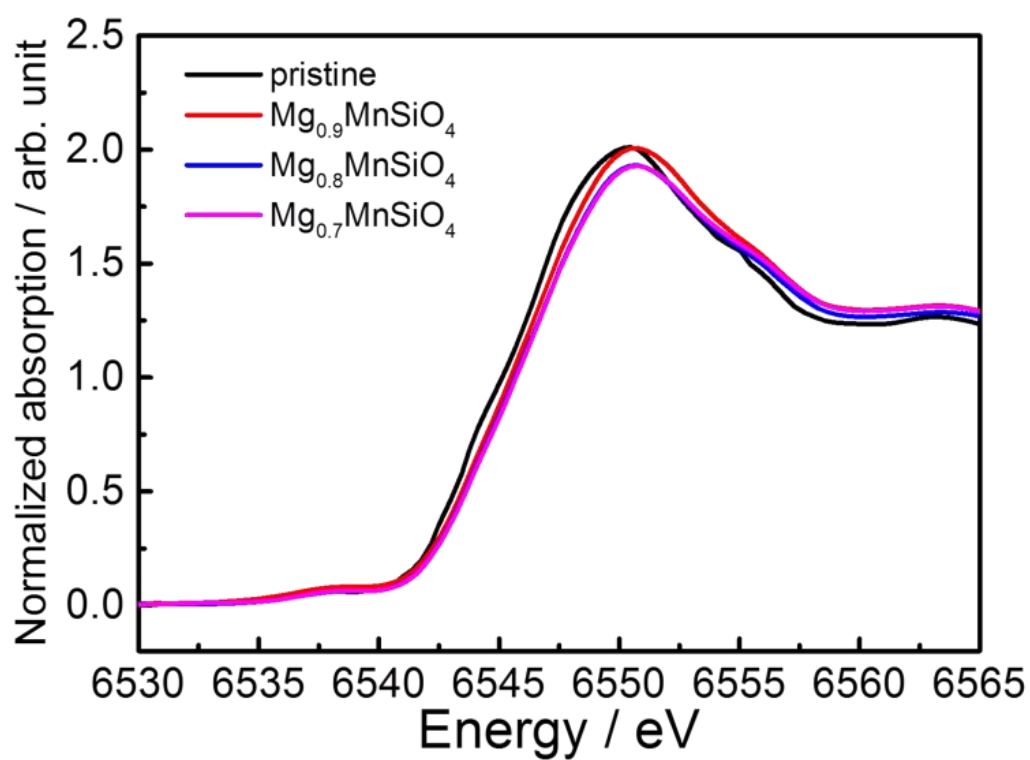


Fig.5-11. Mn K-edge XANES spectra of $\text{Mg}_x\text{MnSiO}_4$ ($x = 1.0, 0.9, 0.8, 0.7$) during charging process.

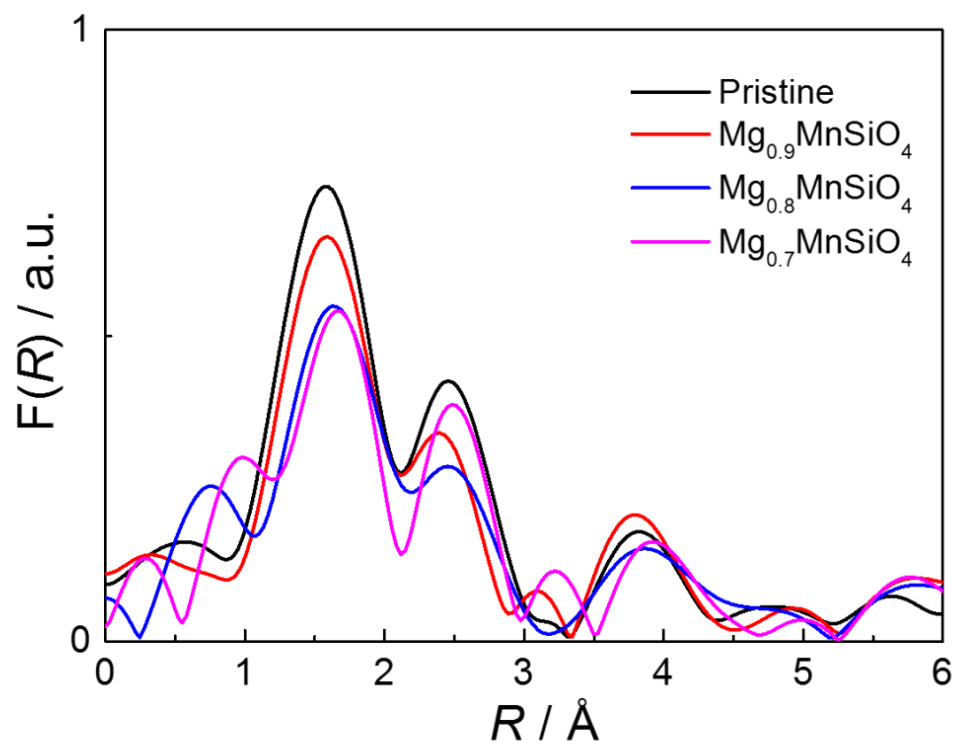


Fig.5-12. Mn-K edge EXAFS spectra of $\text{Mg}_x\text{MnSiO}_4$ ($x = 1.0, 0.9, 0.8, 0.7$) during charging process

Appendix

Rietveld refinement

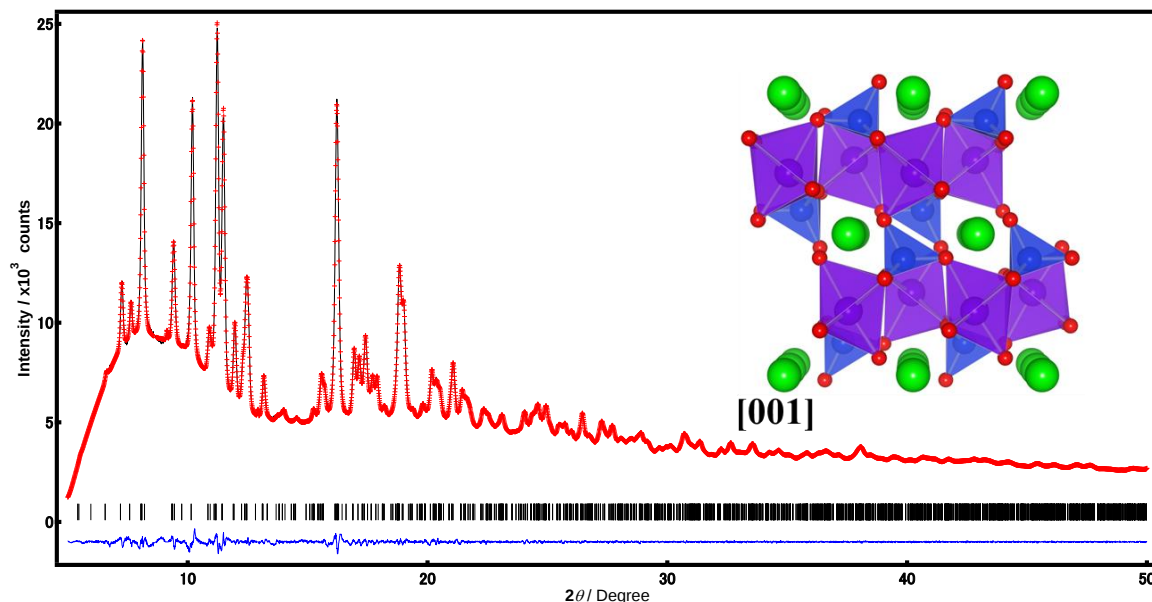


Fig.A5-1. Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 450°C . Inset shows the refined crystal structure of MgMnSiO_4 . Blue and purple polyhedral indicate the SiO_4 tetrahedra and FeO_6 octahedra, respectively. Magnesium atoms are indicated in green.

Table A5-1. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 450°C .

Atom	Wickoff site	g	x	y	z	B
Si1	4c	1.00	0.0920	0.25	0.4244	0.36
O1	4c	1.00	0.0900	0.25	0.7548	0.50
O2	4c	1.00	0.4469	0.25	0.2274	0.48
O3	8d	1.00	0.1629	0.0412	0.2815	0.50
Mg1	4a	0.81	0	0	0	0.42
Mn1	4c	0.81	0.2787	0.25	0.9857	0.42
Mn2	4a	0.19	0	0	0	0.42
Mg2	4c	0.19	0.2787	0.25	0.9857	0.42

$$R_{wp} = 3.04\% \quad R_p = 2.39\% \quad R_e = 1.75\% \quad GOF = 1.74$$

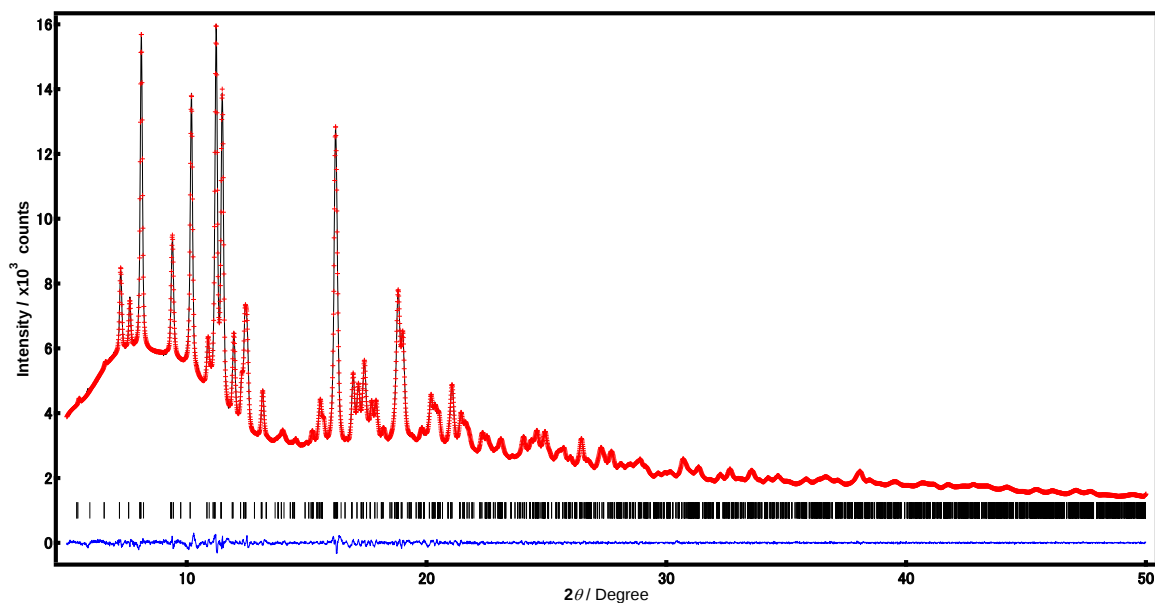


Fig.A5-2. Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 500 °C.

Table A5-2. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 500 °C.

Atom	Wickoff site	g	x	y	z	B
Si1	4c	1.00	0.0917	0.25	0.4248	0.36
O1	4c	1.00	0.0914	0.25	0.7500	0.50
O2	4c	1.00	0.4485	0.25	0.226	0.48
O3	8d	1.00	0.1622	0.0422	0.2839	0.50
Mg1	4a	0.78	0	0	0	0.42
Mn1	4c	0.78	0.2792	0.25	0.9854	0.42
Mn2	4a	0.22	0	0	0	0.42
Mg2	4c	0.22	0.2792	0.25	0.9854	0.42

$$R_{wp} = 2.83\% \quad R_p = 2.19\% \quad R_e = 1.77\% \quad GOF = 1.59$$

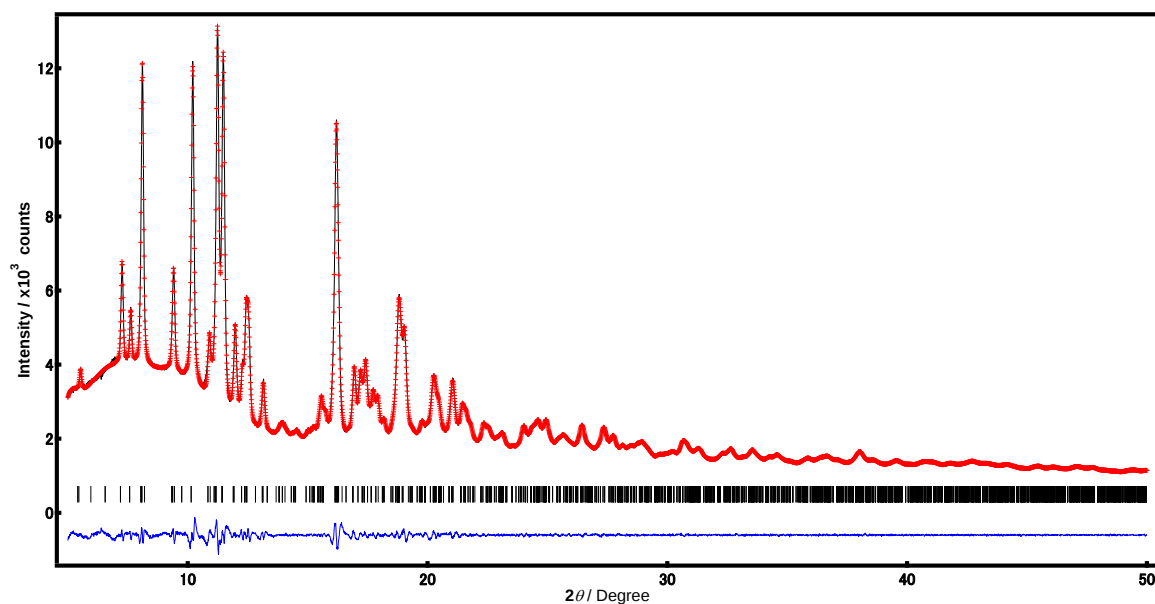


Fig.A5-3. Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 700 °C.

Table A5-3. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 700 °C.

Atom	Wickoff site	g	x	y	z	B
Si1	4c	1.00	0.0924	0.25	0.4266	0.36
O1	4c	1.00	0.0908	0.25	0.7509	0.50
O2	4c	1.00	0.4487	0.25	0.2225	0.48
O3	8d	1.00	0.1628	0.0420	0.2850	0.50
Mg1	4a	0.70	0	0	0	0.42
Mn1	4c	0.70	0.2798	0.25	0.9856	0.42
Mn2	4a	0.30	0	0	0	0.42
Mg2	4c	0.30	0.2798	0.25	0.9856	0.42

$$R_{wp} = 3.02\% \quad R_p = 2.36\% \quad R_p = 2.04\% \quad GOF = 1.48$$

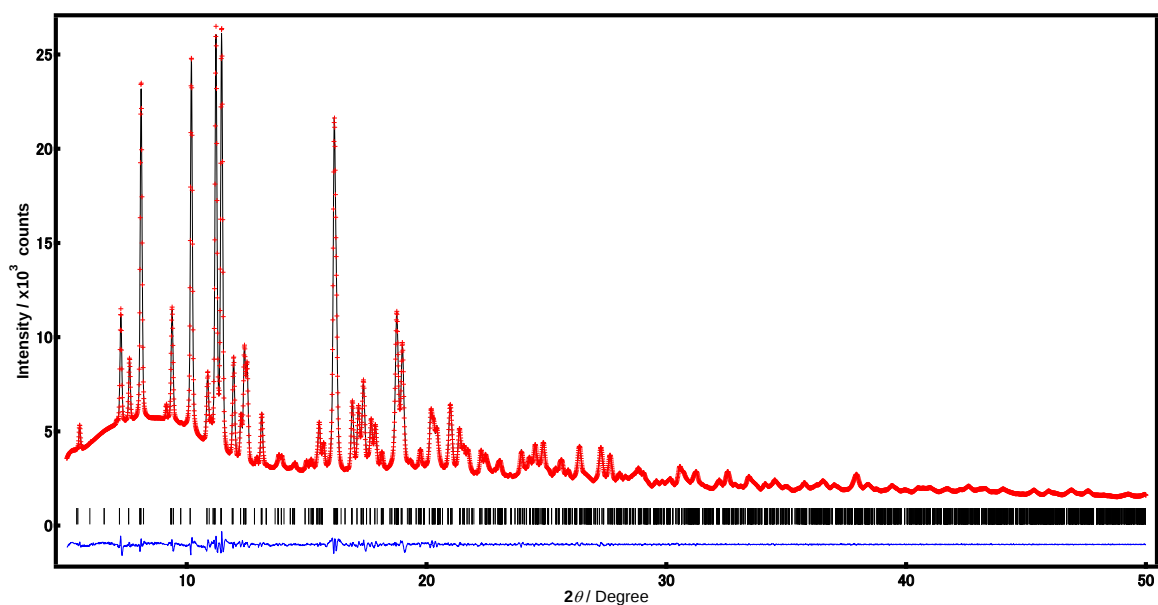


Fig.A5-4. Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 900°C .

Table A5-4. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 900°C .

