

Establishment of Chemical Oxidation
Procedure of Olivine Iron Phosphate Materials
for Next-Generation Secondary Batteries

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Chapter 1

General Introduction

1.1 Olivine-group materials

Olivine, which was named after its olive-green color by A. G. Werner in 1790, is a common mineral on the earth and its physical and chemical properties have been investigated for ages [1]. Mineral olivine is mainly characterized by $(\text{Mg}_x\text{Fe}_{1-x})_2\text{SiO}_4$ solid solutions between Mg-rich rock (forsterite, Mg_2SiO_4) and Fe-rich rock (fayalite, Fe_2SiO_4), which are abundant in the upper mantle of the Earth [1, 2]. Highly crystalline olivine is even valuable as gemstones called peridot [1, 3]. LiFePO_4 and LiMnPO_4 , which are currently well-known olivine-group electrode materials, were recognized as minerals (triphylite and lithiophilite, respectively) over 120 years ago and their structures were studied in the 1960s [4-6] before Goodenough's group firstly reported the electrochemical performances of them in 1997 [7]. The historical milestones of olivine-group materials are illustrated in **Figure 1-1**. Before the 1990s, olivines had been geologically common minerals constituting rocks and the crystal properties of many kinds of mineral olivine including forsterite and fayalite were investigated [8-13]. In 1997, Goodenough's group reported the electrochemical performances of LiFePO_4 and LiMnPO_4 for the first time [7], triggering extensive research on olivine-group materials as battery applications. In the late 1990s and 2000s, many efforts were made to improve the electrochemical properties of LiFePO_4 , wherein some modification

strategies such as temperature elevation [14], carbon-coating [15, 16], doping [17, 18], and synthesis optimization [19] were investigated. In the 2010s, research expanded beyond lithium-based materials to sodium-based materials. In 2010, triphylite NaFePO_4 was first obtained by electrochemically inserting sodium into heterosite FePO_4 , the delithiated form of triphylite LiFePO_4 , and structurally characterized [20]. In 2015, it was found that maricite NaFePO_4 , which had been regarded as an electrochemically inactive material, worked as an electrode material for Na ion batteries, where nano-sized maricite NaFePO_4 transformed into amorphous FePO_4 during charging [21]. In the 2020s, the demand for batteries has been increasing annually, primarily due to the widespread adoption of electric vehicles (EVs) all over the world [22]. In the middle of the 2020s, commercialization of $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ (LMFP), which offers higher energy density compared to LiFePO_4 deriving from the higher redox potential of $\text{Mn}^{3+}/\text{Mn}^{2+}$ than $\text{Fe}^{3+}/\text{Fe}^{2+}$, is anticipated as the promising positive electrode material [23].

Olivine M_2XO_4 belongs to an orthorhombic crystal system (space group: $Pnma$) and consists of a hexagonal close-packed framework containing two octahedral sites for M (M1 and M2) and a tetrahedral site for X (**Figures 1-2a** and **1-2b**). The M1 sites (4a site) form linear chains of edge-sharing octahedra along the b axis (**Figure 1-2c**), while the M2 sites (4c site) form tortuous lines of corner-sharing octahedra perpendicular to the a axis (**Figure 1-2d**) [7, 24, 25]. While some papers refer to different symbols such as $Pbnm$ and $Pmnb$, they are crystallographically identical to $Pnma$ and the variation of symbols simply arises from the choice of axis. [3, 26, 27]. In

mineral olivine, Si cation occupies the X site and divalent cations such as Mg, Ca, Mn, and Fe occupy the M1 and M2 sites [1-3, 8-10, 28]. On the other hand, a typical structure of olivine-group materials used for the energy storage system is AMPO_4 , where A is an alkali metal and M are transition metals. In the case of LiFePO_4 , the M1 and M2 sites are occupied by Li and Fe respectively, where Li ions have one-dimensional diffusion paths along the b axis [7, 24, 29]. This structure is referred to as triphylite [7, 17, 25, 30, 31]. Similarly, the structures of LiMPO_4 (where M = Mn, Co, and Ni) also follow the triphylite type, with Li occupying the M1 sites and M occupying the M2 sites [7, 29, 32]. Heterosite FePO_4 , the Li-extracted form of LiFePO_4 , also belongs to the olivine group, characterized by the absence of the atom in the M1 site and the presence of Fe in the M2 site [7, 25, 30]. In addition to olivine-group LiMPO_4 materials, NaMPO_4 (M = Mn, Fe, Co, and Ni) compounds were reported [20, 33-37]. Contrary to LiMPO_4 , olivine-group NaMPO_4 has two distinct polymorphs, triphylite and maricite. In triphylite NaMPO_4 , akin to triphylite LiMPO_4 , Na and transition metal M occupy the M1 and M2 sites, respectively. In the maricite NaMPO_4 structure, on the other hand, metal distribution is reversed (M in the M1 site and Na in the M2 site) [25, 38].

1.2 Electrochemical energy storage systems

In recent years, the push for decarbonization, carbon neutrality, and sustainable society has gained momentum globally [39]. The primary driver behind this shift is the

emission of greenhouse gases, like carbon dioxide, resulting from fossil fuel use, which contributes to global warming and extreme weather patterns [40, 41]. Additionally, fossil fuels are finite resources, raising concerns about future energy supply and security. This factor further drives the need for the development of alternative sustainable energy sources [42, 43]. Renewable energy resources such as wind and solar energy are being highlighted as sustainable alternatives to fossil fuels. However, these sources can be inconsistent depending on weather conditions, necessitating their integration with systems capable of storing generated energy [44]. Consequently, energy storage systems (ESSs) are becoming increasingly vital to promote renewable energy usage. ESS technology is now widely applied, from small portable devices to electric vehicles (EVs) and large-scale grid.

1.2.1 Lithium/sodium-ion batteries

Among various ESS options, batteries and supercapacitors, which store energy through redox reactions or electrostatic mechanisms, have emerged as promising solutions to address energy challenges [45]. Lithium-ion batteries (LIBs) have been widely used as a mainstream energy storage technology since Sony Corporation first commercialized them using a LiCoO_2 positive electrode in the 1990s [46, 47]. They have become the preferred power source for various small electronic devices such as laptops, smartphones, and digital cameras, and more recently LIB applications have expanded to EVs and stationary energy storage [48, 49]. **Figure 1-3** shows the schematic

illustration of LIB [48]. LIB consists of the positive electrode (so-called cathode) and the negative electrode (so-called anode), separated by an electrolyte. The electrolyte is responsible for transporting lithium ions and can be either in the liquid or solid form. In particular, batteries using solid electrolyte is called solid-state batteries [50]. A rechargeable battery has a reversible chemical reaction between the two electrodes. During charging, lithium ions are extracted from the positive electrode and inserted into the negative electrode. This process raises the oxidation state of the transition metal in the positive active material. Conversely, during discharging, lithium ions are released from the negative electrode and reinserted into the positive electrode. Positive active materials for LIBs include layered oxide types like LiMO_2 ($M = \text{Mn, Co, Ni, etc.}$), spinel types such as LiM_2O_4 ($M = \text{Mn, Ni, etc.}$), and polyanion types like LiMPO_4 ($M = \text{Mn, Fe, etc.}$) [51-53]. In contrast, negative active materials include carbon-based materials like graphite, oxides such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [54, 55].

Sodium-ion batteries (SIBs) have gained attention as a possible alternative to LIBs due to the abundance and low cost of Na resources [56, 57]. The three main families of positive electrode materials are the layered oxides like NaMO_2 ($M = \text{Mn, Fe, Co, Ni, etc.}$), polyanion compounds such as $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, and prussian blue analogues (PBAs) [57, 58]. While graphite is often used as a negative electrode for LIBs, it is thermodynamically unsuitable for SIBs [59], therefore hard carbon is expected to be a promising material for SIB negative electrode. In addition, titanium-based oxides are also considered potential candidates [57, 58]. Although the working principle of SIBs,

involving the reversible insertion and extraction of sodium ions, is similar to that of LIBs, the energy density of SIBs is generally lower [60]. Moreover, SIBs face challenges related to the diffusion kinetics of sodium ions and the stability of electrodes, which impose limitations on practical energy density and cycle stability [61, 62].

1.2.2 Lithium/sodium metal batteries

Lithium/sodium metal batteries (LMBs/SMBs) have emerged as anticipated candidates for next-generation energy storage systems. Unlike LIBs and SIBs, metal batteries use lithium/sodium metal as the negative electrode. Since the theoretical capacities of Li metal (3860 mAh g^{-1}) and Na metal (1166 mAh g^{-1}) are by far higher than those of conventional carbon-based materials [63, 64], equivalent cell capacity can be achieved with a smaller amount of negative active material, leading to improved energy density. Also, the low redox potentials of Li^+/Li (-3.04 V vs SHE) and Na^+/Na (-2.71 V vs SHE) enable higher operating cell voltage, contributing to superior energy density [63, 64]. Due to these characteristics of metallic lithium and sodium, metal batteries are expected to be applicable in a variety of fields such as EVs, where high-energy-density batteries are in demand. The ideal metal batteries are called metal-free batteries (so-called anode-free batteries), where all the metal sources stem from the positive active material and Li/Na metal deposits on the negative current collector during charging [65, 66]. As a result, metal-free batteries can theoretically achieve the highest energy density because they eliminate the need for excess material on the negative electrode side,

thereby reducing the overall weight and volume of the cell [66-68]. Additionally, they can reduce manufacturing costs related to the negative electrode and alleviate safety concerns associated with excess Li/Na metal in typical metal batteries [65, 67].