Atom	Wickoff site	g	x	y	z	B
Si1	4c	1.00	0.0935	0.25	0.4257	0.36
O1	4c	1.00	0.0895	0.25	0.7561	0.50
O2	4c	1.00	0.4513	0.25	0.2223	0.48
O3	8d	1.00	0.1607	0.0425	0.2837	0.50
Mg1	4a	0.68	0	0	0	0.42
Mn1	4c	0.68	0.2792	0.25	0.9871	0.42
Mn2	4a	0.32	0	0	0	0.42
Mg2	4c	0.32	0.2792	0.25	0.9871	0.42

$$R_{wp} = 2.68\% \quad R_p = 2.07\% \quad R_e = 1.71\% \quad GOF = 1.57$$

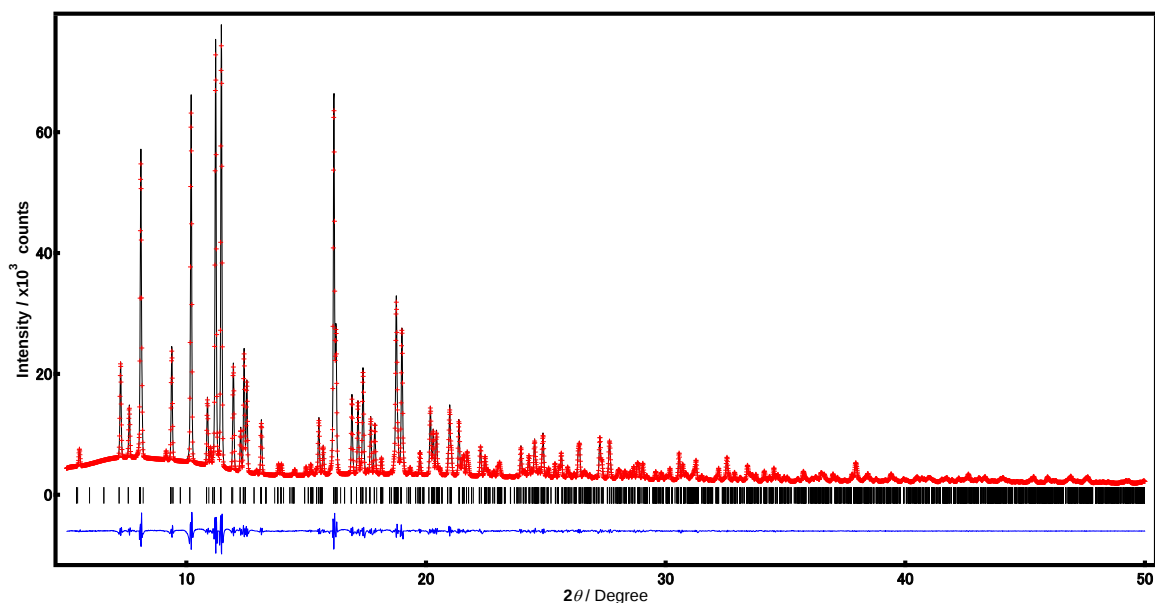


Fig.A5-5. Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 1000 °C.

Table A5-5. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO_4 synthesised at 1000 °C.

Atom	Wickoff site	g	x	y	z	B
Si1	4c	1.00	0.0933	0.25	0.4254	0.36
O1	4c	1.00	0.0904	0.25	0.7585	0.50
O2	4c	1.00	0.4527	0.25	0.2227	0.48
O3	8d	1.00	0.1606	0.0404	0.2823	0.50
Mg1	4a	0.67	0	0	0	0.42
Mn1	4c	0.67	0.2794	0.25	0.9876	0.42
Mn2	4a	0.33	0	0	0	0.42
Mg2	4c	0.33	0.2794	0.25	0.9876	0.42
$R_{wp} = 2.93\%$ $R_p = 2.25\%$ $R_e = 1.49\%$ $GOF = 1.96$						

Table A5-6. Structural parameters obtained from Rietveld refinement of MgMnSiO_4 synthesised at various temperatures

Annealing Temperature (°C)	Space group	a (Å)	b (Å)	c (Å)	$\alpha = \beta = \gamma$ (°)	V (Å ³)
450	<i>Pnma</i>	10.4643(1)	6.1131(1)	4.7971(1)	90	308.87(0)
500	<i>Pnma</i>	10.4527(0)	6.1136(1)	4.7961(1)	90	306.49(0)
700	<i>Pnma</i>	10.4352(2)	6.1158(1)	4.8059(1)	90	306.71(0)
900	<i>Pnma</i>	10.4821(2)	6.1505(2)	4.8273(1)	90	311.22(0)
1000	<i>Pnma</i>	10.4888(3)	6.1536(2)	4.8293(2)	90	311.72(0)

Chapter 6: MgFePO_4F as a feasible cathode material for magnesium batteries

6.1. Introduction

Recently, the high price ($\sim 69\,000$ \$ per ton)¹ and low abundance ($\sim 7 \times 10^{-4}\%$)² of lithium have been viewed as impediments to the further large-scale application of lithium ion batteries (LIBs). To meet the ever-increasing demand on large-scale energy storage/conversion devices, paramount attention has been paid to the development of alternative rechargeable battery systems based on magnesium, as they are of much lower cost (3020 \$ per ton)¹ and much higher abundance (13.9%)² and they exhibit higher theoretical volumetric energy density ($3832 \text{ mA h cm}^{-3}$) than Li ($2062 \text{ mA h cm}^{-3}$).¹ Moreover, Mg is stable upon air exposure and is free of dendritic deposition during repeated cycling, thus, inherently safer than Li.^{1, 2} A prototype Mg battery (MB) was first demonstrated in 2000,³ but its feasibility strongly relies on the development of suitable cathode materials and electrolyte. Recently, much effort has been made to develop a suitable Mg^{2+} electrolyte with broad electrochemical window, while studies related to new cathode materials remain scarce. Owing to strong Mg interactions with the anions and the cations of the hosts or to the polarization effect of Mg^{2+} cations with a high charge/radius ratio, the intrinsically slow solid-state diffusion kinetics of Mg^{2+} hampers most of the intercalation compounds as cathodes for MBs.¹ Until now, only a few cathode materials, such as the Chevrel phases $\text{Mg}_x\text{Mo}_6\text{T}_8$ ($\text{T} = \text{S, Se}$),^{4, 5} Mg_xMSiO_4 ($\text{M} = \text{Fe,}^6 \text{ Mn,}^{7, 8} \text{ Co}^9$), transition metal oxides (such as V_2O_5 (ref. 10 and 11) and MnO_2 (ref. 12 and 13)) and metal chalcogenides (such as MoS_2 , (ref. 14 and 15) TiS_2 (ref. 16)

and WSe₂ (ref. 17)) have been proven to be plausible (de)intercalation hosts of Mg²⁺. A majority of research studies have been directed toward the synthesis of nanostructured cathode materials in order to reduce the diffusion distance of Mg²⁺. However, only a few studies have been directed toward evaluating the feasibility of using new compounds as possible cathodes for MBs. This is the focus of this study. Fluoro-polyanionic cathode materials, such as Na₂FePO₄F,¹⁸ LiFePO₄F,¹⁹ and LiVPO₄F,²⁰ have attracted prime attention as promising alternative cathode materials for sodium and lithium ion batteries, respectively, on the basis of their three-dimensional (3D) framework, good thermal stability, and remarkable electrochemical properties. Recently, a novel lithium transitional bimetal fluoro-phosphate with highly ordered cations of V³⁺ and Fe³⁺, viz. LiV_{0.5}Fe_{0.5}PO₄F, was developed by our group and exhibited a single-phase solid-solution behavior over the entire lithium composition range of Li_{1-x}V_{0.5}Fe_{0.5}PO₄F (0 < x < 0.5).²¹ Inspired by the high Li⁺ conductivity of the fluoro-polyanionic compounds, a stoichiometric fluoro-phosphate analogue, *i.e.* MgFePO₄F (MFPF), is herein synthesized *via* a ball-milling assisted solid-state reaction. In pursuit of high performance cathode materials for rechargeable MBs as well as establishing the basic correlation between their crystal structure and Mg storage performance, the synthesis, crystal structure of MFPF and its correlation with the electrochemical properties as cathode materials for both Mg and Li batteries are discussed herein.

6.2. Experimental

Material Synthesis

Stoichiometric MgFePO₄F (MFPF) powders were prepared via the conventional

solid-state carbothemal method. MFPF was obtained starting from a rigorous mixing of stoichiometric quantities of MgHPO_4 (received from Sigma), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (2N — Junsei Chemical) and NH_4F (received from Wako) powders which were weighed in a molar ratio of 1:1:1. A dispersion of 5 wt% carbon nanotubes in $\text{C}_2\text{H}_5\text{OH}$ (received from Wako) was added and mixed intimately using an agate mortar and pestle. The mixture was poured into a 250 mL zirconia-lined Cr-hardened stainless steel (Cr-SS) milling pot with zirconia (YSZ) milling media ($\phi 10 \text{ mm} \times 100 \text{ ZrO}_2$ balls), and 50 mL of ethanol added. Mixing was performed using a Fritsch LP-6 at 400 rpm for 8 h with reverse rotation every 30 min. The obtained slurry was dried at 80°C in oven. The dried powder was pulverised using an agate mortar and pestle for 1 h, after which the powder was pelletised at 50 MPa using an isostatic press machine. Using an annealing rate of $50^\circ\text{C}/\text{min}$, the pellets were fired in a horizontal quartz tubular furnace and calcined at temperatures ranging from 600°C to 850°C for 5 h with a fixed Ar flux. The obtained pellets were thereafter transferred to the zirconia-lined Cr-hardened stainless steel milling pot with zirconia milling ball. After 24h ball-milling at 400rpm, the final MFPF/CNT composite material was prepared. The content of CNT was determined to be ~5%.

Characterization of morphology, crystal structure and valence state

The morphology of the as-prepared MFPF was characterized by using scanning electron microscopy (JEOL, JSM-890) at an acceleration voltage of 15 kV. The diffraction pattern of the as-prepared MFPF was measured on an X-ray diffractometer (RIGAKU, RINT-ULTIMA III) using $\text{Cu } K\alpha$ radiation ($\lambda = 1.54051 \text{ \AA}$). The diffraction patterns were recorded in the 2θ range of 10° – 80° with a step size of 0.01° . Synchrotron X-ray diffraction (SXRD) patterns of MFPF were collected at the beam line BL02B2

(SPring-8 in Japan), equipped with a large Debye-Scherrer camera. MFPF powder was filled in a glass capillary and sealed by a resin. Based on the obtained SXRD patterns, the crystal structure was further refined by the Rietveld method with the program JANA2006 using the pseudo-Voigt function of Finger *et al*^{22, 23} and drawn by the software of VESTA.²⁴ To determine the occupations of M1 and M2 sites by Fe and Mg within the lattice structure, the crystallographic information files of MFPF with different occupations were built by fixing the atomic positions and created by using VESTA. The corresponding X-ray diffraction patterns of these simulated MFPFs were predicted by using the Reflex program implemented in the software of Materials Studio 6.1 suite. X-ray absorption near edge spectra (XANES) measurement was employed to determine the valence state of Fe within MFPF. X-ray absorption spectra of MFPF sample and the reference compound ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) were measured in the energy region of the Fe *K*-edge at room temperature in transmission mode at the beam line of the SPring-8 synchrotron radiation facility (BL14B2). The intensity of X-ray beam was measured by ionization detectors. Treatment of the raw X-ray absorption data was performed with Athena package.²⁵ Analysis of Fe *K*-edge XANES spectra was performed with the Rigaku REX 2000 program package.²⁶

Electrochemical characterization

The composite electrodes of MgFePO_4F were prepared by mixing the obtained MFPF/CNT composite with acetylene black (AB) and polytetrafluoroethylene (PTFE) in a weight ratio of 5:4:1. The electrode was then pressed and disks with a diameter of 6 mm were punched out. The punched out electrodes were pressed in between Pt meshes as the working electrode, and the typical mass loading of the active powder was *ca.* 5 mg/cm^2 . Thereafter, the electrode was dried *in vacuo* at 80°C. Hermetically sealed three

electrode cells were assembled in an Ar-filled glove box. 0.5 M of Magnesium bis(trifluoromethanesulfonyl)imide ($\text{Mg}(\text{TFSA})_2$) in super dehydrated acetonitrile (all from Wako chemicals) was used as the electrolyte. Mg rod and Pt mesh were used as the anode (counter electrode) and the current collector, respectively. As a reference electrode, a silver wire was inserted into a solution of 0.01 M AgNO_3 and 0.5 M $\text{Mg}(\text{TFSA})_2$ in super dehydrated acetonitrile. This solution, contained in an additional glass tube, was brought into contact with $\text{Mg}(\text{TFSA})_2$ / acetonitrile solution via a microporous glass membrane. To minimise the effect of the ohmic IR drop associated with the electrolyte resistance, the tip of the capillary was placed as close as possible to the working electrode. Galvanostatic charge and discharge measurements in the electrolytic window range of -1.2 V to 1.5 V vs. Ag/Ag^+ were carried out at 25°C at a current density of C/20 and C/30. As a comparison, two electrode cells were assembled to study the cathodic performance of MFPPF in Li^+ electrolyte. 1 M LiClO_4 in mixed solvent of EC and DMC was used as electrolyte. Lithium discs were used as counter and reference electrodes. Galvanostatic charge and discharge measurements in the electrolytic window range of 1.3 V to 4.6 V vs. Li/Li^+ were carried out at 25°C at a current density of C/30. Prior to repeated galvanostatic measurements, MFPPF was first pre-cycled to facilitate electrolyte ingress into the composite electrodes and separators. All the capacities presented in this paper were calculated based on MFPPF only.

6.3. Results & Discussions

As shown in Fig. 6-1a and b, scanning electron microscopy (SEM) images of the ball-milled MFPPF reveal a uniform particle size distribution centered at ~50 nm. Uniformly dispersed carbon nanotubes (CNTs) are effective for enhancing the

conductivity of the composite materials. Moreover, the addition of ~5 wt% CNTs can effectively decrease the interparticle fusion degree and serve as a reductive agent to avoid the formation of Fe^{3+} during the calcination process. Fig.6-2 shows the Fe K-edge XANES spectra of the MFPPF and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ as a reference compounds of the divalent iron species in the octahedral site. Iron in the MFPPF is in a divalent (Fe^{2+}) state in the as-prepared MFPPF and that Fe^{2+} is in an octahedral coordination.

The synchrotron X-ray diffraction (SXRD) pattern of MFPPF synthesised at 650°C, shown in Fig. 6-3a, indicates a monoclinic structure fully indexed in the $I2/a$ space group, which is isostructural with both triplite and wagnerite phases. The refined atomic parameters obtained from Rietveld refinement of the SXRD pattern are shown in Table 6-1. An entire Mg/Fe antisite mixing in the M1 and M2 sites was revealed by the Rietveld refinement results. Its 3D crystallographic representation projected along [010] and [001] is shown in Fig. 6-3b and c, respectively. Furthermore, the monoclinic framework exhibits a unique arrangement of atoms. As shown in Fig. 6-3 and also Fig. 6-4, the lattice framework consists of highly distorted octahedra of MO_4F_2 ($\text{M} = \text{Mg}$ or Fe) and tetrahedra of PO_4 . Within the framework, the nearest neighbouring octahedra at the same M1 or M2 sites share the F–F and O–O edges to form alternating centrosymmetrical octahedron pairs of $\text{MO}_4\text{F}_2\text{O}_4\text{M}$ and $\text{F}_2\text{MO}_6\text{MF}_2$. Consequently, the octahedron chains of cations located at M1 and M2 sites are formed along [010], [001] and so on. Along [010], the F–F edges or bonds serve as bridges to crosslink the octahedron chains of M1 and M2 to form a zigzag octahedron network (see Fig. 6-4a and b). The neighbouring octahedra at the different sites of M1 and M2 share the F–O edge with each other forming an octahedron pair (*i.e.*, $\text{F}_2\text{M1O}_6\text{M2F}_2$). The tetrahedral PO_4 share their vertices with two octahedron pairs ($\text{F}_2\text{MO}_6\text{MF}_2$) and two F–O edge

shared octahedron pairs ($F_2M1O_6M2F_2$). Finally, the 3D lattice framework, as seen in Fig. 6-3b and c, is formed. To investigate the evolution of crystal structures of MFPP with various occupations of Fe and Mg in M1 and M2 sites, respectively, simulations of their corresponding XRD diffraction patterns were conducted by using the lattice parameters and crystallographic information data obtained from Rietveld refinement of the experimental data. As are apparent in Fig. 6-5 and 6-6, the simulated XRD patterns of MFPP vary with the change of site occupations of M1 and M2. The diffraction pattern of simulated MFPP with Fe and Mg antisite occupations of ca. 50% in both M1 and M2 sites coincides with the observed pattern of as-prepared MFPP (see Fig. 6-6a and 6-7). The simulation results further confirm the immense Mg/Fe antisite mixing intrinsic in the obtained monoclinic framework derived from the Rietveld refinement analyses. This phenomenon is ascribed to the similarity in ionic radii of Mg^{2+} (0.72Å) and Fe^{2+} (0.78Å), akin to that observed in the fayalite- $MgFeSiO_4$.⁶ It is important to point out that wide 3D channels for migration of Mg^{2+} could obviously be observed from the simulated cationic orderings of MFPP. As shown in Fig. 6-5b and 6-6b, when the M1 and M2 sites are fully occupied by Mg^{2+} and Fe^{2+} , respectively, wide channels for Mg^{2+} to traverse could be found along [010] and [001]. Analogous migration channels for Mg^{2+} can also be observed along [100] and [111] whereby Fe^{2+} and Mg^{2+} occupy M1 and M2 sites, respectively (see Fig. 6-5c and 6-6c). To further understand the effect of calcination temperature on the crystal structure of MFPP, various calcination temperatures ranging from 600°C to 850°C were used to prepare MFPP. As presented in Fig. 6-7, all corresponding XRD patterns are similar. The crystal grain sizes of MFPP increase from ~24 nm following a near-linear relationship of the grain size increment versus the increase in sintering temperature, see Fig. 6-8. No obvious