Despite such promising characteristics, achieving stable cycling performance to keep a high energy density for LMBs and SMBs remains a challenge due to the limited reversibility of metal deposition/dissolution during cycling, ununiform metal growth, and side reactions with electrolytes [66, 68-70]. To address these issues, a lot of efforts such as the current collector and electrolyte modifications have been made by various groups [66, 68, 70-74].

1.3 Olivine-group materials for battery applications

1.3.1 Lithium-based materials

Since the discovery of the promising potential of LiFePO_4 as a battery application in 1997 [7], many investigations have been conducted to improve the electrochemical properties of LiFePO_4 . These days, due to the rising prices of transition metal resources such as Co and Ni, the resource-advantageous LiFePO_4 is gaining renewed attention. There has been a significant increase in LiFePO_4 demand for light-duty EV batteries with almost 30% in 2022 from 7% in 2020 primarily driven by increasing LiFePO_4 uptake by Chinese manufacturers [75]. Following Chinese manufacturers including BYD, European and American automotive manufacturers such as Volkswagen and Tesla have recently announced the application of LiFePO_4 to onboard batteries [76, 77].

Given these industrial backgrounds, it is estimated that the market share of LiFePO_4 will increase from 28% in 2021 to 38% by 2030 [78].

During charge, Li is extracted from LiFePO_4 to form heterosite FePO_4 (space group: $Pnma$), which retains the FePO_4 framework of the olivine-group structure. Heterosite FePO_4 is a metastable phase that irreversibly transforms into a trigonal FePO_4 phase at temperatures exceeding 580°C , indicating that the trigonal phase is thermally stable [79]. The lattice parameters of heterosite FePO_4 are $(a, b, c) = (9.8142 \text{ \AA}, 5.7893 \text{ \AA}, 4.7820 \text{ \AA})$ [30]. The rigid framework of heterosite FePO_4 ensures stable reversibility of Li extraction/insertion and results in good cycle performance [7].

The typical charge–discharge curves of LiFePO_4 at room temperature are shown in **Figure 1-4a** [80]. The very flat shape indicates a two-phase coexistence reaction. At the beginning and end of the charge–discharge, however, steep slopes indicate that most of the reaction is dominated by the two-phase region between $\text{Li}_\alpha\text{FePO}_4$ and $\text{Li}_{1-\beta}\text{FePO}_4$ and the very narrow single phases of Li_xFePO_4 ($0 < x < \alpha$ and $1-\beta < x < 1$) close to LiFePO_4 and FePO_4 appear at the beginning and end of the charge–discharge [80-82]. The miscibility gap is influenced by the particle size. As shown in **Figure 1-4b**, the single-phase areas ($\text{Li}_\alpha\text{FePO}_4$ and $\text{Li}_{1-\beta}\text{FePO}_4$) are extended with decreasing particle size, and therefore the miscibility gap decreases [83, 84]. Temperature also affects the solid solution ranges. Upon heating, the $x\text{LiFePO}_4/(1-x)\text{FePO}_4$ mixture transforms into a single Li_xFePO_4 phase from about $200\text{--}350^\circ\text{C}$ and then decomposes into a mixture of non-triphylite phases above around 500°C [85].

Doping of different elements is a general strategy to improve electrochemical performance of electrode materials; transition metal element in positive electrode materials is partly substituted to enhance redox potential, electronic or ionic conductivity, and cycle stability based on the difference in size and electronic state [86, 87]. Doping to LiFePO_4 has also been attempted extensively with a variety of dopants, including alkali earth and transition metal elements, and many studies indicated doping lead to the improvement of its electrochemical performance [17, 18, 87-92]. Doping with Mg is one of the most attractive approaches, through the increase in electronic conductivity, due to the cost effectiveness of Mg resources [17, 88, 91-93].

There are several models to explain the delithiation/lithiation mechanism of LiFePO_4 such as the core-shell model [7], mosaic model [94], and domino-cascade model [95], although it is difficult to establish a single mechanism model [96]. The two-phase region in $\text{Li}_{0.45}\text{FePO}_4$ is directly observed using high-resolution transmission electron microscopy (HRTEM), revealing that FePO_4 is predominantly located in the core of the particle, while LiFePO_4 is found in the edge region, with a two-phase area existing between them [97]. Based on the HRTEM and high-resolution electron energy loss spectroscopy (HREELS), a phase transition mechanism was proposed, where Li is successively extracted from the Li channels along the b axis during charging, leading to partially delithiated particles made of both FePO_4 and LiFePO_4 [97]. Whether charging or discharging, FePO_4 is always located in the particle's core, whereas LiFePO_4 is positioned in the shell of the partially delithiated particle because the phase

having the smaller unit-cell volume is more likely to be located in the core of the particles rather than on the outside of the particle [98]. A recent study used operando scanning transmission X-ray microscopy (STXM) to visualize the dynamic lithiation and delithiation pathways in single LiFePO_4 particles during cycling [99]. The observations revealed that surface and bulk phase separation depends on the direction and magnitude of current densities, addressing contradictions in existing phase transition models. At intermediate current rates, the asymmetry in Li composition during delithiation and lithiation was noted. Delithiation involves a small surface area, allowing rapid Li extraction through the [010] channels, triggering adjacent delithiation and creating intercalation-wave kinetics. In contrast, lithiation is auto-inhibited, causing Li insertion into nearby surfaces before the activated channels are fully lithiated. Although bulk Li transport along [010] channels is fast enough to match the insertion flux, lithiation currents spread over a larger surface area, resulting in shrinking-core features. At faster rates, higher current density activates most surface regions, leading to poorer Li composition during delithiation and richer composition during lithiation, stabilizing phase-separated surfaces. In regions where surface reactions are rate-determining step, these phases control lithium insertion and extraction rates, contributing to significant hysteresis in overpotential and rate capability between lithiation and delithiation.

LiMnPO_4 demonstrates higher operational voltage because of the higher redox potential of $\text{Mn}^{3+}/\text{Mn}^{2+}$ (4.1 V vs. Li^+/Li [100]) than $\text{Fe}^{3+}/\text{Fe}^{2+}$ (3.5 V vs. Li^+/Li [30]),

leading to higher energy density. Similar to LiFePO_4 , both LiMnPO_4 and MnPO_4 coexist during charge–discharge [101-103]. The lattice parameters of MnPO_4 are $(a, b, c) = (9.69 \text{ \AA}, 5.93 \text{ \AA}, 4.78 \text{ \AA})$ [102]. Compared to FePO_4 , however, MnPO_4 seems less stable probably caused by Jahn-Teller distortion [101, 104]. Jahn-Teller distortions are most commonly associated with transition metal centers, whether in molecular complexes or ionic lattices. In these centers, the splitting of the d-energy levels within a ligand field can lead to the degeneration of electron configurations, resulting in a net reduction in electronic energy. In octahedral symmetry, d^1 , d^2 , d^4 (both spin-states), d^5 (low-spin), d^6 (high-spin), d^7 (both spin-states), and d^9 transition ions are Jahn-Teller-active [105], but strong Jahn-Teller distortion appears for the high-spin d^4 , low-spin d^7 , and d^9 configurations. In the case of MnO_6 octahedra in MnPO_4 , Mn^{3+} is considered Jahn-Teller-active because of its high spin configuration ($t_{2g}^3 e_g^1$). This electron configuration results in the split of both t_{2g} and e_g subshell to reduce electronic energy and the Mn–O bond length changes. Typically, the axial Mn–O bond elongates, and the basal Mn–O bond contracts in the D_{4h} symmetry [106]. Moreover, thermally unstable MnPO_4 decomposes into $\text{Mn}_2\text{P}_2\text{O}_7$ and O_2 gas by heating above 210°C [103]. To simultaneously enhance structural stability and energy density, solid solutions of Mn and Fe ($\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$) have been deeply investigated since the early 2000s [101, 104, 107-121]. Transition metals occupying the M2 site can form solid solutions in a wide proportion, thus various combinations of transition metals have been investigated thus far [122-131].

While there is a report on calculating the lattice constants and redox potentials of silicate olivine-group LiMSiO_4 ($M = \text{Mn, Fe, Co, and Ni}$) [132], it seems challenging to directly synthesize them in practice. Theoretical calculation on the relative stability of four possible polymorphs of LiFeSiO_4 , delithiated- $\text{Li}_2\text{FeSiO}_4$, olivine, Na_2CrO_4 -like, and spinel, indicated that the olivine type LiFeSiO_4 is the most stable phase, but the experimental syntheses of olivine LiFeSiO_4 were unsuccessful [133]. Preparation of olivine LiFeSiO_4 from a mixture of reactants (Fe_2O_3 , Li_2SiO_3 , and SiO_2) at ambient pressure at 600–1100 °C resulted in a mixture of quartz- SiO_2 , Li_2SiO_3 , LiFe_5O_8 and $\text{LiFeSi}_2\text{O}_6$. High-pressure synthesis (40 kbar) resulted in the formation of $\text{LiFeSi}_2\text{O}_6$ as a main phase, which was confirmed by the first principle calculation indicating that the preparation of the olivine LiFeSiO_4 is thermodynamically hindered due to the competition with the more stable $\text{LiFeSi}_2\text{O}_6$ phase [133]. Another study demonstrated orthorhombic LiFeSiO_4 (space group: $Pnma$) can be obtained via electrochemical delithiation of monoclinic $\text{Li}_2\text{FeSiO}_4$ at 0.02C, while monoclinic LiFeSiO_4 is obtained when delithiated at 0.1C [134].

1.3.2 Sodium-based materials

NaFePO_4 is the most investigated material among Na-based olivine-group materials. As mentioned above, NaFePO_4 has two polymorphs, triphylite and maricite. In triphylite NaFePO_4 , much like triphylite LiMPO_4 , Na and Fe occupy the M1 and M2 sites respectively. In contrast, maricite NaFePO_4 has a reversed metal distribution [25,

38]. Computational studies suggested that the thermal stabilities of triphylite and maricite phases are relatively similar, allowing both phases to exist stably [20, 38]. Although the triphylite NaFePO_4 phase possesses sufficient stability to maintain its structure during charge–discharge, this phase is metastable and irreversibly converts to maricite above 480 °C [20, 25, 135]. Therefore, triphylite NaFePO_4 is generally produced from triphylite LiFePO_4 , where it is obtained by sodiation of heterosite FePO_4 , the delithiated form of triphylite LiFePO_4 [20]. The structural properties of triphylite NaFePO_4 have been studied since its first structural report in 2010 [20]. XRD investigations of triphylite Na_xFePO_4 ($0 \leq x \leq 1$) revealed Na_xFePO_4 involves two regions, two-phase region (FePO_4 and $\text{Na}_{2/3}\text{FePO}_4$) for $0 \leq x \leq 2/3$ and solid-solution region for $2/3 \leq x \leq 1$ at room temperature [135], which validates its voltage profile two plateaus during charging [20, 136-138]. Rietveld refinements (**Figure 1-5**) revealed that lattice parameters of the single-phase Na_xFePO_4 ($2/3 \leq x \leq 1$) continuously decrease, following the Vegard’s rule, and those of the $\text{FePO}_4/\text{Na}_{2/3}\text{FePO}_4$ two-phase region ($0 \leq x \leq 2/3$) are almost constant along Na extraction [135]. The intermediate phase is considered to exist to mitigate the large volume expansion from FePO_4 to NaFePO_4 (about 17%) [135, 136]. Although the expansion from FePO_4 to $\text{Na}_{2/3}\text{FePO}_4$ is still large (12.8%) and almost twice as large as that from FePO_4 to LiFePO_4 (6.8%), there is no further intermediate phase. This can be explained by the more isotropic expansion in Na_xFePO_4 ($0 \leq x \leq 2/3$), where lattice expansion of each axis is relatively even compared to Li_xFePO_4 ($0 \leq x \leq 1$) and less than 5% mismatch of each axis may sustain a coherent

interface [135]. To elucidate the large lattice mismatch between FePO_4 and NaFePO_4 , a strain-accommodation mechanism has also been proposed, wherein an amorphous phase forms to buffer the large lattice mismatch between the primary phases. This mechanism was identified by synchrotron radiation powder XRD, pair distribution function (PDF) analysis, and TEM observations [139]. Triphylite NaFePO_4 faces a significant challenge, particularly at room temperature, where its practical capacity is limited to only 70%–80% of the theoretical capacity. To address this issue, doping, similar to that used for LiFePO_4 , has been explored [140]. However, research on doping for triphylite NaFePO_4 is relatively scarce compared to LiFePO_4 .

In contrast to the triphylite phase, maricite NaFePO_4 , the structure of which was already investigated before the 1990s [36, 141, 142], had been considered electrochemically inactive and unsuitable as electrode materials due to the limited Na^+ diffusion paths [38, 143, 144]. However, electrochemically active maricite NaFePO_4 was reported for the first time in 2015 [21]. Here, nano-sized maricite NaFePO_4 successfully worked as a positive electrode material as it transformed to amorphous FePO_4 after the initial charge in Na-ion cells according to XRD analysis, although theoretical calculation showed activation energies of two possible Na^+ diffusion paths are too high to enable Na^+ diffusion in maricite NaFePO_4 . This was further confirmed by TEM observations of charged maricite NaFePO_4 , which revealed a two-phase reaction between maricite NaFePO_4 and amorphous FePO_4 . Additional calculations concluded that the transformation into amorphous FePO_4 is the key step for reversible

Na insertion and extraction in the electrode because amorphous FePO_4 allows substantially smaller barriers than maricite NaFePO_4 for Na^+ to diffuse from site to site. In a subsequent study, it was revealed that the XRD peaks of the ball-milled maricite NaFePO_4 electrode could shift slightly upon charge–discharge at 90 °C, suggesting crystalline maricite NaFePO_4 can be electrochemically activated through downsizing and high-temperature operation [145].

1.3.3 Potassium- and magnesium-based materials

Crystalline KFePO_4 is known to be electrochemically inactive. Electrochemical insertion of K^+ into heterosite FePO_4 to obtain crystalline triphylite KFePO_4 was unsuccessful because of the larger ionic radius of K^+ compared to Li^+ and Na^+ [146–148]. Recent studies have shown that the potassiation of heterosite FePO_4 leads to amorphization. The XRD patterns of the K-inserted sample revealed irreversible structural degradation, indicating the amorphization or significant decrease in crystallinity after initial potassiation [148]. Another study claimed that downsized and amorphized monoclinic KFePO_4 can be a potassium storage material [149].

Crystalline olivine-group $\text{Mg}_{0.5}\text{FePO}_4$ seems also difficult to obtain although insertion of Mg^{2+} into heretosite FePO_4 is partially possible [146, 150]. Ex-situ XRD results showed neither peak shift of the original FePO_4 nor emergence of new peaks for a Mg^{2+} -inserted phase, suggesting that the Mg^{2+} -intercalated FePO_4 phase becomes an amorphous phase [150]. Another study demonstrated that surface amorphization of

FePO₄ upon Mg²⁺ insertion prevents magnesiation into the bulk FePO₄, which leads to the low charge–discharge capacity [151]. Density functional theory (DFT) calculation also showed Mg_{0.5}FePO₄ is unstable and an experimental attempt to synthesize Mg_{0.5}FePO₄ resulted in the formation of a solid solution between Mg₃(PO₄)₂ and Fe₃(PO₄)₂ [151].

Several olivine-group silicates MgMSiO₄ (M = Mn, Fe, and Co) have been reported for Mg-based energy storage materials [152-157]. Occupation of Mg and transition metals in M1 or M2 sites is mixed. A structural study of MgMSiO₄ (M = Mn and Co) revealed the mixed site occupation of Mg and Mn/Co atoms, where Mg is mainly located at the edge-sharing octahedral M1 sites and Mn/Co is mainly found in the corner-sharing octahedral M2 sites [154].

1.4 Chemical oxidation of electrode materials

When charging, the valence of the transition metal in the positive electrode material increases, equivalent to oxidation of the material. For example, LiFePO₄ transforms to FePO₄ during charging, with the change in Fe oxidation state from II to III. Such oxidation can proceed not only electrochemically within the cell but also chemically with oxidizing agents. Oxidizing agents used for the chemical oxidation of positive electrode materials include NO₂BF₄, Na₂S₂O₈, Cl₂, O₂, and Br₂, as shown in **Figure 1-6** [158-162]. It is thermodynamically feasible to oxidize (chemically charge) positive electrode materials with a lower redox potential than these oxidizing agents, although

considerations such as reactions between materials and solvents are essential in practice. NO_2BF_4 is commonly used in lab scale, but it is expensive and difficult to handle due to its high reactivity. $\text{Na}_2\text{S}_2\text{O}_8$, which can only be used in aqueous systems, has limited applicability for electrode materials that are often unstable in water. Cl_2 can be used in an acetonitrile solvent, making it more suitable for the oxidation of electrode materials. Furthermore, as a gaseous oxidizing agent, it offers advantages of high scalability, separability, and recovery rate after the reaction, compared to the other oxidizing agents. Similarly, O_2 gas, which is readily available, is also a gaseous oxidizing agent, making it suitable for scaling up. However, since it is used in aqueous systems, careful selection of materials is required. Br_2 poses difficulties in handling since it is a liquid with high vapor pressure.