correlation could be found between the calcination temperature and the anti-site mixing degree within MFPP. Rietveld refinement of the sample synthesized at 800°C also indicates an entire Fe/Mg anti-site mixing (see Fig. 6-9 and Table 6-2). We are aware that anti-site mixing may impose a limitation in the (de)intercalation of cations; however, the 3D framework conferred by MFPP may be beneficial to allow cations to traverse easily. As a proof-of-concept, the feasibility of using MFPP as a cathode material for MBs was examined in a three-electrode cell configuration. The composite electrodes prepared from MFPP were used as the working electrodes. Room-temperature galvanostatic measurements were carried out between -1.2 V and 1.5 V vs. Ag/Ag^+ at current densities corresponding to C/20 and C/30 rates. In order to obtain stable electrochemical performances both in Mg- and Li-ion cells, a pre-charge/discharge process was performed to promote the ingress of electrolyte into composite electrodes and separators. As shown in Fig. 6-10, the subsequent charge/discharge profiles neatly superimpose to attain a stable cyclic performance. MFPP exhibits a reversible capacity of 35 mA h g^{-1} at C/20 rate in a Mg-ion cell (see Fig. 6-10a and 6-11a). A discharge capacity of approximately 53 mA h g^{-1} could be attained in a Mg-ion cell (see Fig. 6-12a, which is lower than the sustainable capacity of ca. 86 mA h g^{-1} achieved in a Li ion cell (Fig. 6-10 and 6-11b) at the same current density corresponding to the C/30 rate. The cyclic performance and coulombic efficiency of the as-prepared MFPP electrodes are given in Fig. 6-11. The lower coulombic efficiency of the MFPP electrode in 0.5 M $\text{Mg}(\text{TFSA})_2$ electrolyte should be ascribed to electrolyte-related side reactions upon charging the electrode to a high potential region (see the differential capacity dQ/dV plots shown in Fig. 6-13a). Additionally, the electrochemical performance of a control electrode consisting of

carbon (acetylene black) and binder (PTFE) is shown in Fig. 6-12b. The obtained small capacity of 5 mA h g^{-1} corresponds to the supercapacitive behaviour of carbon. It is also interesting to note that the average working potentials are $-2.6 \text{ V vs. Mg/Mg}^{2+}$ and $-3.1 \text{ V vs. Li/Li}^+$. To the best of our knowledge, this potential is higher than that reported in most cathode materials for MBs.⁴⁻¹⁷ The potential exhibited is also slightly higher than that of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple in LiFePO_4F (2.75 V) due to the higher charge/radius ratio of Mg^{2+} than that of Li^+ .¹⁹ The sloping voltage (dis)charge profiles of MFPPF in both Mg- and Li-ion cells suggest a solid solution (single-phase) behaviour, which is distinct from the two-phase behaviour exhibited in LiFePO_4F .¹⁹ As presented in Fig. 6-13, one pair of oxidation/reduction peaks can be found in the differential capacity dQ/dV plots corresponding to the tenth charge/discharge cycle of the as-prepared MFPPF electrodes in the three-electrode Mg cell (Fig. 6-13a) and the two-electrode lithium cell (Fig. 6-13b). The extremely broad oxidation and reduction peaks, instead of extremely narrow and sharp peaks, are characteristic of a single-phase electrochemical behaviour of MFPPF in both Mg and Li ion cells.^{27, 28} Furthermore, smaller polarization and more distinct plateaus can be found from the voltage (dis)charge profiles of MFPPF in Li-ion than in Mg-ion cells. This could also be confirmed by the smaller peak-to-peak voltage difference between the oxidation and reduction peaks observed from the dQ/dV plots of lithium ion batteries (-0.17 V) than that of Mg batteries (-0.93 V). The much wider peak-to-peak separation of dQ/dV curves of MFPPF in the Mg system than that of the Li system should be ascribed to the stronger interactions with the anions and the cations of the hosts, as well as the more sluggish solid-state diffusion of Mg^{2+} cations than that of Li^+ within the disordered host crystal structure of MFPPF arising from higher charge-to-radius ratio of Mg^{2+} than that of Li^+ .¹ Moreover, it is worth noting that the

contribution of charge/discharge capacity from the electrochemical double layer capacitance (EDLC) is very limited. As shown in Fig. 6-12, the capacity of the as-prepared composite electrode and acetylene black stemming from the EDLC is lower than 10 mA h g^{-1} and 5 mA h g^{-1} , respectively. Moreover, the achieved discharge capacity based on MFPP only is $\sim 53 \text{ mA h g}^{-1}$ close to 38.4% of the theoretical capacity of MFPP (138 mA h g^{-1}). Thus, merely the surface process, including EDLC and pseudocapacitance (resulting from the surface (de)intercalation of Mg^{2+}), seems not able to provide such capacity. In view of this, most of the capacity of the composite electrodes stems from the redox reaction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ caused by the (de)intercalation of Mg^{2+} , as confirmed by the differential capacity dQ/dV plots shown in Fig. 6-13a. In other words, limited extraction/intercalation of Mg^{2+} from/into the host structure of MFPP takes place during the charge/discharge process even though the full intercalation is limited by the entirely cationic mixing of $\text{Fe}^{2+}/\text{Mg}^{2+}$ within the crystal structure of MFPP (which block the migration pathways for Mg^{2+} diffusion of Mg^{2+}) and the sluggish solid state diffusion kinetics of Mg^{2+} . Therefore, judicious design of a cationic ordered MFPP possessing straight pathways for the 3D migration of Mg^{2+} , as presented in Fig. 6-3b and c, might be essential to further improve the electrochemical performance of MFPP.

5.4. Conclusions

Stoichiometric MgFePO_4F was successfully synthesized using a solid-state carbothermal method. The experimental and simulated XRD results confirmed that the obtained monoclinic MFPP exhibit immense $\text{Mg}^{2+}/\text{Fe}^{2+}$ antisite mixing, which in turn results in a relatively low utilization ratio and capacity of MFPP. Nonetheless, the

relatively high potential (~ 2.6 V vs. Mg/Mg^{2+}) augmented with good cyclic stability at an encouraging capacity (~ 60 mA h g^{-1}) deems MFPF a promising high voltage cathode material contender for rechargeable magnesium batteries. A reduction of the $\text{Mg}^{2+}/\text{Fe}^{2+}$ antisite mixing degree by use of a suitable synthetic strategy as well as cycling at elevated temperature could be a necessary prelude to anticipating profound electrochemical performance in MFPF. Such efforts are subject of our future work, as are investigations relating to the mechanism of Mg^{2+} (de)intercalation.

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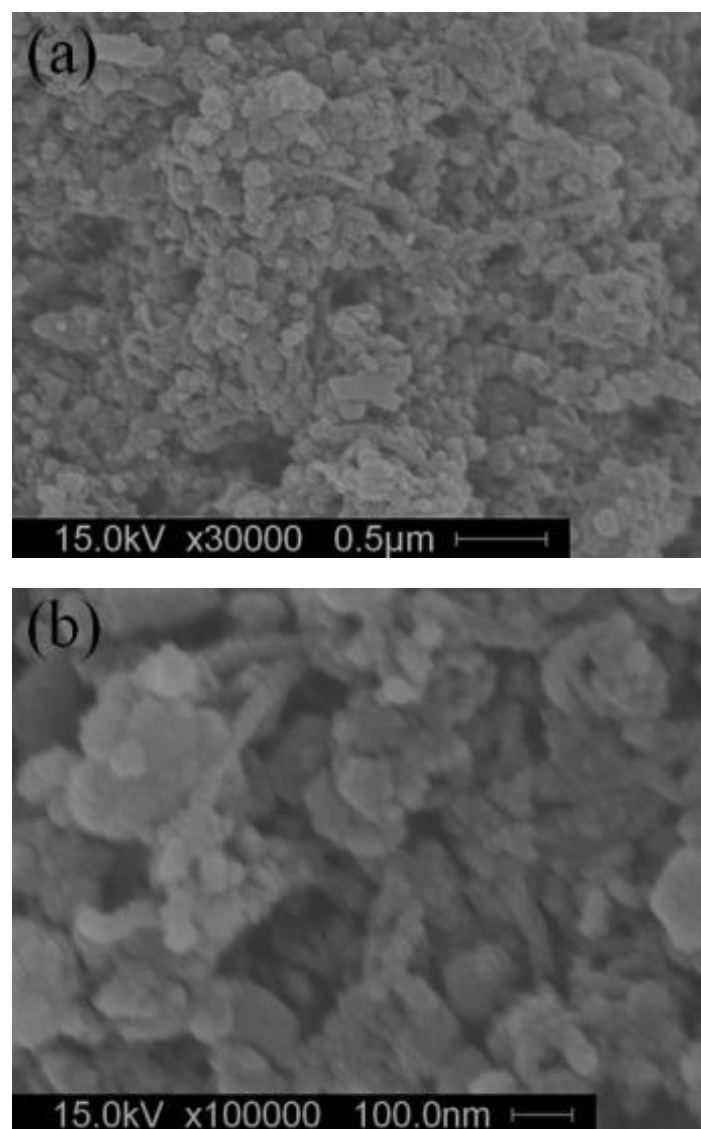


Fig. 6-1. Scanning electron microscopy (SEM) images at different magnifications for as-prepared MFPP: (a) $\times 30000$ and (b) $\times 10^5$.

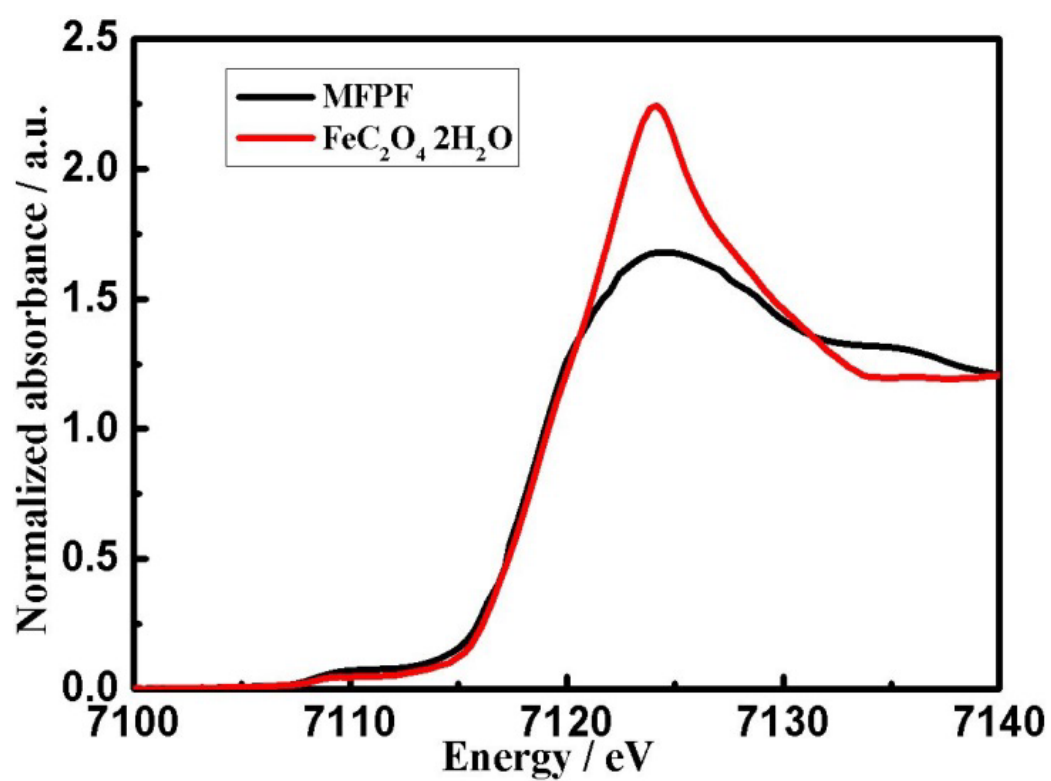


Fig. 6-2. Fe *K*-edge X-ray absorption near edge spectra of as-prepared MFPF and FeC₂O₄ · 2H₂O validating the octahedral coordination of Fe²⁺ in MFPF framework

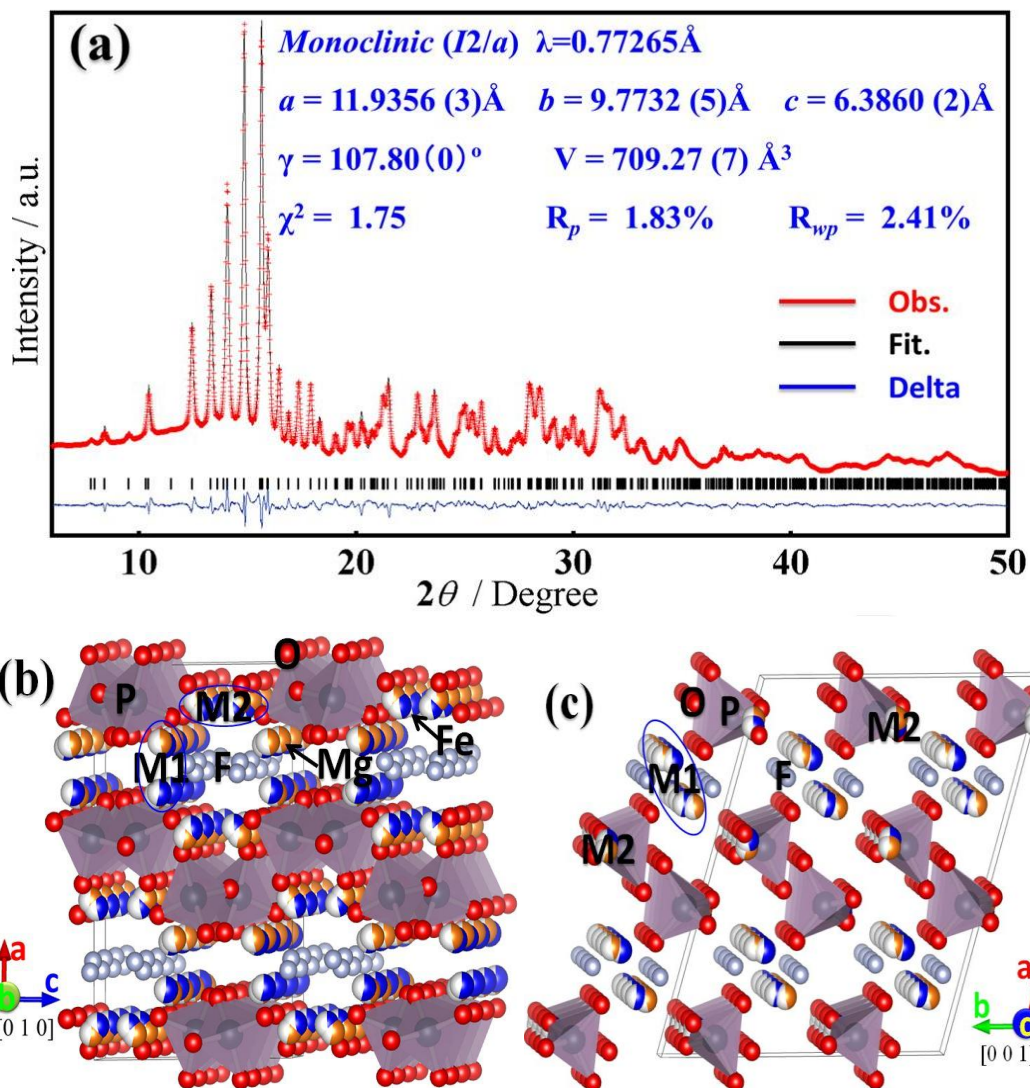


Fig. 6-3. (a) Rietveld refinement of synchrotron X-ray diffraction pattern of MFPP and the 3D crystallographic representation of monoclinic MFPP projected along (b) [010] and (c) [001].

Table 6-1. Atomic parameters obtained from Rietveld refinement of the SXRD patterns for as prepared MgFePO_4F synthesized at 650 °C.

Atom	g	x	y	z	U^*
Mg1	0.475	0.1831(7)	0.1683(7)	0.9636(12)	0.005
Fe1	0.525	0.1906(3)	0.2041(3)	0.9823(5)	0.005
Mg2	0.525	0.0809(7)	0.4506(10)	0.1271(13)	0.005
Fe2	0.475	0.0994(3)	0.4548(5)	0.1555(7)	0.005
P	1.000	0.0761(2)	0.3819(4)	0.6507(3)	0.010
O1	1.000	0.0567(3)	0.4734(4)	0.8297(7)	0.010
O2	1.000	0.9616(4)	0.2689(5)	0.6005(6)	0.010
O3	1.000	0.1682(5)	0.3156(6)	0.7169(5)	0.010
O4	1.000	0.1204(3)	0.4786(4)	0.4672(7)	0.010
F	1.000	0.2633(3)	0.3725(4)	0.1300(7)	0.005

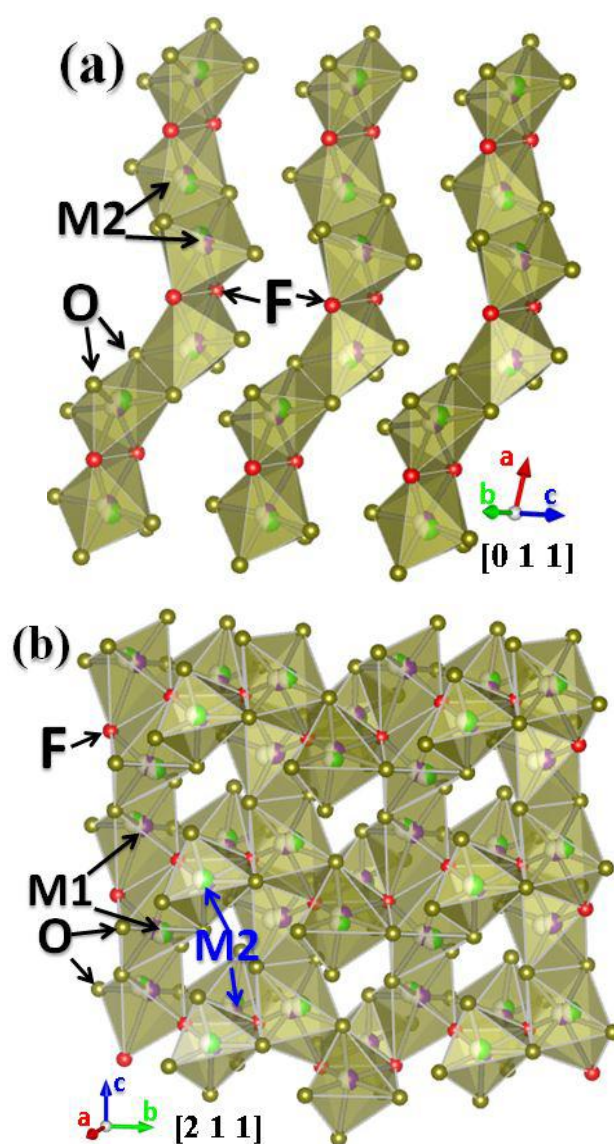


Fig. 6-4. 3D crystallographic representation of cationic-disordered MFPF monoclinic framework projected along (a) [011] and (b) [211].