The advantage of chemical oxidation is that it allows for the bulk processing of materials at once, enabling comprehensive investigation of the resulting material. Furthermore, it can also be applied to extract lithium from used LIB electrode materials, contributing to lithium recycling and material reuse [162, 163].

1.5 Aim of this study

To address the growing societal demand for sustainability, the development of environmentally friendly and cost-effective secondary batteries is required. With the rising prices of Co and Ni, which are primarily found in layered oxide type electrode materials, LiFePO_4 has regained attention as a resource-advantaged alternative.

Chemical oxidation using oxidizing agents is an intriguing technique with the potential to unlock insights unattainable through electrochemical oxidation methods, paving new paths for material development. This research aims to establish the chemical oxidation process of LiFePO_4 and investigate its applications for next-generation secondary batteries including SIBs, SMBs, and LMBs as shown in **Figure 1-7**.

Chapter 2 describes the experimental methods, characterization techniques, and testing conditions that serve as the foundation for the investigations undertaken in Chapters 3 to 6.

Chapter 3 proposes the LiFePO_4 delithiation technique using Cl_2 gas and investigates the properties of the delithiated FePO_4 as an electrode for SIBs. Cl_2 gas does not damage the host framework of LiFePO_4 , and the delithiated FePO_4 demonstrates highly stable sodium insertion/extraction reaction between heterosite FePO_4 and triphylite NaFePO_4 over 1000 cycles.

Chapter 4 develops a sustainable FePO_4 production route from LiFePO_4 using O_2 gas. While the obtained FePO_4 is utilized as a positive electrode for SMBs, the extracted lithium during the delithiation process is recovered as lithium acetate (CH_3COOLi) that can be used to resynthesize LiFePO_4 , which enables a closed-loop lithium recycling and a more sustainable FePO_4 production. SMB full cell (Na/FePO_4) exhibits a relatively high gravimetric energy density comparable to the conventional SMBs.

Chapter 5 further extends the technique developed in Chapter 4 by utilizing FePO_4 as a positive electrode for LMBs, which implies the reuse of FePO_4 from spent LiFePO_4 .

Here, a concept of charged-state lithium metal batteries (CSLMBs), which showcase superior cycle stability and higher energy density, is discussed.

Chapter 6 explores the effect of Mg doping into heterosite FePO_4 to enhance the electrochemical performance of triphylite NaFePO_4 and heretosite FePO_4 as SIBs. Mg-doped FePO_4 is produced from Mg-doped LiFePO_4 by delithiation using O_2 gas. Improved electrochemical properties are achieved by 1% and 2% of Mg doping, resulting from the enhanced electronic and ionic conductivity.

Chapter 7 summarizes the thesis and highlights future prospects related to this research.

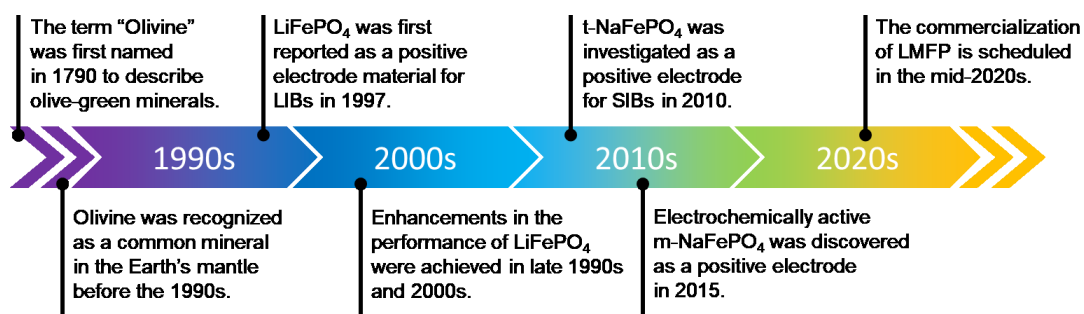
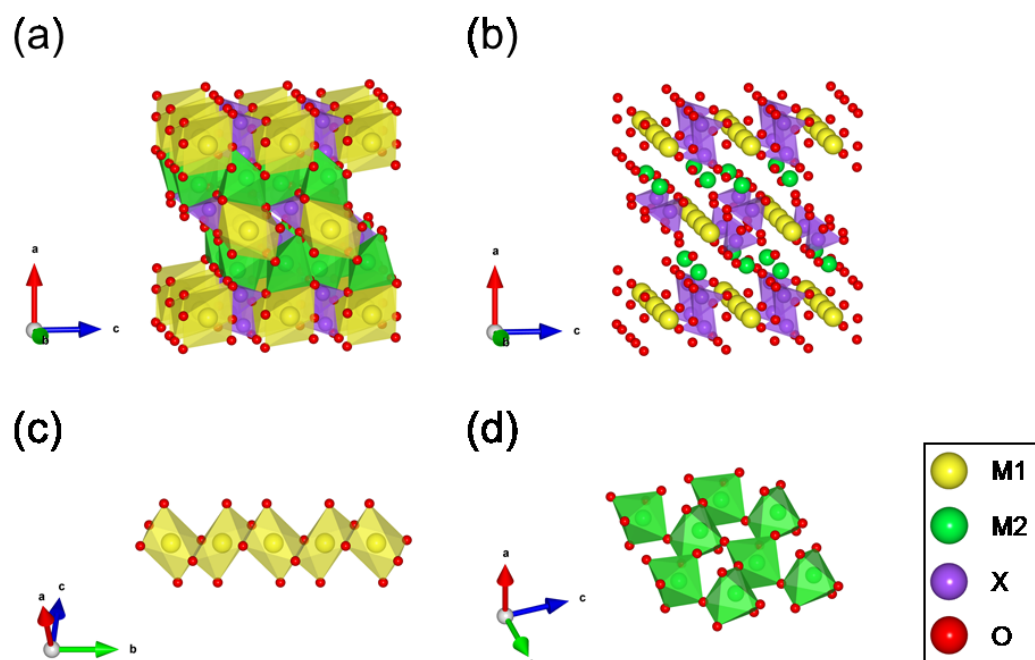


Figure 1-1. The milestones for developing olivine-group materials for secondary batteries.



Structure (S. G.: <i>Pnma</i>)	Representative material	Site			Electrochemical activity
		M1	M2	X	
Olivine	Mg_2SiO_4	Mg	Mg	Si	Inactive
	Fe_2SiO_4	Fe	Fe	Si	Inactive
Triphylite	LiFePO_4	Li	Fe	P	Active
	NaFePO_4	Na	Fe	P	Active
Maricite	NaFePO_4	Fe	Na	P	Inactive
Heterosite	FePO_4	-	Fe	P	Active

Figure 1-2. The crystal structure of olivine-group M_2XO_4 . Yellow, green, purple, and red denote M1 (M1 = Mg, Fe, Li, Na), M2 (M2 = Mg, Fe, Na), X (X = Si, P), and O, respectively. (a) Octahedra in M1 and M2 sites and tetrahedra in X sites are illustrated. (b) Illustrations of octahedra in M1 and M2 sites are omitted, showing linear diffusion channels in M1 sites along the b axis. (c) Edge-sharing octahedra in M1 sites. (d) Corner-sharing octahedra in M2 sites.

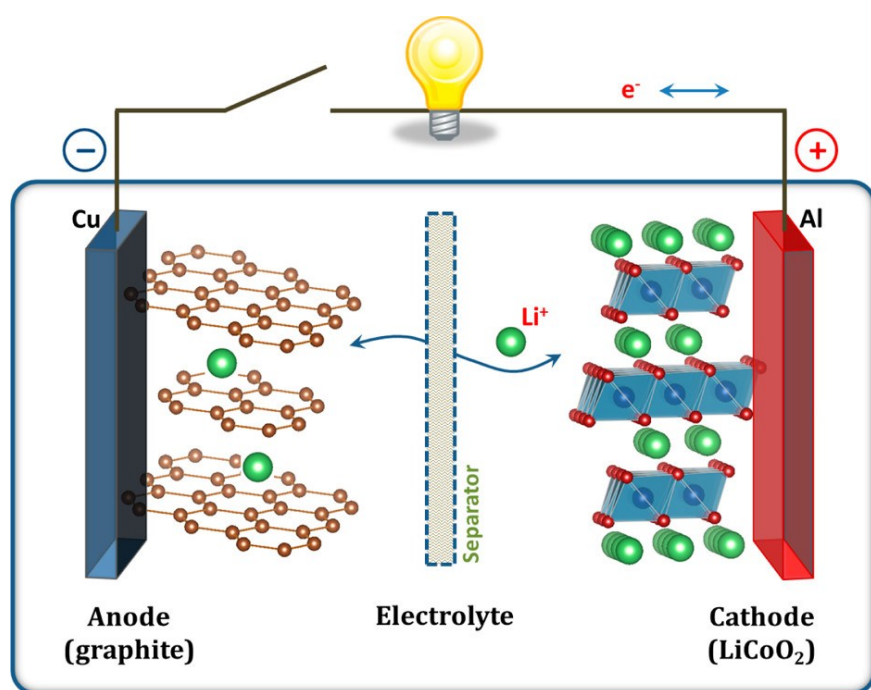


Figure 1-3. Schematic illustration of the Li-ion battery (LiCoO₂/Li⁺ electrolyte/graphite). Reproduced with permission [48]. Copyright 2013, American Chemical Society.

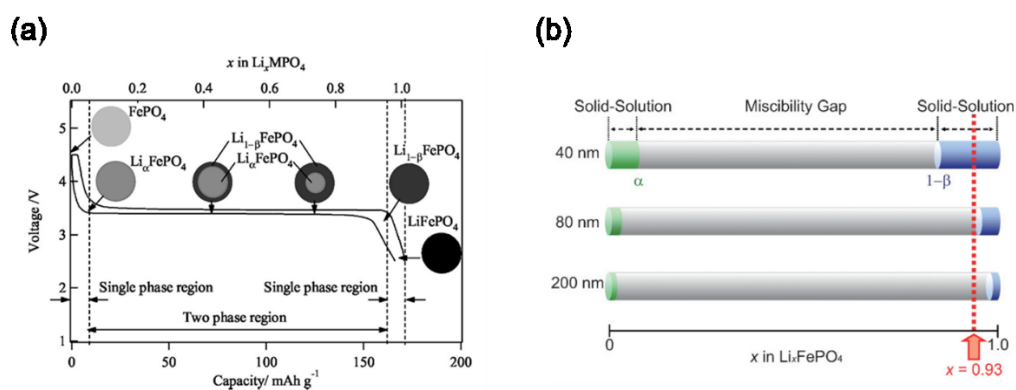


Figure 1-4. (a) Charge–discharge curves of the LiFePO₄. Reproduced with permission [80]. Copyright 2005, The Electrochemical Society. (b) Schematic illustration of the size-dependent FePO₄–LiFePO₄ binary phase diagram. Reproduced with permission [84]. Copyright 2009, Wiley-VCH.

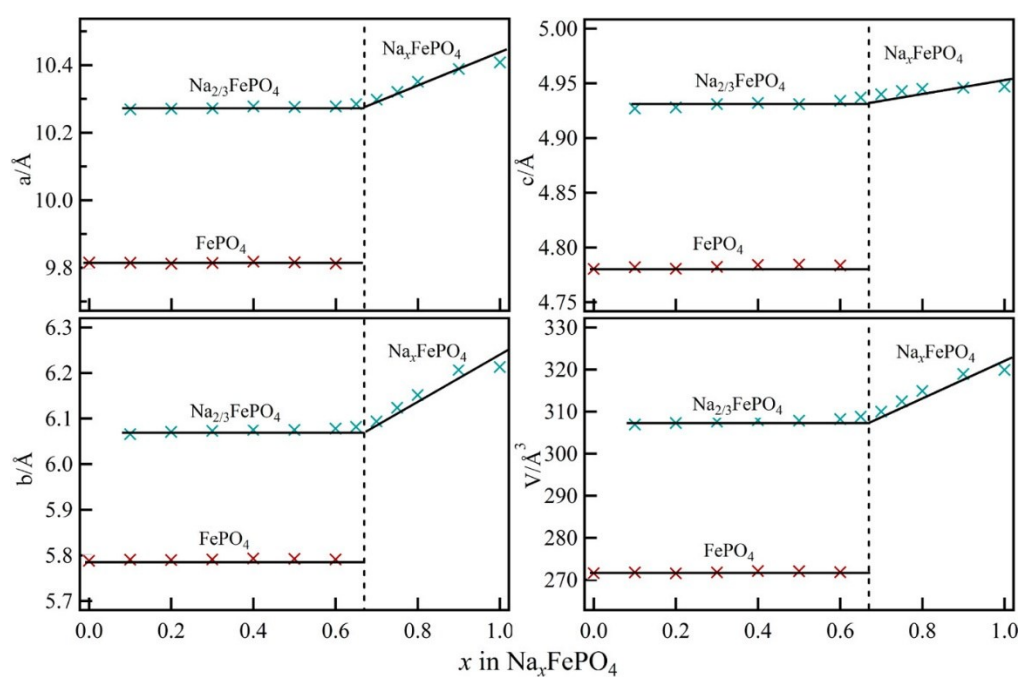


Figure 1-5. Unit cell parameters (a , b , and c) and volume as functions of x in Na_xFePO_4 . Reproduced with permission [127]. Copyright 2013, American Chemical Society.

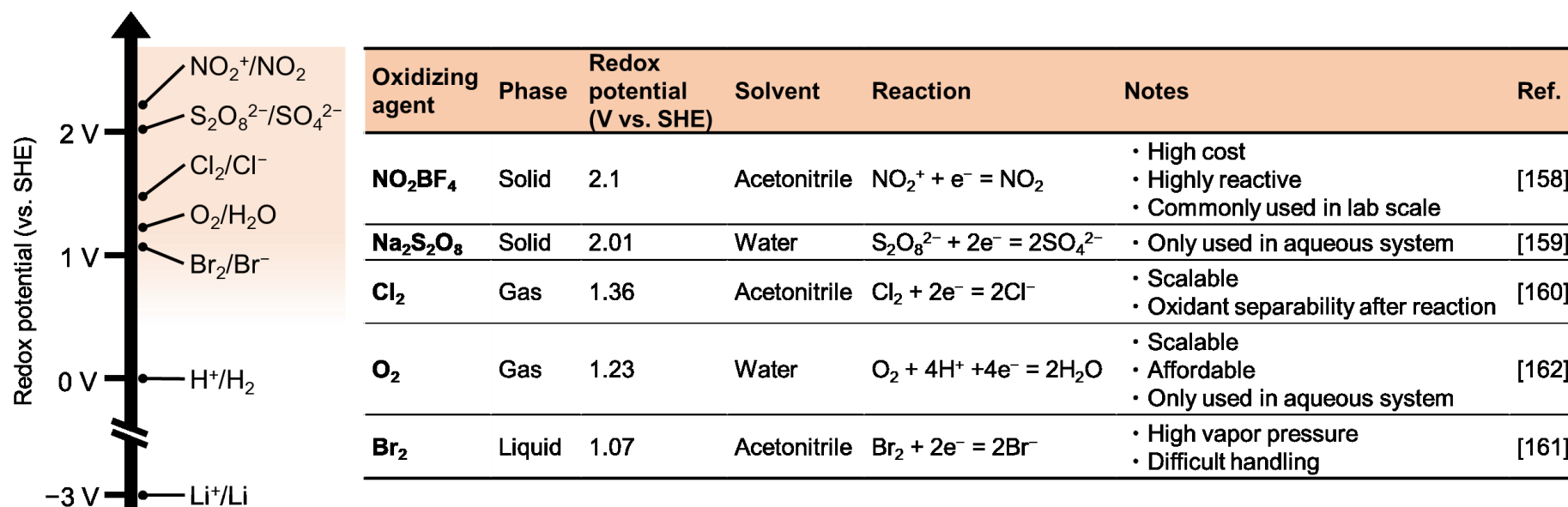


Figure 1-6. Redox potentials of oxidizing agents for chemical delithiation of positive electrode materials.

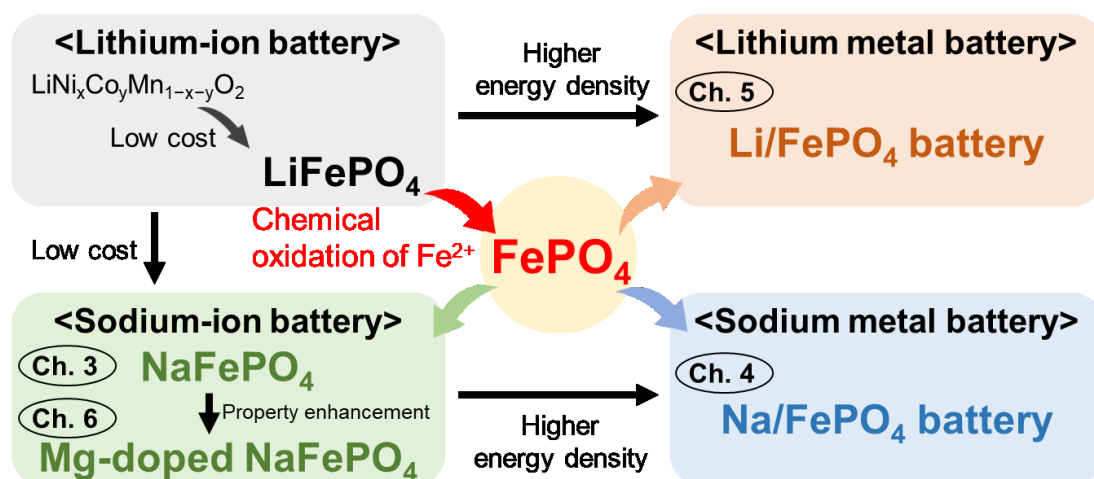


Figure 1-7. Overview diagram of the relationships between the chapters.