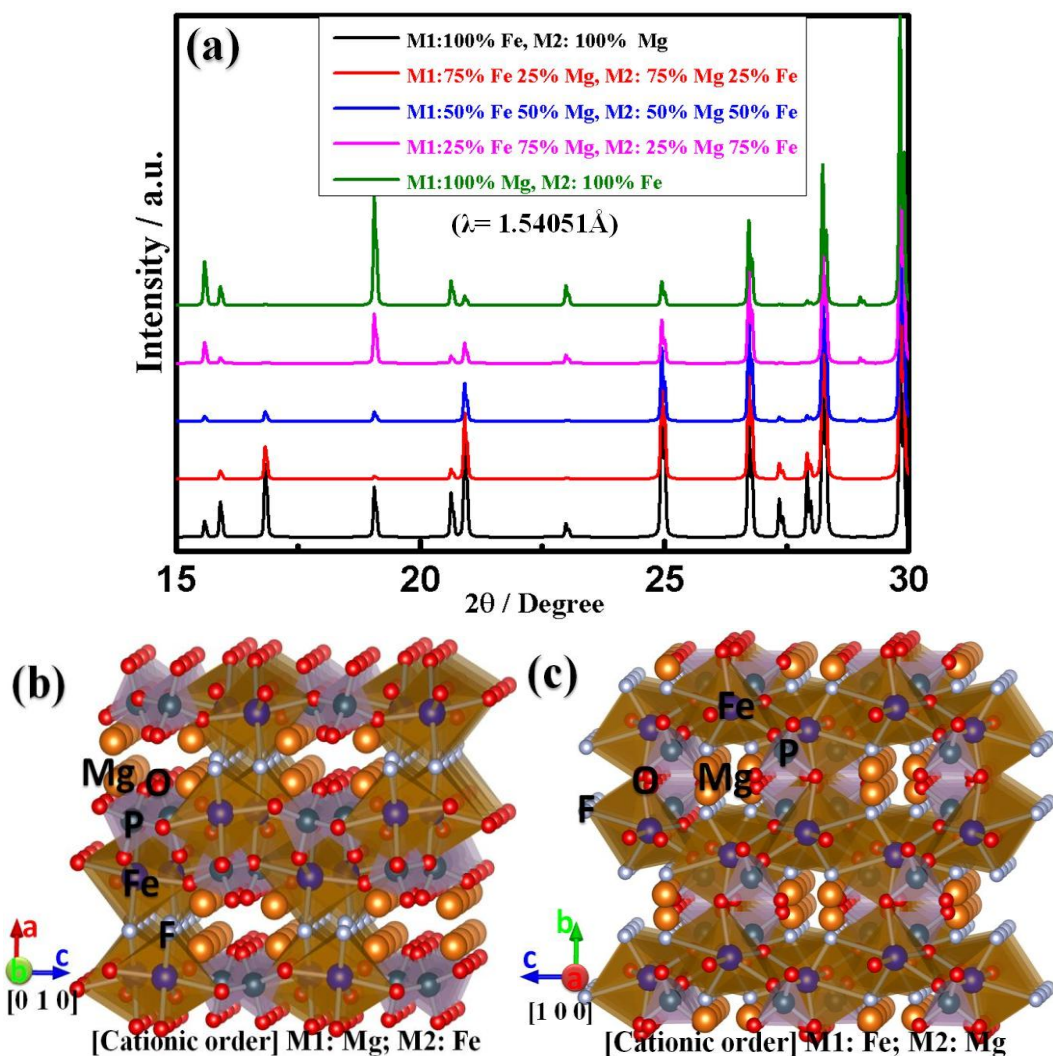


Fig. 6-5. (a) Simulated X-ray diffraction patterns of MFPPF ranging from 15° to 30° with various occupations of Fe and Mg in M1 and M2 sites, while the corresponding 3D crystallographic representations of simulated MFPPF in two different cationic orderings are shown in (b) and (c).

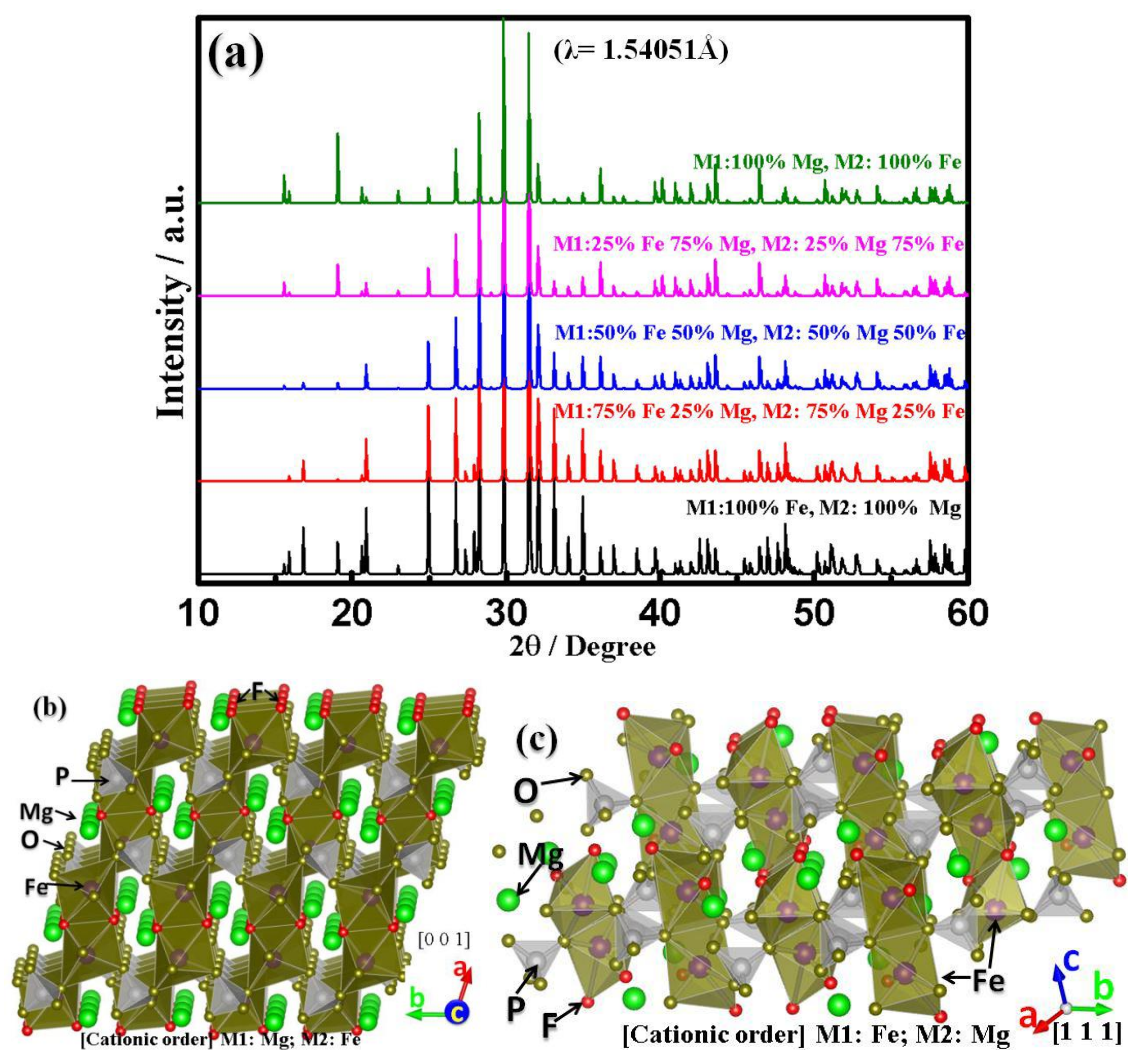


Fig. 6-6. (a) Simulated X-ray diffraction patterns ranging from 10° to 60° of MFPPF with various occupations of Fe and Mg in M1 and M2 sites. The corresponding 3D crystallographic representations of simulated MFPPF in two different cationic orderings are shown in (b) and (c).

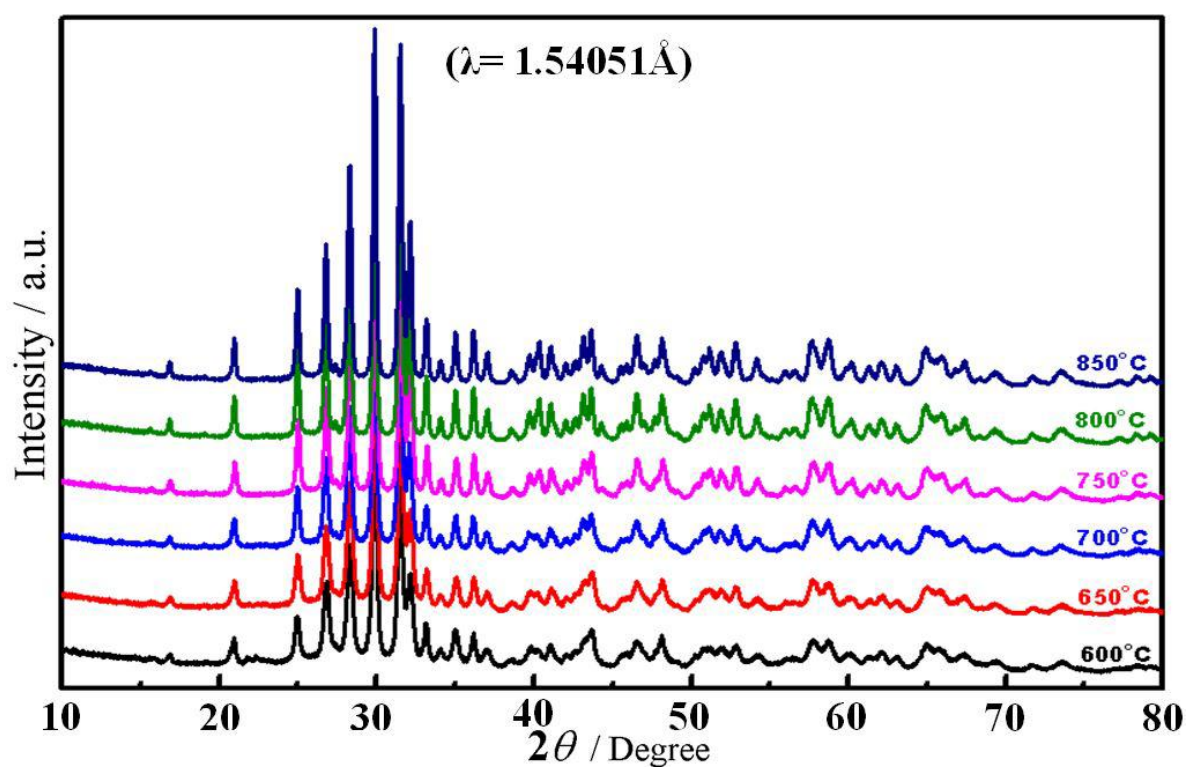


Fig. 6-7. X-ray diffraction patterns of MgFePO₄F prepared at different temperatures (*viz.* 600°C, 650°C, 700°C, 750°C, 800°C and 850°C).

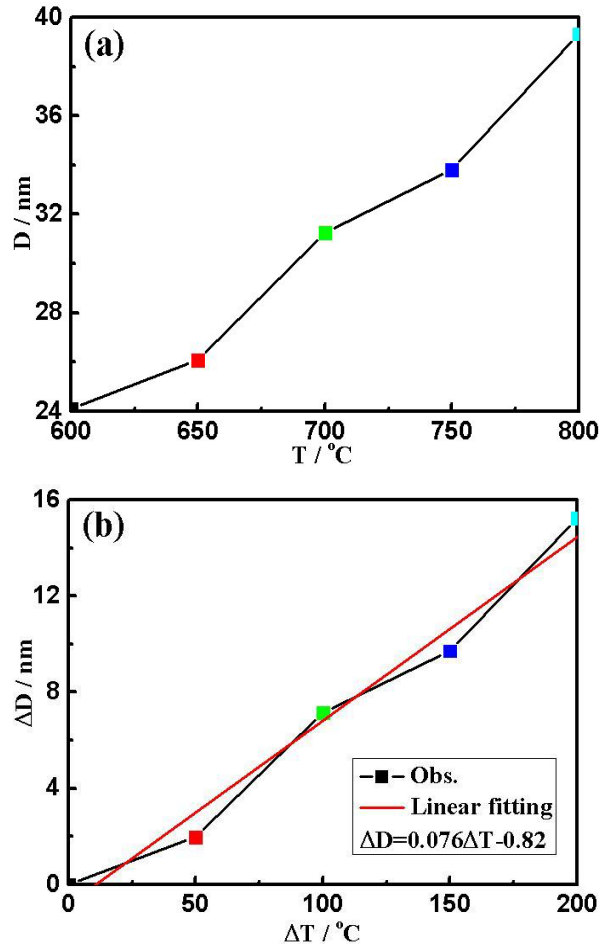


Fig. 6-8. (a) The crystal grain size of MFPP sintered for 5h from 600 to 800°C calculated by the Scherrer equation ($D=K\lambda/\beta\cos\theta$). K is a dimensionless shape factor, has a typical value of about 0.9. λ is the X-ray wavelength, equal to 0.154 nm. β and θ are the full-width at halfmaximum and the Bragg angle of the diffraction peak (2θ) centered at 29.8°, respectively. (b) The linear relationship of the grain size increment vs the rising of sintering temperature.

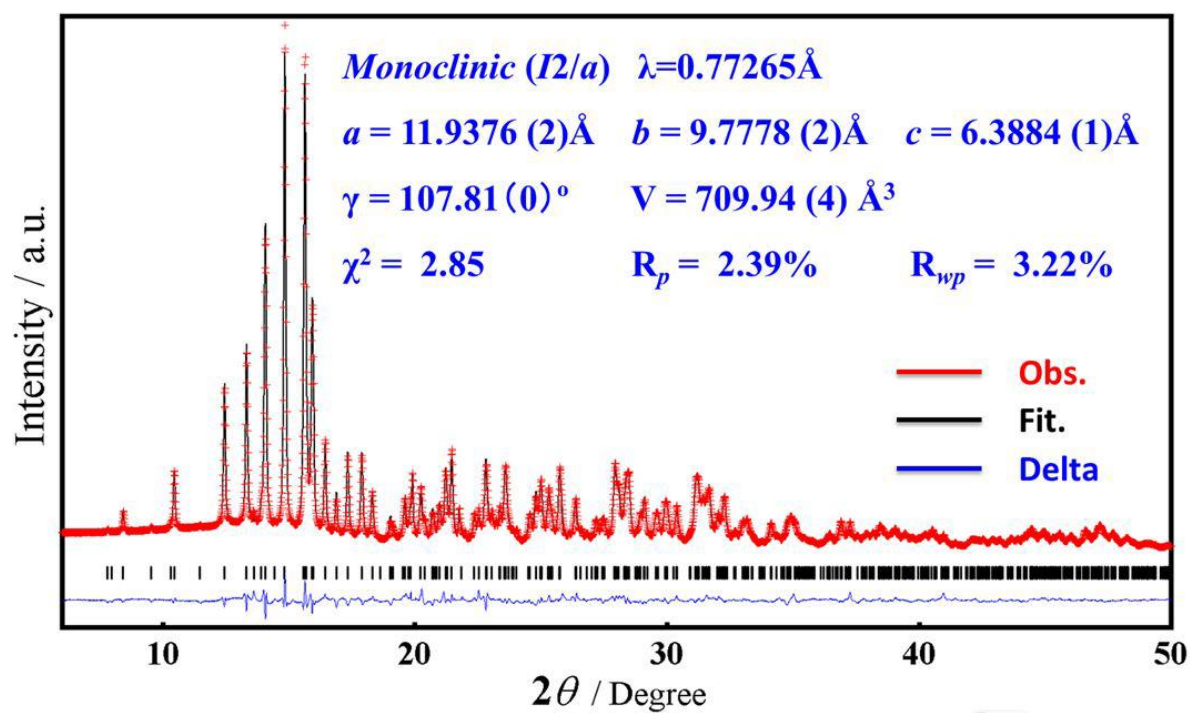


Fig. 6-9. Rietveld refinement result of the synchrotron XRD pattern of MFPP prepared at 800°C.

Table 6-2. Atomic parameters obtained from Rietveld refinement of the SXRD patterns for as prepared MgFePO_4F synthesized at 800 °C.