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Chapter 2

Experimental

2.1 Apparatus and material handling

The tools used in the experiments, including cutting knives, medicine spoons, tweezers, scissors, beakers, and measuring cylinders, were cleaned with ion-exchanged water and ethanol in turn, and dried in an oven at 60 °C for more than 2 h.

All moisture- and oxygen-sensitive materials were handled under a dry Ar atmosphere ($\text{H}_2\text{O} < 1 \text{ ppm}$ and $\text{O}_2 < 1 \text{ ppm}$) in a glove box (Miwa Manufacturing, DBO-2LKH-HNBR) with a gas-refining instrument. An electronic balance (Sartorius, CPA225D) was installed in the glove box, which was used for measuring the weights of chemicals. The materials sensitive to the moisture in air were handled under a dry air atmosphere in an open dry chamber (Daikin, HRW-60AR).

A separable vacuum flask (**Figure 2-1**) and vacuum line (**Figure 2-2**) systems were used to dry chemicals and impregnate ionic liquid (IL) electrolytes into electrodes and separators [1]. This vacuum line is connected with a pressure gauge, a cold trap, and a vacuum pump in sequence. The cold trap was cooled with liquid nitrogen to capture volatiles. The final vacuum degree of the system was below 1 Pa.

The heating devices used in the experiments are hot plate (AS ONE, REXIM RSH-1DN), oil bath (below 150 °C, Advantec, TBX183SB), mantle heater (above 150 °C, TAIKA, GB-5), and tubular furnace (Koyo Thermo System, KTF045N1).

The materials for organic and IL electrolytes included Na[FSA] ([FSA][−] = bis(fluorosulfonyl)amide, Mitsubishi Materials), [C₂C₁im][FSA] ([C₂C₁im]⁺ = 1-ethyl-3-methylimidazolium, Kanto Chemical), 1 mol dm^{−3} Na[PF₆]-EC/DMC (1:1 v/v) (EC: ethylene carbonate, DMC: dimethyl carbonate, Kishida Chemical), and 1 mol dm^{−3} Li[PF₆]-EC/DMC (1:1 v/v) (Kishida chemical). Here, 3wt% of FEC (fluoroethylene carbonate, Wako Pure Chemical) additive was added in 1 mol dm^{−3} Na[PF₆]-EC/DMC (1:1 v/v). Additionally, Na[PF₆] (Sigma-Aldrich), Li[FSA] (Kishida Chemical), and DME (1,2-dimethoxyethane, Kishida Chemical) were utilized. All salts were dried under a vacuum at 80 °C. These commercial reagents and materials had purities of over 99%.

Carbon-coated LiFePO₄ (LiFePO₄/C, purity 99.9%, carbon coating 1.15%) was purchased from Toshima Manufacturing. In addition, LiFePO₄/C and Mg-doped LiFePO₄/C were also synthesized from purchased CH₃COOLi·2H₂O (Fujifilm Wako Pure Chemicals, purity > 98%), FeC₂O₄·2H₂O (Sigma-Aldrich, purity > 90%), (CH₃COO)₂Mg·4H₂O (Fujifilm Wako Pure Chemicals, purity 99%), (NH₄)₂HPO₄ (Fujifilm Wako Pure Chemicals, purity 99%), and glucose (C₆H₁₂O₆, Fujifilm Wako Pure Chemicals) in molar ratios of 1 : 1−*x* : *x* : 1 : 0.1 (*x* = 0, 0.01, 0.02, 0.03, and 0.04). They were ball-milled in ethanol for 12 h. The mixed slurry was dried at 70 °C and the obtained precursor powder was sintered at 300 °C for 3h, then at 700 °C for 6 h under Ar atmosphere.

The delithiation process using Cl_2 was performed with the above-mentioned LiFePO_4/C , AlCl_3 (Fujifilm Wako Pure Chemicals, purity 98.0%), acetonitrile (Fujifilm Wako Pure Chemicals, super dehydrated, $\text{H}_2\text{O} < 10$ ppm, purity $> 99.8\%$), and Cl_2 gas (Sumitomo Seika Chemicals, purity $> 99.4\%$). The delithiation process using O_2 was performed with LiFePO_4/C , CH_3COOH (acetic acid, Fujifilm Wako Pure Chemicals, purity 99.7%), distilled water, and O_2 gas (Air Liquide Japan, purity $> 99.995\%$).

2.2 Chemical oxidation of LiFePO_4

2.2.1 Chemical oxidation using Cl_2 gas

Under a dry air atmosphere, LiFePO_4/C , AlCl_3 , and acetonitrile were added into an air-tight glass reaction vessel. The vessel was evacuated before slowly introducing 100 kPa of Cl_2 gas from a storage cylinder via a reaction manifold [2]. The mixture was left undisturbed in the reaction vessel for 72 h. After the reaction, all the volatile gases were evacuated through a liquid nitrogen cold trap. The reaction product was washed and centrifuged with acetonitrile several times to separate the powder from solvent, then dried at $60\text{ }^\circ\text{C}$ under a vacuum overnight to obtain carbon-coated FePO_4 (FePO_4/C) powder.

2.2.2 Chemical oxidation using O_2 gas

Under an air atmosphere, LiFePO_4/C , acetic acid, and distilled water were added into an air-tight glass reaction vessel (volume: 1.2 dm^3). The vessel was slowly evacuated

and 1.5 atm of O₂ gas was introduced. After the mixture was stirred for 72 h, the delithiated product (FePO₄/C) was obtained by centrifuging, washing with distilled water several times, and then drying overnight at 80 °C under a vacuum.

2.3 Electrode preparation

2.3.1 Preparation of positive electrodes

The positive electrode was prepared by mixing the active materials (LiFePO₄/C or FePO₄/C) with Super C65 conductive carbon (MTI) and polyvinylidene fluoride (PVDF, Kureha) (80:15:5wt%) in *N*-methylpyrrolidone (NMP, Fujifilm Wako Pure Chemicals, purity > 99.0%) using a planetary mixer (Thinky, AR-100). The mixture was thereafter pasted onto an Al foil using a coating machine (Hohsen) and dried for 4 h at 70 °C. The dried electrode was punched into discs (diameter: 10 mm) using a hand punch (Nogami Giken), and then vacuum dried overnight at 80 °C to remove residual solvent.

The positive electrodes were also prepared by mixing the active materials (LiFePO₄/C, FePO₄/C, or Mg-doped FePO₄/C) with Super C65 carbon and the single wall carbon nanotube (SWCNT) dispersion in NMP with PVDF (TUBALL) in the weight ratio of LiFePO₄/C (or FePO₄/C) : Super C65 : SWCNT : PVDF = 91:3:2:4 using a planetary mixer. The mixture was pasted onto an Al foil and dried overnight at room temperature. The electrode was punched into discs (diameter: 10 mm) and then vacuum-dried overnight at 80 °C to completely remove NMP.

2.3.2 Preparation of negative electrodes

Sodium metal (Sigma-Aldrich, purity 99.9%) or lithium metal (Sigma-Aldrich, purity 99.9%) were thinly rolled out, punched, and crimped onto a current collector to obtain negative electrodes. They were punched into disks of 13 mm diameter and 10 mm diameter for the half-cell and full-cell tests, respectively. For the full-cell tests, metals were weighed accurately with a restricted amount. Al current collectors were used for Na metal. Stainless steel and Cu current collectors were used for Li metal with the half-cell and full-cell tests, respectively.

2.4 Material characterizations

2.4.1 X-ray diffraction

X-ray diffraction (XRD) patterns of the samples were collected using a Rigaku SmartLab diffractometer (Ni filtered Cu-K α , 40 kV-30 mA) with a silicon strip high-speed detector (Rigaku, D/teX Ultra 250). The Rietveld refinements of the obtained XRD patterns were performed using the FullProf software to calculate the detailed crystallographic parameters of the samples [3].

2.4.2 Scanning electron microscopy/energy dispersive X-ray spectroscopy

Particle size, morphological properties, and elemental composition were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy.

The samples were examined through a field-emission SEM (FE-SEM, Hitachi, SU-8020) and an EDX spectrometer (Horiba, EMAXEvolution X-max).

2.4.3 Fourier transform infrared spectroscopy

Fourier transform infrared (FT-IR) spectra were recorded using an FT-IR spectrometer (Bruker, Alpha II) by the attenuated total reflection (ATR) method and with the aid of the single reflection diamond. The wavenumber range was calibrated to 4000–400 cm^{-1} , and the resolution was set to 4 cm^{-1} .

2.4.4 Organic elemental analysis

Organic elemental analyses (H and C) were performed using an organic elemental analyzer (Jay Science Lab, JM-11) at Organic Microanalysis Laboratory, Kyoto University.

2.4.5 Atomic absorption spectrometry

Atomic absorption spectrometry (AAS) was conducted to quantitatively determine the Li composition of the samples using atomic absorption spectrometer (Hitachi, ZA3300) at Toray Research Center.

2.4.6 Inductively coupled plasma atomic emission spectroscopy

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was carried out to quantitatively determine the elements other than Li in the samples using an ICP-AES device (Hitachi, PS3520VDD II) at Toray Research Center.

2.4.7 X-ray photoelectron spectroscopy

The surface components of the samples were analyzed using an X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9030) with a Mg- $K\alpha$ source. The collected data were processed and analyzed with an analytical software (JEOL, SpecSurf version 1.8.3.7).

2.4.8 Specific surface area analysis

The specific surface area of the samples was analyzed using the surface and porosity analyzer (Shimadzu, TriStar II) with the Brunauer-Emmett-Teller (BET) method.

2.5 Electrochemical measurements

2.5.1 Galvanostatic charge–discharge test

The charge–discharge performances of the cells were evaluated by using a charge–discharge test device (Hokuto Denko, HJ1001SD8). The cells were subjected to multiple charge–discharge cycles to determine their capacity, Coulombic efficiency, cycle stability, and energy density. The tests were conducted at controlled temperatures in an environmental test chamber (ESPEC, SU221).

2.5.2 Galvanostatic intermittent titration technique

The diffusivity of Na^+ ions in the electrodes was evaluated using a galvanostatic intermittent titration technique (GITT). The GITT measurements were conducted in the following manner. The Na/FePO_4 half cell was discharged at $10 \text{ mA (g-FePO}_4\text{)}^{-1}$ for 1 h, followed by the open circuit relaxation for 5 h. This procedure was repeated until the voltage reached the cutoff voltage (2.0 V). Then, the cell was charged in the same manner until the voltage reached the cutoff voltage (3.8 V).

2.5.3 Electrochemical impedance spectroscopy

In-situ electrochemical impedance spectroscopy (EIS) measurements were conducted using the electrochemical measurement system (BioLogic, VSP) at 25°C with a three-electrode cell. The frequency range was 100 mHz–100 kHz, and an AC amplitude was 10 mV. The EIS measurements were first performed after constant voltage discharging from the open circuit voltage to 2 V at regular intervals, until the current dropped below $3 \mu\text{A}/\text{cm}^2$. Subsequently, EIS measurements were also conducted after constant voltage charging from 2 V to 3.8 V in the same manner.

2.6 Computational study

The computational investigation was carried out using density functional theory (DFT) calculations. The calculations were performed with the Vienna Ab initio Simulation Package (VASP) version 6.4.0 [4], which uses the projected-augmented plane-wave

(PAW) approach to describe the electron-ion interaction. The Perdew-Burke-Ernzerhof (PBE) functional was used with an energy cutoff of 650 eV and a smearing width of 0.05 eV [5]. The convergence threshold of the electronic self-consistent loop was set to 10^{-6} eV, while the threshold for the ionic relaxation convergence was set to have the maximal force acting on the atom be below 0.03 eV/Å. All of the calculations were spin-polarized, and the nudged elastic band (NEB) calculations were performed using an Atomic Simulation Environment without the climbing image [6].

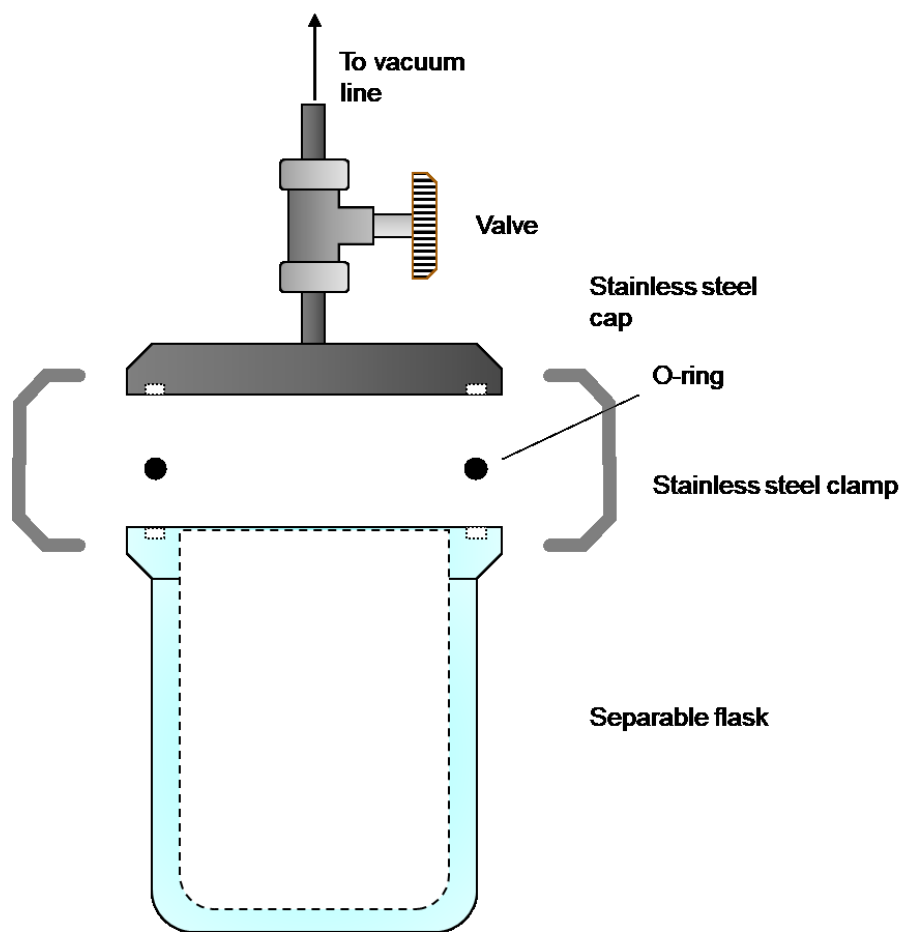


Figure 2-1. Schematic drawing of the separable vacuum flask [1].

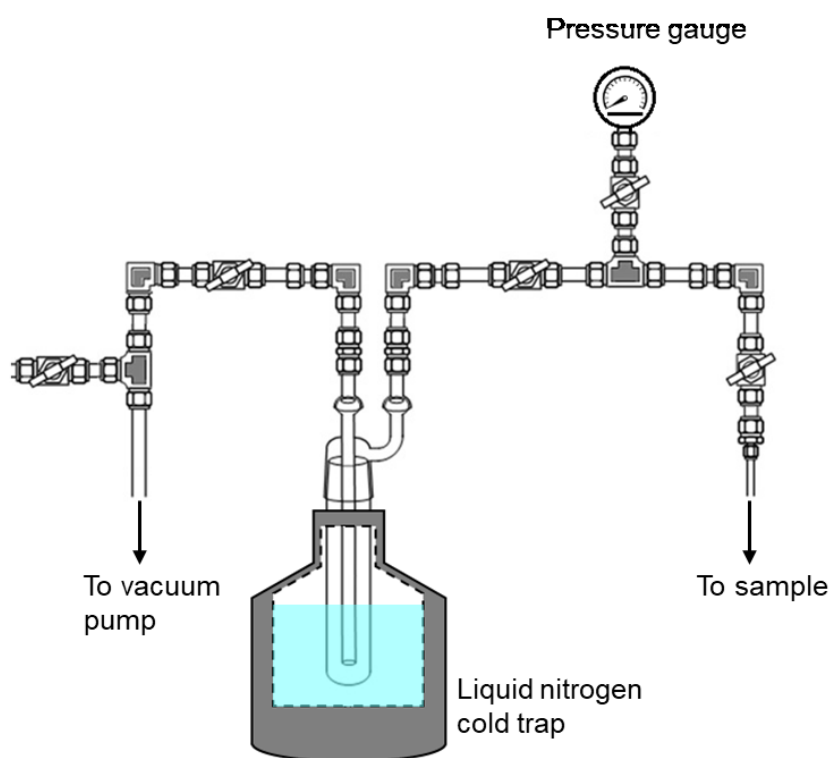


Figure 2-2. Schematic drawing of the vacuum line [1].