Atom	q	x	y	z	U^*
Mg1	0.440	0.1794(6)	0.1663(6)	0.9551(10)	0.005
Fe1	0.560	0.1928(2)	0.2029(2)	0.9839(4)	0.005
Mg2	0.560	0.0855(7)	0.4585(9)	0.1281(11)	0.005
Fe2	0.440	0.0972(4)	0.4504(5)	0.1530(6)	0.005
P	1.000	0.0755(2)	0.3823(2)	0.6521(3)	0.010
O1	1.000	0.0558(3)	0.4761(3)	0.8274(6)	0.010
O2	1.000	0.9570(3)	0.2648(4)	0.6038(5)	0.010
O3	1.000	0.1722(4)	0.3078(4)	0.7111(4)	0.010
O4	1.000	0.1192(3)	0.4749(3)	0.4629(6)	0.010
F	1.000	0.2699(3)	0.3746(4)	0.1287(5)	0.005

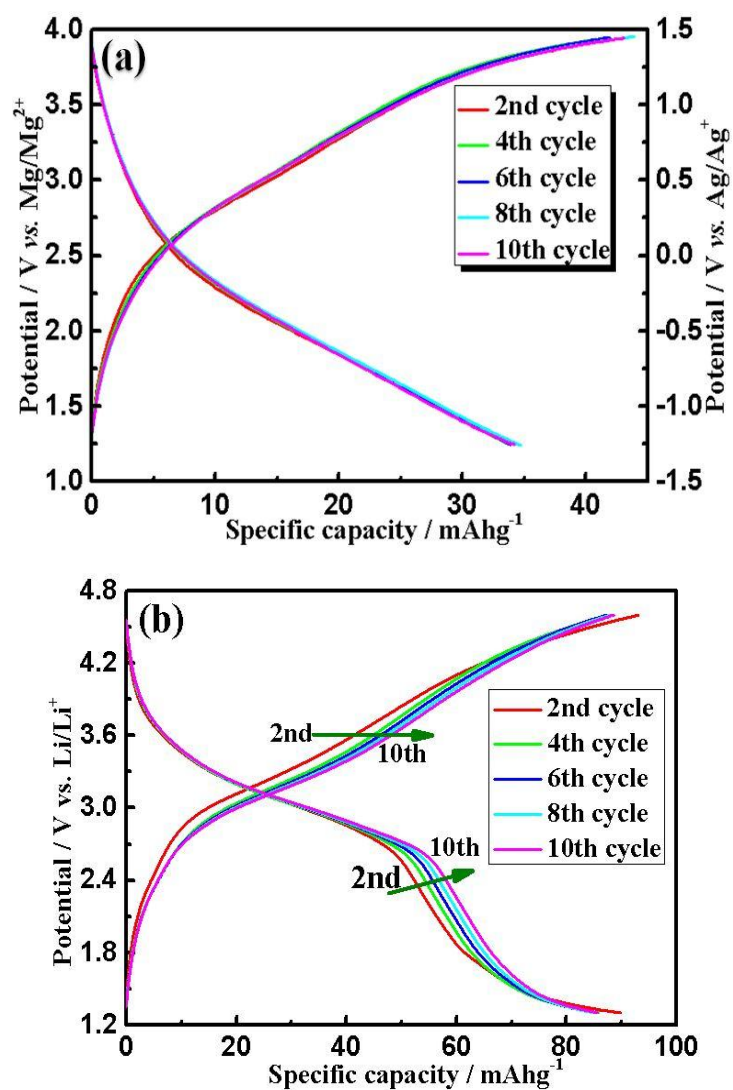


Fig. 6-10. Voltage (dis)charge profiles of MFPP recorded at 25°C in (a) MB at C/20 rate and (b) LIB at C/30 rate.

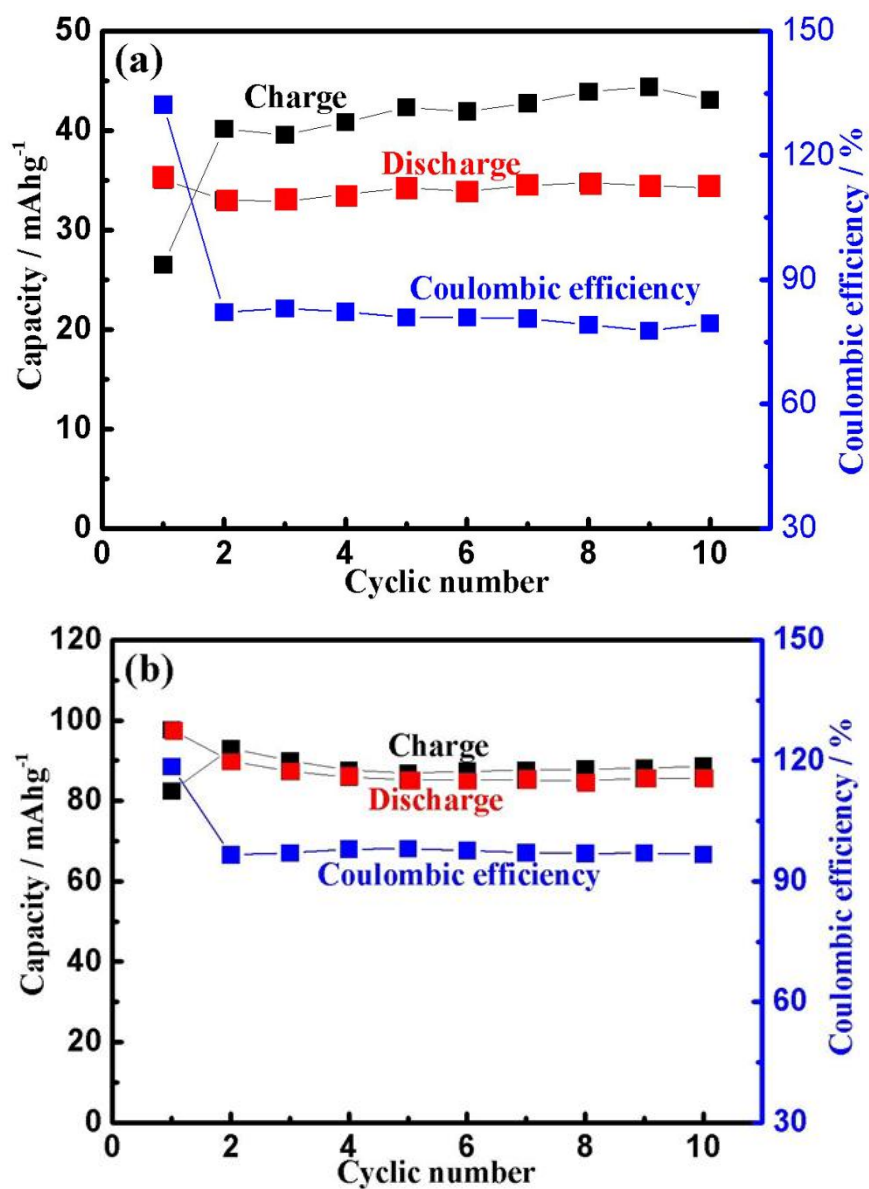


Fig. 6-11. Cyclic performance and coulombic efficiency of the as-prepared MFPE electrodes in a three-electrode Mg-ion cell (a) and two-electrode Li-ion cell (b).

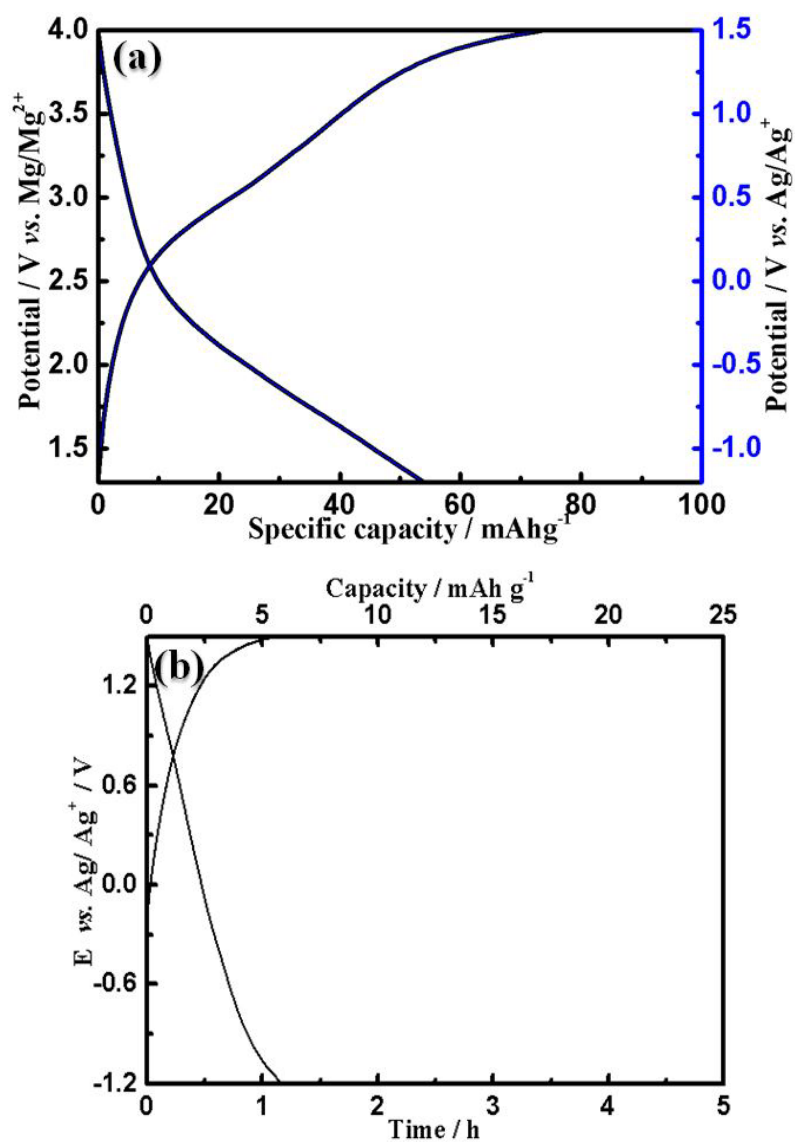


Fig. 6-12. Voltage (dis) charge profiles of (a) MFPPF and (b) AB recorded at a current density corresponding to C/30 rate at 25°C in a Mg-ion cell

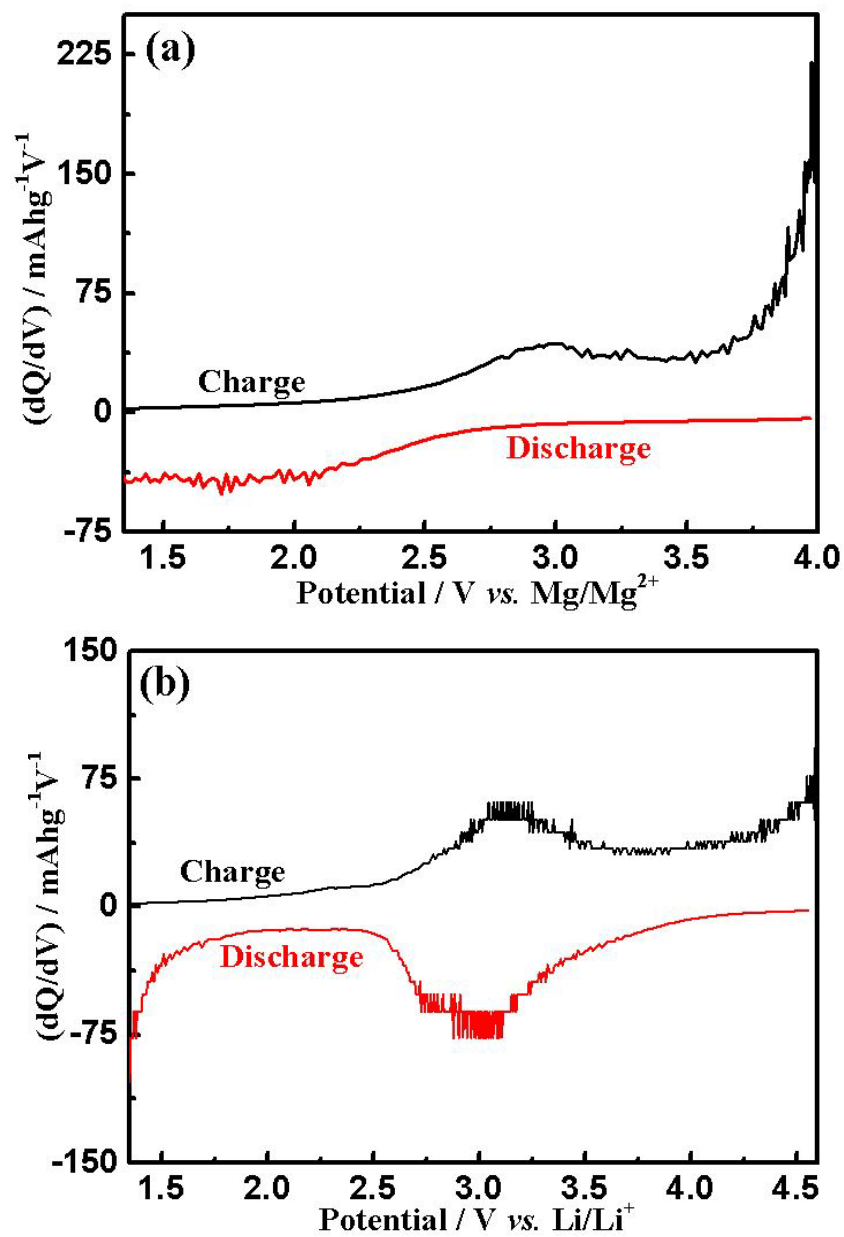


Fig. 6-13. Differential capacity dQ/dV plots corresponding to the tenth charge/discharge cycle of the as-prepared MFPF electrode in a three-electrode Mg-ion cell (a) and a two-electrode Li-ion cell (b).

Chapter 7 : Vanadium phosphate as a promising high-voltage magnesium ion (de)-intercalation cathode host

5.1. Introduction

Prime attention has been inclined towards the development of alternative energy storage devices, which have a comparable electrochemical performance, but are safer and of considerably lower cost than lithium ion batteries, in order to meet the escalating new energy demand in the future low carbon society. Mg batteries have gained considerable concerns since the development of a prototype rechargeable Mg battery, where Mg^{2+} ions replace Li^+ as the charge carrier, in 2000.¹ Compared to Li anode, Mg anode is low-cost and shows (3020 \$ per ton, vs. ~69 000 \$ per ton for Li) much higher abundance (13.9%, vs. $7 \times 10^{-4}\%$ for Li) and higher theoretical volumetric energy density ($3832 \text{ mA h cm}^{-3}$, vs. $2062 \text{ mA h cm}^{-3}$ for Li).^{1, 2} Moreover, Mg is stable upon air exposure and is free of dendritic deposition during repeated cycling, and thus, is inherently safer than Li.^{1, 2} Although Mg batteries are deemed as promising alternatives for a gamut of large-scale storage devices that could couple with renewable energy sources to load the electric grid, and the low working voltage, as well as low capacity of the cathode material limits the attainable energy; thereby, hampering the commercial realization of Mg batteries.³ One of the most effective and direct solutions is to find a proper cathode host with high average working voltages, as well as high capacities. Several cathode materials, including Chevrel phases $\text{A}_x\text{Mo}_6\text{T}_8$ (A = metal, T = S, Se)^{4, 5} Mg_xMSiO_4 (M = Fe, Mn, Co),⁶⁻⁹ transition metal oxides (V_2O_5 ,¹⁰⁻¹⁴ MnO_2 ,¹⁵⁻¹⁷) and

transition metal chalcogenides (MoS_2 , TiS_2 and WSe_2),¹⁸⁻²¹ have been reported as feasible cathode materials for Mg batteries, which exhibit reasonable reversible capacities. Considerable effort has been devoted to bypassing the intrinsically sluggish solid-state diffusion of Mg^{2+} within the host cathodes via morphological design strategies, such as nano-sizing and carbon-coating.¹⁸⁻²¹ However, most of the reported cathode materials show relatively low working voltages. Therefore, the pursuit for novel high voltage cathode materials that exhibit a high capacity is crucial for the development of high energy density Mg battery systems. Vanadium phosphates (*viz.*, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (hereafter denoted as LVP)) has proven to be promising high performance cathode materials for lithium ion batteries, due to their high working voltage (~ 4 V), high theoretical capacity (197 mA h g^{-1}), three-dimensional (3D) crystal structural framework, good thermal stability and remarkable rate capability.²²⁻²⁴ It was reported that the average working potential of Mg^{2+} -based compounds vs. Mg/Mg^{2+} is about 1 V lower than that of their Li^+ -based analogues in lithium ion battery systems.² Thus, the expected average working voltage of $\text{Mg}_x\text{V}_2(\text{PO}_4)_3$ (the Mg^{2+} intercalated counterparts of LVP) could be up to ~ 3 V, which is considerably higher than the reported cathode materials shown in Table S1.† Therefore, we anticipate to employ LVP and/or $\text{Mg}_x\text{V}_2(\text{PO}_4)_3$ as high voltage cathode materials to couple with the Mg anode. Worthy to mention is that, to date, no attention has been paid to exploring the $\text{A}_x\text{V}_2(\text{PO}_4)_3$ system (where $\text{A} = \text{Li}, \text{Na}$ ($0 < x < 3$) or Mg ($0 < x < 1.5$)) as potential cathode materials for Mg batteries. In this communication, we report on the feasibility of using electrochemically delithiated $\text{V}_2(\text{PO}_4)_3$ (hereafter denoted as ED-VP) as a promising magnesium ion (de)-intercalation host and provide promising high voltage cathode host material contenders for Mg batteries. Here, ED-VP was prepared by the electrochemical

delithiation of all three lithiums from the host structure of carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (hereafter denoted as C-LVP). Electrochemical measurements, crystal and electronic structural, as well as composition analyses indicate that ED-VP demonstrate an exceptionally high average working voltage with reasonable capacity in an Mg^{2+} electrolyte. Reversible Mg^{2+} (de)-intercalation into (from) the host frameworks of ED-VP have been verified by our findings.

5.2. Experimental

Preparation and electrochemical delithiation of C- $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composites

Carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (C-LVP) was prepared by using the conventional ball-milling assisted carbothermal method. Stoichiometric amounts of LiH_2PO_4 (97%, STREM Chemicals), V_2O_5 (98+%, Sigma-Aldrich) powders corresponding to 0.01 mol of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, citric acid (anhydrous, Wako) and Ketjen carbon black (KB) were sealed into a zirconia (ZrO_2) pot with 10 ml ethanol and 15.9 g zirconia ball. Subsequently, the mixture was ball-milled on a planetary pulverizer (FRITSCH, Pulverisette 7) at 300 rpm for 10 h with reverse rotation every 15 min. After being dried at 70°C for 10 h, the dried slurry was separated with zirconia ball and pulverized using an agate mortar, thereafter pelletized at 50 MPa using a hydraulic press machine. The pellet was pre-calcined at 300°C for 6 h followed by final calcination at 750°C for 5 h in a tube furnace with a fixed Ar flux. The final product was pulverized by ball-milling at 500rpm for 12 h.

The as-prepared C-LVP powders were used to prepare the electrodes by mixing the ball-milled active powder with KB and polytetrafluoroethylene (PTFE). The final weight ratio of LVP/C+KB/PTFE was 75:15:10. Subsequently, the obtained sheet was

punched into 6 mm discs (the typical mass loading is ~ 3 mg per disc) and pressed between two Pt meshes. The final electrodes were vacuum dried at 70°C for 12 h. C-LVP electrodes were electrochemically delithiated in three-electrode Mg cells assembled in an Ar-filled glove box (MIWA). Polished Mg rod was used as counter electrode. Ag/Ag⁺ electrode prepared by inserting a silver wire into a glass tube containing a solution of 0.1M AgNO₃ in acetonitrile was used as reference electrode. 0.5M Mg(TFSA)₂ in acetonitrile (solvent) was used as electrolyte. The solution of 0.1 M AgNO₃ in acetonitrile was brought into contact with Mg(TFSI)₂/acetonitrile solution via a microporous glass membrane. Electrochemically delithiated V₂(PO₄)₃ (ED-VP) was obtained by charging the assembled Mg cells at a current density commensurate to 0.05C (1C = 197 mA g⁻¹) rate at 55°C. The delithiated ED-VP was disassembled from the fully charged Mg cell, followed by washing with acetonitrile for several times. As a control experiment, C-LVP was also delithiated in two-electrode lithium ion cells with Li sheet as anode, microporous polypropylene membrane as separator and 1 mol L⁻³ solution of LiClO₄ in ethylene carbonate/diethyl carbonate (1:1 ratio by volume, all received from Kishida chemical) as electrolyte.

Electrochemical characterization

The electrochemical performances of C-LVP and ED-VP as cathode material for Mg battery were characterized in three-electrode cells shown in Figure S4. The protocols for preparation of the electrode and cell assembly were the same as those employed during the delithiation process of LVP. Galvanostatic charge and discharge measurements in an appropriate potential window vs. Ag/Ag⁺ were carried out at a current density corresponding to 0.05C rate at 55°C. After being fully charged, the charged C-LVP electrodes were discharged to various capacities corresponding to 39.4 mAh g⁻¹, 78.8

mAh g⁻¹, 118.2 mAh g⁻¹, 157.6 mAh g⁻¹ and 197 mAh g⁻¹. The fully charged and discharged electrodes were rinsed several times with super-dehydrated acetonitrile followed by vacuum drying for 12 h. The compositions of discharged LVP were analyzed by using inductively coupled plasma (ICP) measurements. Synchrotron X-ray diffraction (SXRD) and X-ray absorption spectroscopy (XAS) measurements were performed on pristine and charged /discharged C-LVP to assess the crystal and electronic structures after the electrochemical measurement. The cyclic voltammograms during the initial 7 cycles of LVP in three-electrode Mg cells and V₂(PO₄)₃ electrodes obtained via the electrochemical delithiation of Li₃V₂(PO₄)₃ electrodes (ED-VP) using newly assembled three-electrode cells were performed at a scanning rate of 0.1 mV s⁻¹ at 55°C, respectively. Characterization of morphology, crystal structure and Rietveld refinement of synchrotron X-ray diffraction patterns (SXRD) The morphology of the as-prepared C/LVP was characterized by using scanning electron microscopy (JEOL, JSM-890) at an acceleration voltage of 15 kV. Synchrotron X-ray diffraction patterns of C-LVP were collected at the beam line BL02B2 (SPring-8 in Japan), equipped with a large Debye-Scherrer camera. C-LVP powder and the charged/discharged LVP electrodes were sealed in a glass capillary in an Ar-filled glove box to prevent the sample's exposure to air. To minimise the effect of X-ray absorption by the 3 samples, the wavelength (λ) of the incident X-ray beam was set to 0.49971(1) Å using a Si monochromator, which was calibrated with a CeO₂ standard. X-ray diffraction data were recorded on an imaging plate for 1h. The crystal structure was further refined by the Rietveld method with the program JANA2006 using the pseudo-Voigt function of Finger *et al*^{25, 26} and drawn by the software of VESTA.²⁷ X-ray absorption measurements X-ray absorption spectra of pristine and charged/discharged LVP

electrodes were measured in the energy region of the V-K edge at room temperature in transmission mode at the beam line BL14B2 of SPring-8. The intensity of X-ray beam was measured by ionization detectors. Treatment of the raw X-ray absorption data was performed with Athena package.²⁸ Analysis of V-K and Fe-K edge XANES spectra was performed with the Rigaku REX 2000 program package.²⁹

5.3. Results & Discussions

Fig. 7-1 shows the Scanning Electron Microscopy (SEM) images and synchrotron X-ray diffraction (SXRD) patterns of pristine CLVP. Citric acid and high surface area carbon (Ketjen black) were used as the carbon source for the carbothermal reduction process.³⁰ The total carbon content obtained from the trace elements analysis was ~4.1 wt%. The SEM images shown in Fig. 7-1a and b indicate a uniform C-LVP composite. The particle size of LVP is in the range of 150–400 nm. Fig. 7-1c presents the Rietveld refinement of the SXRD pattern and the inset shows a 3D graphical representation of the crystal structure of the as prepared LVP. The observed pattern coincides with the calculated pattern with low reliability factors, validating the quality of the fit. The lattice parameters of the as-prepared C-LVP ($a = 8.6080(2) \text{ \AA}$; $b = 8.5939(2) \text{ \AA}$; $c = 14.7263(4) \text{ \AA}$; $\beta = 125.180(1)^\circ$) are much closer to that reported for LVP.³¹ The atomic parameters are listed in Table 7-1. Isostructural to the monoclinic structure of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ ($P_{21/c}$ space group), LVP entails VO_6 octahedrons and PO_4 tetrahedrons, which share their apical O atoms to form a 3D framework. The positions of the Li^+ ions in the empty channels (voids) vary depending on the synthetic conditions.³¹

The as-prepared C-LVP composite electrodes were electrochemically delithiated using both two-electrode Li cells and three-electrode Mg cells. The electrochemical

measurements were performed at 55°C, in order to fully delithiate the three Li^+ from LVP. Fig. 7-2a shows the initial charge profile of C-LVP in the Li cell, which corresponds to the delithiation of LVP. Four typical two-phase plateaus observed at ~ 3.592 V, ~ 3.679 V, ~ 4.075 V and ~ 4.489 V, respectively, correspond to the extraction of Li^+ from three different crystallographic sites of LVP.^{22, 23} The initial charge capacity of LVP is 197 mA h g^{-1} , which indicates that all three Li^+ ions have been fully extracted from LVP host structure. A similar initial charge profile with four two phase plateaus exhibiting a charge capacity of 197 mA h g^{-1} is also observed during the initial charge process of LVP in a three electrode Mg cell (see Fig. 7-2b). The results shown in Fig. 7-2a and b indicate that the asprepared C-LVP composite can be fully delithiated in both Li and Mg cells at a current density corresponding to the C/20 rate at 55°C. It is worth noting that a similar charge behaviour of LVP, but lower capacity, can be observed when the tests were conducted at room temperature. The SXRD pattern of the fully charged LVP was shown in Fig. 7-3. Upon delithiation of all three Li^+ , the crystallinity of ED-VP apparently decreases. This observation is in line with the previous report.²⁴ For the sake of clarity, the four delithiation plateau voltages vs. Li/Li^+ were also used to calibrate the potential of the LVP and ED-VP working electrodes vs. Ag/Ag^+ and Mg/Mg^{2+} .

In this work, galvanostatic measurements were conducted for both C-LVP and ED-VP working electrodes in a threeelectrode Mg ion cell using an Ag/Ag^+ standard electrode and Mg rod as the reference and counter electrode, respectively. 0.5 M $\text{Mg}(\text{TFSA})_2$ in acetonitrile solution was used as the electrolyte. Fig. 7-4 shows the electrochemical performance of LVP with repeated cycling. Surprisingly, the attained discharge capacity of the LVP electrode is 197 mA h g^{-1} within the same three electrode

Mg cells. Moreover, the average (dis)charge potential of around 3.0 V vs. Mg/Mg^{2+} was determined according to both the delithiation potential vs. Li/Li^+ anode and the reference potential vs. Ag/Ag^+ , which further confirms that the voltage expected with a Mg battery is about 1 V lower than that of a lithium ion battery using the same cathode materials.² It is notable that the average working voltage vs. Mg/Mg^{2+} (~ 3.0 V) and the reasonable capacity (197 mA h g^{-1}) of LVP outclasses the hitherto reported cathode host materials for rechargeable MBs. Furthermore, two plateaus were observed when the cell was discharged to 197 mA h g^{-1} (see Fig. 2b). Interestingly, during the subsequent cycles, the quasi plateau charge profiles (typical of a two-phase electrochemical behaviour) gradually transform to sloping single-phase profiles (Fig. 7-4.), due to the gradually decreasing contribution from the Li^+ intercalation and slight structure variation caused by the intercalation of Mg^{2+} . Fig. 7-2c shows the shifts of the absorption edges of the V-K edge XAS spectra, which correspond to the oxidation or reduction of vanadium ions; this is univocal evidence for the intercalation of Mg^{2+} and Li^+ during the discharge process. Further intercalation of more Mg^{2+} and Li^+ into the outer layer of LVP active particles should account for the further shift of the V-K edge absorption spectra to a lower absorption energy beyond that of pristine LVP upon discharging to 197 mA h g^{-1} . This phenomenon does not come entirely as a surprise, taking into account the sluggish diffusion kinetics of Mg^{2+} and the multivalent nature of vanadium ions. The crystallinity of delithiated LVP recovered in a certain degree with the varying amount of inserted Mg^{2+} and/or Li^+ . For example, the electrode discharged to a capacity of $118.2 \text{ mA h g}^{-1}$ exhibits the highest crystallinity in the same monoclinic $P2_1/c$ space group as LVP. Its refined SXRD pattern and 3D graphical representation of the crystal structure are presented in Fig. 7-5. The refined atomic coordinates are

furnished in Table 7-2. The composition formula estimated from the Rietveld refinement is $\text{Li}_{0.7}\text{Mg}_{0.55}\text{V}_2(\text{PO}_4)_3$, which is slightly different from the composition formula calculated based on the results of the ICP measurements shown in Table 7-3. The calculated composition formulas for the electrodes discharged to a capacity of 78.8 mA h g⁻¹ and 118.2 mA h g⁻¹ are $\text{Li}_{1.32}\text{Mg}_{0.37}\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_{1.35}\text{Mg}_{0.44}\text{V}_2(\text{PO}_4)_3$, respectively. These observations are unambiguous proof that Mg^{2+} have been successfully intercalated into the structural framework of the electrochemically de-lithiated $\text{V}_2(\text{PO}_4)_3$. The discrepancy in the composition predicted by the structural refinement and ICP measurement should be caused by the nonuniform composition from surface to core of active particles. More Mg^{2+} should be found from the outer layer of the particles due to the considerably slower diffusion kinetics of Mg^{2+} than Li^+ . Both the ICP analysis results and the over shift of V *K*-edge absorption spectra reveal that the discharge plateau observed at a low potential arises from the further intercalation of Mg^{2+} and Li^+ into the outside layer, rather than the decomposition of the electrolyte. The decreasing discharge capacity of the high potential discharge plateau with cycling should be ascribed to the decreasing intercalation of Li^+ . As presented in Table 7-4, the lattice parameters and lattice volume obviously increase with the rise of the discharge capacity, in other words, with the intercalation of more Li^+ and Mg^{2+} . To investigate the (de)intercalation behaviour of Mg^{2+} within the host structure of ED-VP and avoid the influence of Li^+ , the fully delithiated ED-VP electrodes were characterized using newly assembled three-electrode Mg cells after being washed several times with acetonitrile. Fig. 7-6 shows the galvanostatic discharge/charge profiles (5th cycle) of the ED-VP electrodes. With respect to the discharge process of the ED-VP electrodes in Mg^{2+} electrolyte, an obvious transfer of discharge profiles from an initially linear profile to a

sloping stage profile could be observed from Fig. 7-7, which indicates that the discharge behaviour changed from the surface absorption and outer layer insertion of Mg^{2+} to the ‘inner core’ diffusion of Mg^{2+} . Two discharge plateaus are observed from the 5th discharge profile (see Fig. 6a). The initial charge profile exhibits a typically short flat plateau; however, the subsequent charge profiles gradually change to long sloping profiles. The charge capacity also increased to 197 mA h g^{-1} at the 5th cycle. From the 5th cycle, the electrochemical performance of the ED-VP electrodes were the same as that for the LVP electrodes cycled in Mg^{2+} electrolyte, as shown in Fig. 7-4 and 7-6a. Generally speaking, the consistent evolution of the charge/discharge profiles indicates that the reversible intercalation/de-intercalation of Mg^{2+} into/from the ED-VP electrode is gradually activated during the initial 5 cycles. The apparent shift to lower energies of the absorption edge features for the V-K edge XAS spectra corresponds to the reduction of vanadium ions during the initial discharge process of ED-VP (Fig. 7-6b). This validates the intercalation of Mg^{2+} during the discharge process. Additionally, the CV measurement was performed to further discuss the (de)intercalation mechanisms. Fig. 7-8a depicts the cyclic voltammetry (CV) curves of the LVP cathode material in a three-electrode Mg cell. Four sharp oxidation peaks are observed in the initial cycle, which are indicative of the four two phase plateaus observed during the initial delithiation process. The gradual transformation of electrochemical behaviour from a two- to single-phase is also evident, as manifested by the weakening and broadening of the oxidation peaks. The broad reduction peaks and the sloping discharge profiles are reminiscent of a single-phase electrochemical behaviour. With subsequent cycling, the transitions between the 1st and 2nd reduction peaks become smoother, while the 2nd reduction peaks become narrow and the 3rd reduction peak is more distinct. These

observations clearly reflect the smoother transition from initial discharge profile to the gradually shorter discharge plateau at high potentials, and the extension of the discharge plateau at low potentials. Based on the stabilized CV curves shown in Fig. 7-8a, we expect the charge carriers (Mg^{2+} and/or Li^+) to be reversibly inserted into and extracted from the host structure of delithiated LVP. The evolution of the CV curves of ED-VP with successive cycling (see Fig. 7-5b) is consistent with the evolution of the galvanostatic charge/discharge profiles of ED-VP. Two sharp oxidation peaks observed from the 1st cycle of the CV curve diminish in the subsequent cycles, and the subsequent oxidation peaks slightly shift to a lower potential and become broader. Starting from the 7th cycle, the oxidation peaks centered at different potentials merged into a broad peak. Indifferent to ED-VP, three distinct oxidation peaks were observed from the CV curves of the LVP electrodes in Mg^{2+} electrolyte (see Fig. 7-8a). This difference indicates that the oxidation peaks centered at ~ 0.24 V and 0.34 V correspond to the extraction of Li^+ from the structure of discharged LVP in Mg^{2+} electrolyte. Moreover, the sharper oxidation peak centered at ~ 0.8 V and the slightly higher average working potential (~ 3.0 V vs. Mg/Mg^{2+}) of LVP than that of ED-VP (~ 2.9 V vs. Mg/Mg^{2+}) are due to faster transfer kinetics and the more positive chemical potential of Li^+ than that of Mg^{2+} in the same hosts.² Initially, a reduction peak centered at ~ 0.8 V is observed. Subsequently, the reductive peak gradually broadens and shifts to ~ 0.62 V. Starting from the 4th cycle, two additional broad oxidation peaks centered at ~ -0.06 V and ~ -1.05 V emerge from the 4th and 7th cycles, respectively. The cyclic voltammograms of the ED-VP electrode are the same as that of the LVP electrode tested in Mg^{2+} electrolyte (Fig. 8a and b). Generally speaking, the consistent evolution of both the charge/discharge profiles and CV curves indicate that the reversible intercalation/

de-intercalation of Mg^{2+} into/from the ED-VP electrode is gradually activated during the initial 5 cycles.

5.4. Conclusions

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) was prepared using a ballmilling-assisted solid state carbothermal method. All three lithium ions were electrochemically delithiated from LVP to successfully prepare $\text{V}_2(\text{PO}_4)_3$ (ED-VP). Electrochemical measurements, coupled with crystal structure, electronic structure and composition analyses validate that Mg^{2+} can be reversibly intercalated into and extracted from the host structure of ED-VP. As cathode host materials for Mg batteries, both LVP (~ 3.0 V) and ED-VP (~ 2.9 V) exhibit high average working voltages vs. Mg/Mg^{2+} with a reasonable high capacity (*i.e.*, 197 mA h g^{-1}). To the best of our knowledge, the exhibited voltage by far surpasses other reported cathode materials for Mg batteries. This work not only provides a high-voltage cathode material contender for Mg battery systems, but also highlights the versatility of electrochemical cation exchange for accessing new functional materials for future rechargeable battery systems. Further work is ongoing to understand the evolution of the crystal structure and electrochemical behaviour of LVP and VP as high-rate cathode materials for Mg batteries. Additionally, a stable electrolyte, which is compatible to an Mg anode and possesses a wide voltage window of 0–4 V, or even 0–5 V, should be developed in order to develop high performance prototype two-electrode Mg batteries by using $\text{V}_2(\text{PO}_4)_3$ -based compounds, such as LVP and ED-VP, as cathode materials.

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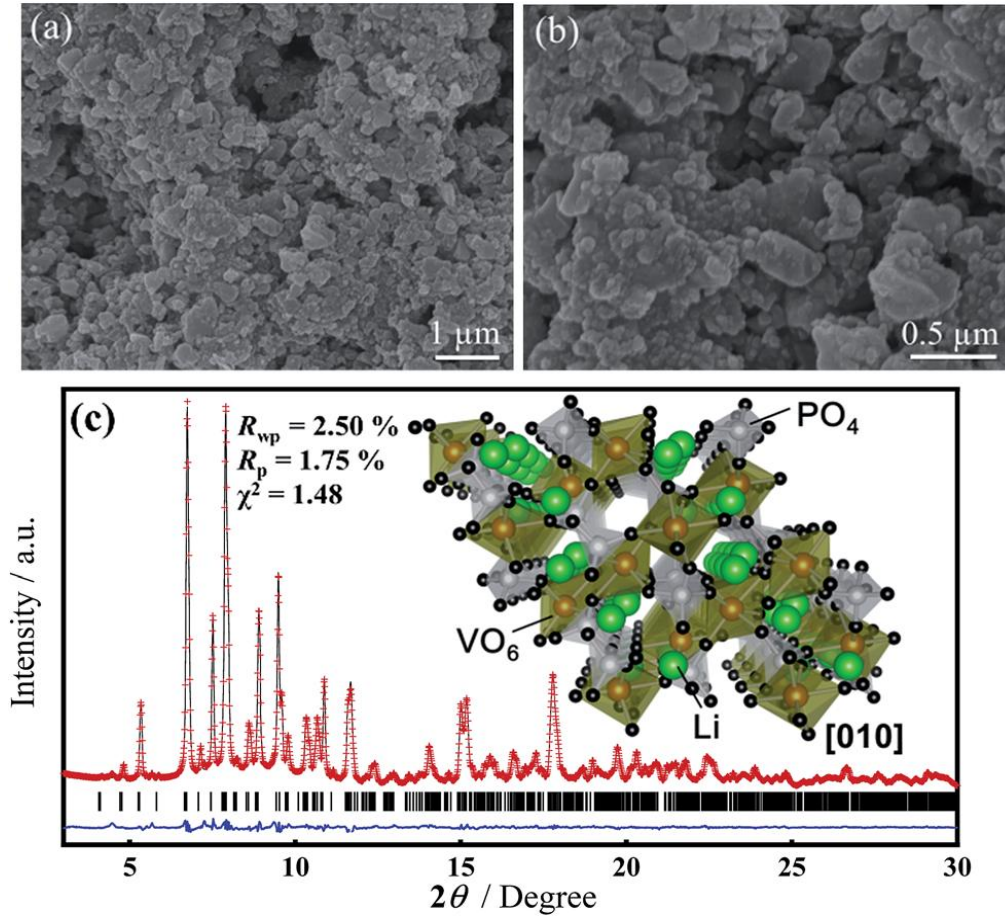


Fig. 7-1. SEM images of the as-prepared C-LVP composite: (a) 15 000, (b) 40 000; (c) Rietveld refinement of the SXRD pattern of C-LVP and a 3D graphical representation of the crystal structure (inset). The wavelength was set at 0.49971 (1) Å. The observed and calculated peaks are indicated in red and black, respectively. The difference between the observed and calculated intensity is indicated in blue, while black ticks indicate the position of the Bragg peaks of the phase. The agreement indices used are $R_{wp} = [\sum w_i (y_{io} - y_{ic})^2 / \sum w_i (y_{io})^2]^{1/2}$, $R_p = \sum |y_{io} - y_{ic}| / \sum y_{io}$ and the goodness of fit, $\chi^2 = [R_{wp} / R_{exp}]^2$ where $R_{exp} = [(N - P) / \sum w_i y_{io}^2]^{1/2}$, y_{io} and y_{ic} are the observed and calculated intensities, w_i is the weighing factor, N is the total number of y_{io} data when the background is refined, and P is the number of adjusted parameters.

Table 7-1. Refined atomic coordinates of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. g and U_{iso} denote the occupancy and isotropic thermal factor, respectively. The atomic positions of Li and isotropic thermal factors (U_{iso}) of atoms were fixed during the Rietveld refinement to the values reported by Kee *et al.*³¹

Atom	g	x	y	z	U_{iso}
Li1	1.000	0.1133(-)	0.5883(-)	0.1934(-)	0.0263(-)
Li2	1.000	0.1891(-)	0.1919(-)	0.2599(-)	0.0362(-)
Li3	1.000	0.4730(-)	0.2213(-)	0.1767(-)	0.0185(-)
V1	1.000	0.1394(3)	0.5278(2)	0.3903(2)	0.0067(-)
V2	1.000	0.3621(4)	0.5399(2)	0.1099(2)	0.0065(-)
P1	1.000	0.0440(4)	0.2502(5)	0.0076(3)	0.0066(-)
P2	1.000	0.4576(5)	0.3961(4)	0.3508(3)	0.0067(-)
P3	1.000	0.7524(5)	0.3836(4)	0.1463(2)	0.0063(-)
O1	1.000	0.0267(10)	0.1747(8)	0.0960(5)	0.0126(-)
O2	1.000	0.0329(9)	0.3608(8)	0.4233(5)	0.0150(-)
O3	1.000	0.0844(8)	0.0001(7)	0.2813(5)	0.0102(-)
O4	1.000	0.1209(9)	0.6351(8)	0.0687(5)	0.0111(-)
O5	1.000	0.1779(9)	0.7126(9)	0.3184(5)	0.0109(-)
O6	1.000	0.2380(10)	0.3268(7)	0.0708(5)	0.0112(-)
O7	1.000	0.2758(10)	0.3860(8)	0.3525(5)	0.0125(-)
O8	1.000	0.3624(9)	0.5482(7)	0.5411(5)	0.0171(-)
O9	1.000	0.4761(9)	0.2340(9)	0.3125(5)	0.099(-)
O10	1.000	0.5911(10)	0.0185(8)	0.2387(5)	0.0115(-)
O11	1.000	0.6000(9)	0.4053(7)	0.1676(5)	0.0110(-)
O12	1.000	0.6748(5)	0.4125(7)	0.0272(9)	0.0128(-)

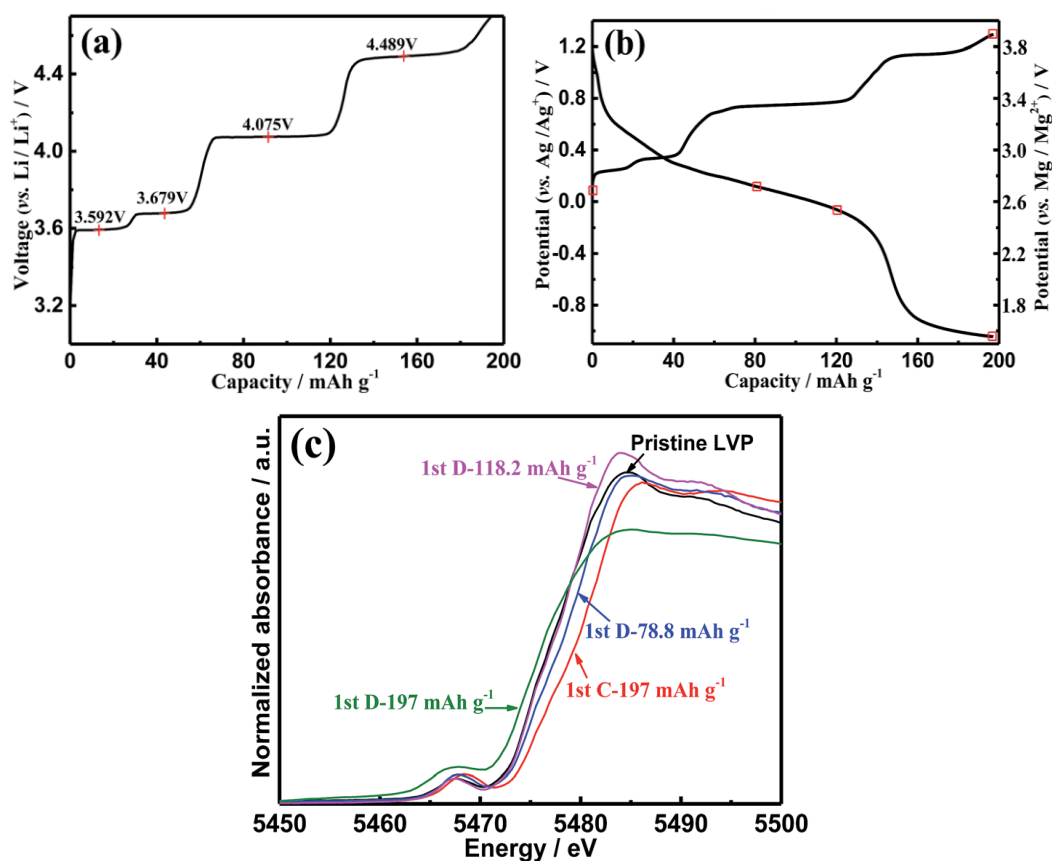


Fig. 7-2. Electrochemical performance of the composite electrodes consisting of LVP (75 wt%), carbon (15 wt%) and polytetrafluoroethylene (10 wt%): (a) the 1st charge profile corresponding to the delithiation process of LVP in two-electrode Li cells, (b) the 1st charge/discharge profiles in three-electrode Mg cells using the Ag/Ag^+ electrode as a reference electrode, and (c) shift of X-ray absorption V-K absorption edges during the 1st discharge process from the fully charged state (1st C-197 mA h g^{-1}) to the fully discharged state (1st D-197 mA h g^{-1}).

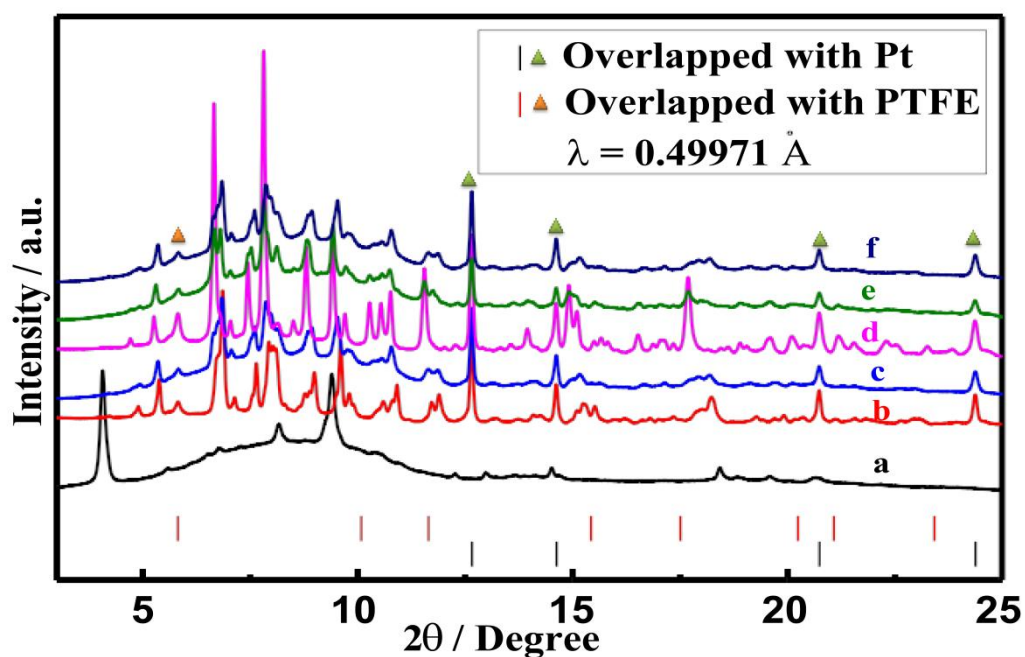


Fig. 7-3. Synchrotron X-ray diffraction patterns of LVP at various states of charge and discharge: (a) 1st charged to 197 mAh g^{-1} (1st C-197), (b) 1st discharge to 39.4 mAh g^{-1} (1st D-39.4), (c) 1st discharge to 78.8 mAh g^{-1} (1st D-78.8), (d) 1st discharge to 118.2 mAh g^{-1} (1st D-118.2), (e) 1st discharge to 157.6 mAh g^{-1} (1st D-157.6) and (f) 1st discharge to 197 mAh g^{-1} (1st D-197).

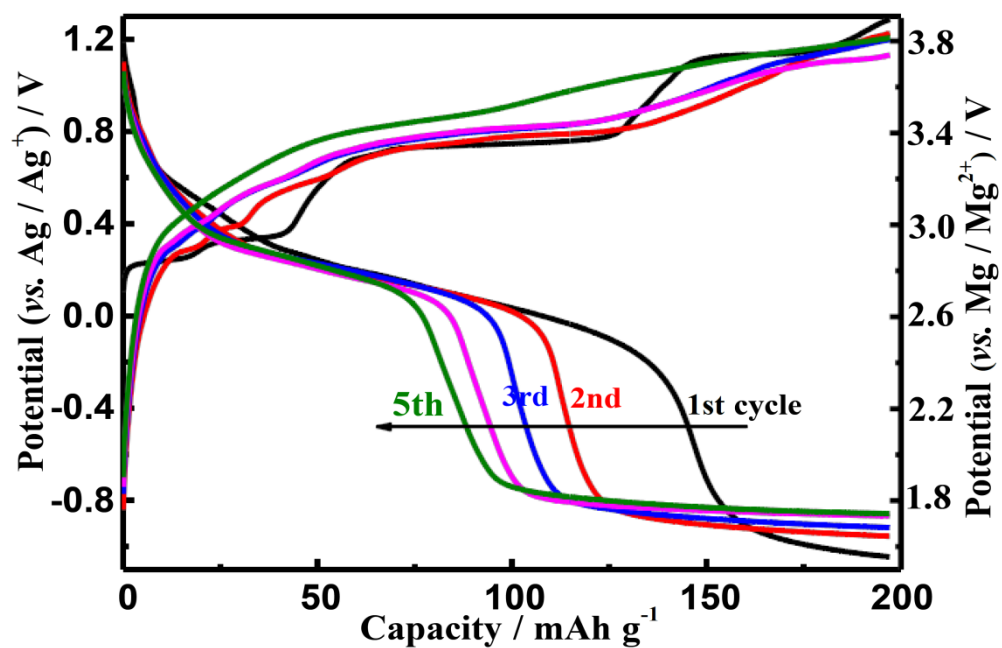


Fig. 7-4. Charge / discharge profiles of LVP in three-electrode Mg cells using Ag/Ag^+ electrode as reference electrode and 0.5 M $\text{Mg}(\text{TFSA})_2$ in acetonitrile as electrolyte at a current density of C/20 at 55°C.

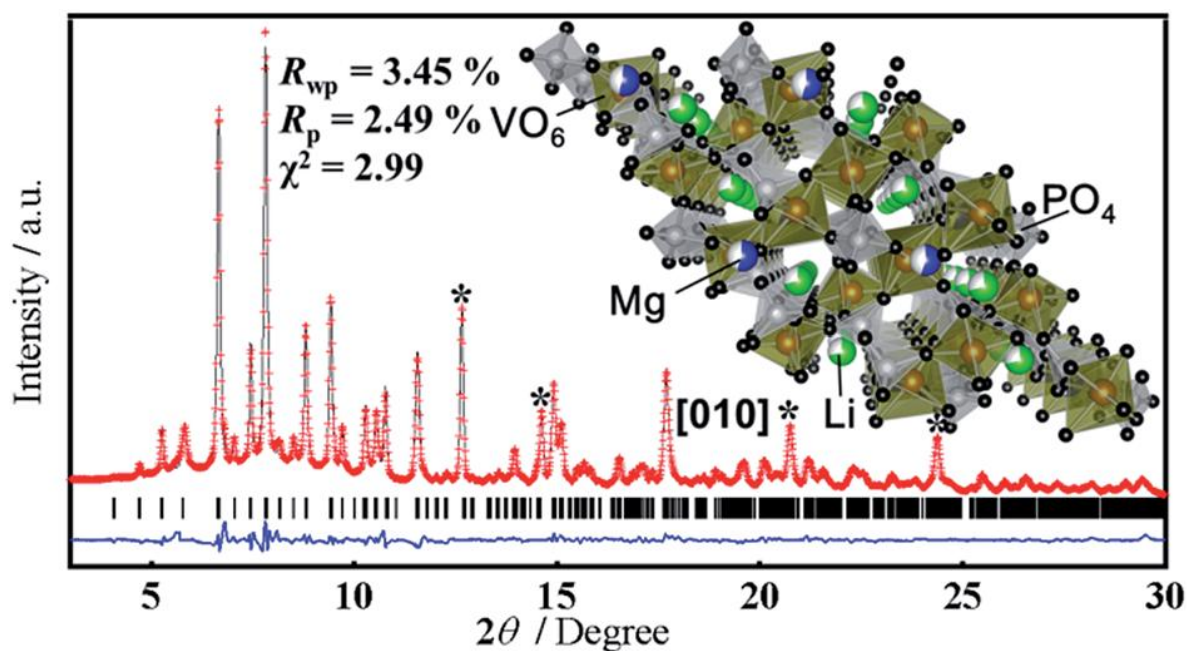


Fig. 7-5. Rietveld refinement SXR D pattern for the electrode discharged to 118.2 mA h g⁻¹ (1st D-118.2). Inset depicts a 3D graphical representation of the crystal structure. The wavelength was set at 0.49971(1) Å. The observed and calculated peaks are indicated in red and black, respectively. The difference between the observed and calculated intensity is indicated in blue, while black ticks indicate the position of the Bragg peaks of the phase. Peaks arising from the Pt metal (current collector), which overlapped with the observed peaks are indicated in asterisks and were excluded from the refinement.

Table 7-2. Refined atomic coordinates within the crystal structure of

$\text{Li}_{0.708}\text{Mg}_{0.546}\text{V}_2(\text{PO}_4)_3$. $*2g\text{Mg} + g\text{Li} = 1.8$

Atom	<i>q</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
Li	0.708(-)*	0.278(11)	0.070(10)	0.240(7)	0.003(-)
Mg	0.546(-)*	-0.138(3)	-0.219(2)	0.346(2)	0.003(-)
V1	1.000	0.142(1)	0.530(1)	0.391(1)	0.003(-)
V2	1.000	0.356(1)	0.538(1)	0.113(1)	0.003(-)
P1	1.000	0.031(2)	0.239(1)	-0.007(1)	0.007(-)
P2	1.000	0.463(2)	0.404(2)	0.352(1)	0.005(-)
P3	1.000	0.752(2)	0.385(2)	0.151(1)	0.005(-)
O1	1.000	0.018(4)	0.142(3)	0.062(2)	0.010(-)
O2	1.000	0.067(4)	0.322(2)	0.403(2)	0.010(-)
O3	1.000	0.103(4)	0.014(3)	0.289(3)	0.010(-)
O4	1.000	-0.185(3)	0.645(3)	-0.066(2)	0.010(-)
O5	1.000	0.165(4)	0.758(3)	0.318(3)	0.010(-)
O6	1.000	0.437(4)	0.512(3)	0.255(2)	0.010(-)
O7	1.000	0.289(4)	0.369(4)	0.340(2)	0.010(-)
O8	1.000	0.376(4)	0.540(3)	0.531(2)	0.010(-)
O9	1.000	0.499(4)	0.787(3)	0.680(3)	0.010(-)
O10	1.000	0.834(4)	0.157(4)	0.411(2)	0.010(-)
O11	1.000	0.587(3)	0.410(3)	0.157(2)	0.010(-)
O12	1.000	0.668(4)	0.421(3)	0.018(2)	0.010(-)

Table 7-3. Results of ICP measurements.

Sample	Test No.	Li/ μg	Mg/ μg	V/ μg
LVP discharged	1	42.2	41.0	471
to 78.8 mAh g ⁻¹	2	42.2	41.3	462
	Average	42.2	41.2	467
LVP discharged	1	44.1	50.1	480
to 118.2 mAh g ⁻¹	2	44.9	50.0	479
	Average	44.5	50.0	479

Table 7-4. The calculated lattice parameters of the pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and the delithiated $\text{V}_2(\text{PO}_4)_3$ at different discharge state.

Discharge state / mAh g ⁻¹	a / Å	b / Å	c / Å	V / Å ³	β / °
0	8.6080	8.5939	14.7263	890.4	125.180
39.4	8.5880	8.3341	11.9354	854.0	91.406
78.8	8.6183	8.3565	12.0352	866.7	90.775
118.2	8.6256	8.5982	12.0655	894.8	90.599
157.6	8.7338	8.6502	12.0634	911.2	91.131
197	8.7327	8.4888	11.7774	873.0	90.763

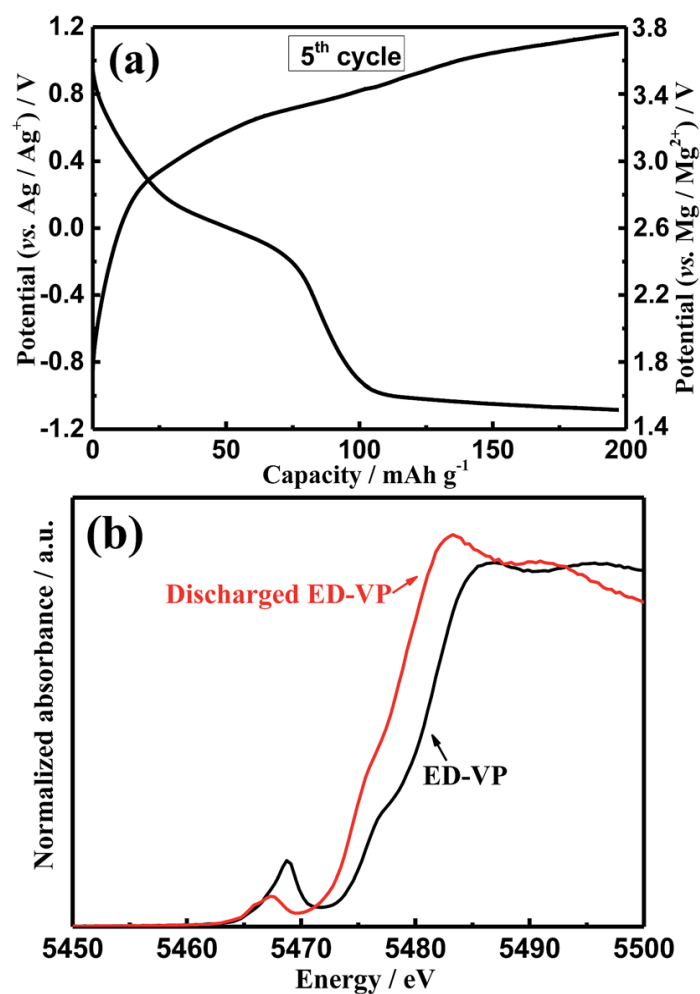


Fig. 7-6. (a) The 5th discharge/charge profile at 10 mA g⁻¹, (b) the 7th cyclic voltammogram of the V₂(PO₄)₃ electrodes obtained by the electrochemical delithiation of Li₃V₂(PO₄)₃ electrodes (ED-VP) within newly assembled three-electrode cells at a scanning rate of 0.1 mV s⁻¹ and (c) shift of the X-ray absorption V-K edge spectrum to low energy during the 1st discharge process of ED-VP. The electrochemical measurements were conducted at 55°C in the three electrode Mg cells. Starting from the 5th cycle, the charge/discharge profile of ED-VP is similar with that of LVP. Additionally, the initial two oxidation peaks merge into one broad peak starting from the 7th cyclic voltammogram of ED-VP.

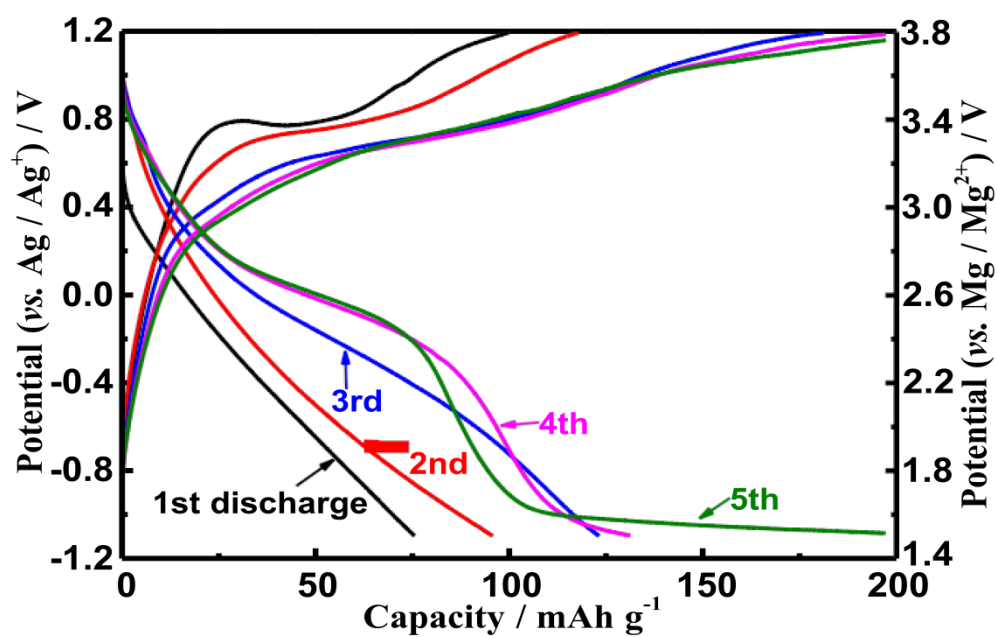


Fig. 7-7. Discharge/charge profiles of $V_2(PO_4)_3$ electrodes obtained via the electrochemical delithiation of $Li_3V_2(PO_4)_3$ electrodes (ED-VP) using newly assembled three-electrode cells at a current density of $C/20$ at $55\text{ }^\circ\text{C}$.

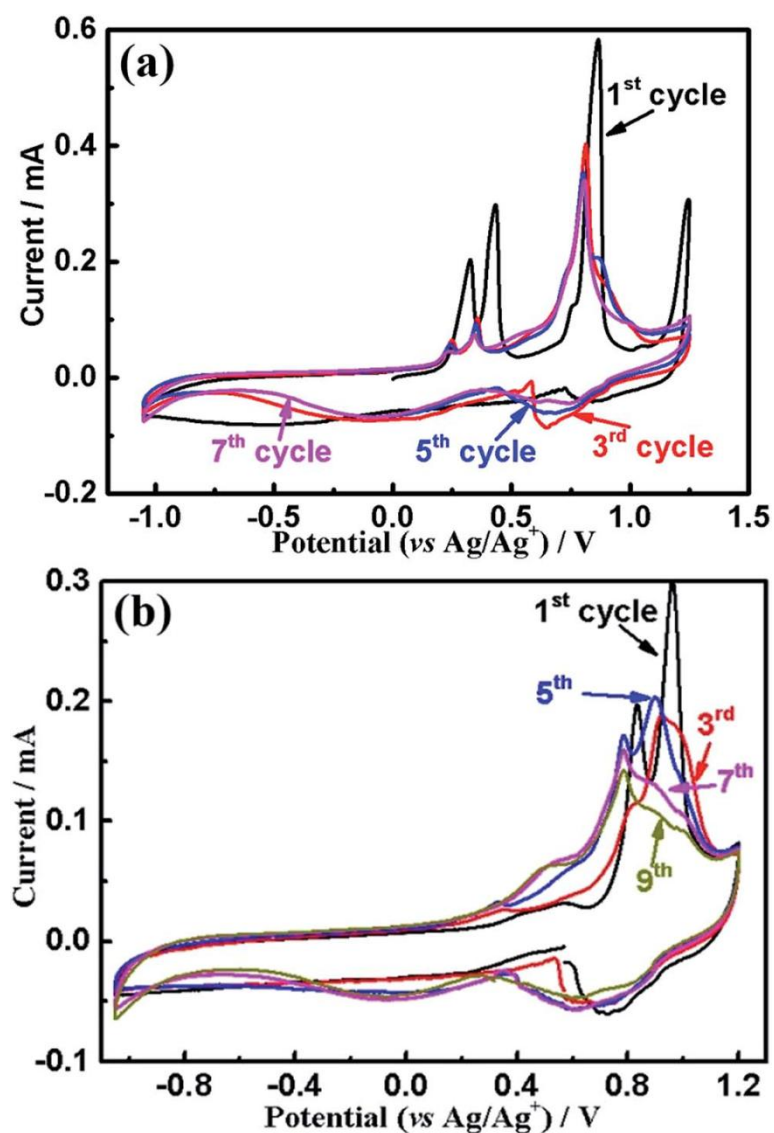


Fig. 7-8 (a) The evolution of cyclic voltammograms during the initial 7 cycles of LVP in three-electrode Mg cells and (b) the cyclic voltammograms of the $V_2(PO_4)_3$ electrodes obtained via the electrochemical delithiation of the $Li_3V_2(PO_4)_3$ electrodes (ED-VP) using newly assembled three-electrode cells at a scanning rate of 0.1 mV s^{-1} at 55°C .

Chapter 8 : General Conclusions

Multivalent cation batteries are deemed as next generation battery systems due to their high energy density, low cost, and safety. However the potential cathode materials are lacking. Then we investigated the reaction mechanisms of the several cathode materials for the multivalent cation battery because of making the design principles of the cathode materials for the multivalent cation battery. In this work, we explored the sulfide and oxide compounds and investigated the crystal structures and electronic structures.

In chapter 1, I revealed the necessity of the multivalent cation battery and explained the problems of the multivalent ions to use the carrier ions for the battery systems. For high energy density battery systems, the developments of the cathode materials are important. Then I reviewed the reported magnesium and aluminum cathode materials, and propose the overview of this thesis.

In part 1, I focused on the sulfide compounds cathode materials.

In chapter 2, I investigated the reaction mechanisms of the FeS_2 reacted with aluminum ions at ambient temperatures by XRD, and XAS. The charge compensation of the FeS_2 is mainly occurred at sulfur atoms during (dis)charging because the FeS_2 has dumbbell shaped S_2^{2-} in the structure. After discharging, FeS_2 are converted to low crystalline FeS and amorphous Al_2S_3 . This obtained phase was different from the lithium ion battery case which is insertion phase of Li_2FeS_2 . Aluminum ion is difficult to insert into the solid, and not to form the insertion phase because of its high charge density.

In chapter 3, the electronic and local structural change of the Mo_6S_8 during insertion of the magnesium ions is investigated by XAS. The charge compensations of this phase are occurred at both atoms which are Mo and S, and the reported two step reactions are

inner site insertion, which is at the site near the sulfur atom, and outer site insertion which is at the site near the molybdenum atom by EXAFS, respectively. Magnesium ions at this inner site are difficult to desert because of strong interactions between magnesium and sulfur atoms.

In this part, the reaction mechanisms of the sulfide compounds are investigated. The charge compensation occurred at sulfur and transition metal atoms (TM) because of the molecular orbitals of TM $3d$ or $4d$ hybridized with S $3p$. These orbitals can be reacted with the multivalent cations, easily. However, the trapping of the anion inhibits the desertion process because the interactions between multivalent cations and host structures are very strong. The properties of the sulfide material are suitable for the cathode materials of the multivalent cation battery, however the potential of the sulfides are relatively low. This is the problems for the high energy density battery systems.

In part 2, I focused on the oxide materials for achievements of the high potential cathode materials.

In chapter 4, I investigated the charge compensation mechanisms and local structural change during charge transfer reaction using Nano-sheet structured MnO_2 electrode. The valence state of the Mn are not $2+$ but $3+$ after adsorbed magnesium ions, and the structural distortions of MnO_2 adsorbed more magnesium ions than it adsorbed lithium ions. Then the structural distortions are affected by the interactions between guest cation and host structure.

In chapter 5, I investigated the possibility of the polyanion cathode materials of the olivine-type MgMnSiO_4 as a host structure because of their structural stability that can achieve structural distortions caused by the electronic interactions by guest multivalent cations, and the correlations between the electrochemical properties and the anti-site

defects of the olivine-type MgMnSiO_4 . The cation mixing between Mg and Mn is a dominant factor of the electrochemical properties of the olivine-type MgMnSiO_4 , which has one dimensional diffusion pathway in the crystal structures. Then the diffusion pathway in the crystal structures is important in utilizing the polyanion compounds as a cathode material for the magnesium battery.

In chapter 6, I prepared the MgFePO_4F which has three dimensional diffusion pathways in the crystal structure. This material shows the relatively high potential, however obtained capacity was still low ($\sim 60 \text{ mAh g}^{-1}$). This low capacity derived from the cation mixing between Mg and Fe.

In chapter 7, I prepared the $\text{V}_2(\text{PO}_4)_3$ as a host structure obtained from the electrochemically delithiated by the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The $\text{V}_2(\text{PO}_4)_3$ host shows the high potential and relatively high capacity ($\sim 200 \text{ mAh g}^{-1}$). The delithiated host from the lithium compounds has no defect in the diffusion pathway and shows the very high performances. Then the good diffusion pathway is very important factor to develop the high capacity polyanion cathode materials for the multivalent cation battery.

The better diffusion pathway and highly stable structure is important to develop the high potential oxide-type cathode materials for the multivalent cation battery. This knowledge leads to develop the high energy density cathode materials for the multivalent cation battery.

Acknowledgements

This work has been carried out at Graduate School of Human and Environmental Studies, Kyoto University.

The author thanks to Prof. Yoshiharu Uchimoto at Graduate School of Human and Environmental Studies, Kyoto University, for his grateful indications and advices, and to Dr. Yuki Orikasa at Graduate School of Human and Environmental Studies, Kyoto University for his discussions and teaching of the several issues.

The author also thanks to Mr. Tetsuya Okado (Panasonic corporation), Mr. Kohei Wada (Nissan Motors corporation), Mr. Takashi Kamijo (Hitachi corporation), Prof. Zhen-dong Huang (Nanjing University of Posts and Telecommunications), Dr. Koji Nakanishi (Kyoto University), Dr. Taketoshi Minato (Kyoto University), Dr. Titus Masese (National Institute of Advanced Industrial Sciences and Technology), and Dr. Kentaro Yamamoto (Kyusyu University) for their grateful helps, discussions and encouragements of this study.

I would like to wish all of the members and the old boys of the Prof. Uchimoto's laboratory for their helps, discussions and encouragements.

Finally, I would like to thank my parents and my wife for their support of my life works in the doctoral course studies.

Takuya Mori

Kyoto, JAPAN