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Chapter 3

Delithiation of LiFePO_4 with Cl_2 Gas: Preparation of FePO_4 for Sodium-Ion Batteries with High Li Recovery

3.1 Introduction

As the world steers toward environmentally benign materials, sodium-ion batteries (SIBs) have emerged as promising alternatives to lithium-ion batteries (LIBs) owing to the abundance and extensive distribution of sodium resources [1, 2]. Besides sustainability, sodium manifests chemical properties similar to lithium because of their proximity in the periodic table (Group 1 elements), betokening the possibility of battery systems comparable to LIBs [3-5]. Even so, SIB advancement is heavily encumbered by insufficient capacities due to the scarcity of positive electrode materials, especially the elements (such as transition metals) for their redox centers. Thus, the possibility of high-performance positive electrodes employing abundant elements would be a significant milestone for high-energy-density SIBs.

The search for SIBs positive electrodes has galvanized explorations into polyanionic materials, such as phosphates and pyrophosphates ($\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, $\text{Na}_2\text{FeP}_2\text{O}_7$, etc.) in attempts to emulate the electrochemical performances of their Li analogs in LIBs [6-11]. In particular, NaFePO_4 positive electrodes have demonstrated remarkable structural stability, high energy density, and stable electrochemical behavior [12-14]. As mentioned in Chapter 1, the olivine-group

NaFePO₄ is known to crystalize in two polymorphs, maricite and triphylite (so-called olivine structures in Li-based systems). The maricite NaFePO₄ has high thermodynamic stability that allows solid-state or hydrothermal syntheses at high temperature. However, this polymorph has limited Na⁺ diffusion paths and a high diffusion barrier which generally results in low electrochemical performance [14-20]. In search for solutions, a study reported that the desodiation of a nano-sized maricite NaFePO₄ formed an amorphous FePO₄ with significantly enhanced Na⁺ mobility [21]. Other studies have also shown that reducing the particle sizes and elevating cell operation temperature to 90 °C partially activated the maricite NaFePO₄ and improved charge–discharge capacity [17, 22].

Against this backdrop, triphylite NaFePO₄ has been reported to embody Na⁺ diffusion paths along the *b* axis ([010] direction), much like triphylite LiFePO₄, which renders positive electrodes with substantial performances (capacity of ~120 mAh g⁻¹) [14-16, 23]. Despite these prospects, the direct synthesis of triphylite NaFePO₄ remains a challenge because the thermodynamically unstable triphylite phase easily converts to the maricite phase when heated above 480 °C [15, 24]. Therefore, triphylite NaFePO₄ is typically prepared through chemical or electrochemical delithiation from triphylite LiFePO₄. **Table 3-1** summarizes the reported delithiation and sodiation methods [15, 23, 25-29]. Delithiation engenders a structure known as heterosite FePO₄ whose framework is identical to that of triphylite LiFePO₄ without the Li atoms. It should be mentioned that although electrochemical delithiation is a common synthesis method in

studies entailing triphylite NaFePO_4 , the process has limited commercial feasibility [23, 25, 30]. Similarly, the practicality of the chemical delithiation process, which uses oxidizing reagents such as nitronium tetrafluoroborate (NO_2BF_4) in acetonitrile [15, 26-28], is heavily limited by the cost and difficulty in handling NO_2BF_4 . In an attempt to alleviate these handicaps, Berlanga et al. recently proposed a low-cost and eco-friendly synthesis method wherein $\text{Na}_2\text{S}_2\text{O}_8$ was used for delithiation and $\text{Na}_2\text{S}_2\text{O}_3$ for sodiation to produce the triphylite NaFePO_4 and sufficiently recover the lithium sources [29]. There is another delithiation method of LiFePO_4 using peracetic acid, and the resulting FePO_4 showed better rate performance than the one delithiated by NO_2BF_4 [30]. Other delithiation methods using $\text{K}_2\text{S}_2\text{O}_8$ solution under microwave condition [31] and formic acid with H_2O_2 [32] have been also reported as a green method. Compared to these methods, Cl_2 gas treatment is also a pro-environmental method because Cl_2 gas has sufficient reactivity to complete the reaction and the extracted lithium source is efficiently recovered. Furthermore, the residual Cl_2 gas can be easily recovered and reused even if excess Cl_2 is employed.

It is worth noting that the desodiation (or delithiation) of polyanion frameworks is not limited to chemical or electrochemical processes. In fact, a previous report demonstrated that Cl_2 gas treatment of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ could effectively produce desodiated $\text{NaV}_2(\text{PO}_4)_3$ (or the two-phase mixture of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and $\text{NaV}_2(\text{PO}_4)_3$, depending on the reaction conditions) which was used to devise a reference electrode for a two-electrode SIB configuration [33]. Compared to the conventional delithiation

(or desodiation) techniques, the use of an oxidative gas shortens the reaction durations and improves the scalability of the process. The use of a nonaqueous medium (acetonitrile here) also has a high applicability to various materials because many positive electrode materials are unstable in aqueous media, especially in the charged state.

In an effort to augment the viability of NaFePO_4 positive electrodes for SIBs, this chapter presents a novel preparation method for heterosite FePO_4 . Here, a triphylite LiFePO_4 is delithiated using Cl_2 gas to produce the heterosite FePO_4 and recover Li in the form of LiAlCl_4 (**Figure 3-1**). The obtained heterosite FePO_4 is characterized through X-ray diffraction (XRD) and the Rietveld refinement to ascertain its crystal structure. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectrometry are employed to confirm the morphology and elemental composition before and after the delithiation process. The electrochemical properties of the positive electrode are further evaluated through a series of electrochemical performance tests.

3.2 Experimental

As described in Chapter 2, LiFePO_4/C was delithiated using Cl_2 gas to obtain FePO_4/C powder. Here, 7.889 g (50.01 mmol) of commercial LiFePO_4/C , 8.016 g (60.11 mmol) of AlCl_3 , approximately 50 mL of acetonitrile, and 660 mL (26.5 mmol) of Cl_2 gas were added into an air-tight glass vessel.

The obtained samples were subjected to SEM for surface observation and EDX for elemental composition analysis. XRD patterns of the samples were also collected and the Rietveld refinement of the obtained XRD patterns was performed to determine the lattice parameters.

Under a dry Ar atmosphere, 2032-type coin cells were assembled. The mixture of the obtained FePO₄/C with Super C65 carbon and PVDF (80:15:5wt%) was served as a positive electrode. The sodium metal and 1 mol dm⁻³ Na[PF₆]-EC/DMC (1:1 v/v) with 3wt% of FEC additive were selected as the negative electrode and electrolyte, respectively. A glass microfiber (Whatman GF/A) was used as a separator.

Charge–discharge properties, rate capabilities, and cycle performance were evaluated at 25 °C. The capacity was calculated based on the weight of the FePO₄ active material. The cutoff voltage for the tests was set in the 2.0 V–3.8 V range. After the charge–discharge tests, the coin cells were disassembled, and the electrodes were characterized by XRD.

3.3 Results and discussion

In this study, FePO₄/C powder was obtained through the delithiation of LiFePO₄/C using Cl₂ gas, in accordance with the following reaction (3-1):



Here, Cl_2 gas works as an oxidizing agent while AlCl_3 acts as a Lewis acid for dissolving the LiCl formed on the surface of LiFePO_4 [33]. Most notably, the Cl_2 gas used in this reaction makes this preparation process uniquely expedient for mass production while ensuring a high recovery efficiency of the lithium source. This reaction can theoretically recover 100% of lithium in the form of LiAlCl_4 using acetonitrile. In the present method, the LiAlCl_4 dissolved in acetonitrile was separated from FePO_4/C through simple filtration or centrifuge. The lithium recovery ratio was calculated based on the fraction of the actual yield of FePO_4 over the theoretical yield of FePO_4 . The pristine LiFePO_4 (7.889 g of 50.01 mmol) was delithiated by Cl_2 . After the delithiation process, 7.498 g of powder was obtained. The weight fractions of FePO_4 (98.0%) and LiFePO_4 (2.0%) were determined through the Rietveld quantitative phase analysis. Considering the theoretical yield of FePO_4 is 7.542 g, the actual lithium recovery ratio can be calculated to be 97.4%. Notably, the recovered LiAlCl_4 is expected to gain utility in various applications that augment the economic viability of this method. For example, the LiAlCl_4 can be used directly as an electrolyte for lithium/thionyl chloride primary batteries which are known for their high energy densities and long lifetimes [34, 35]. Other works have also suggested that this byproduct can be used as electrolytes in solid-state or in SO_2 solutions for LIBs [36-38]. Furthermore, chemical conversion through hydrolysis or metathesis can also yield other lithium compositions.

XRD patterns of the obtained FePO_4/C (heterosite, space group: $Pnma$) and the pristine LiFePO_4/C (triphylite, space group: $Pnma$) are illustrated in **Figure 3-2** for comparison. The patterns were also analyzed through the Rietveld refinement as shown in **Tables 3-2** and **3-3**. The XRD pattern of the obtained FePO_4/C corresponds with that of FePO_4 heterosite, albeit with some impurity peaks assigned to LiFePO_4 [39]. The weight fractions of FePO_4 (98.0%) and LiFePO_4 (2.0%) phases, determined through the Rietveld quantitative phase analysis, verified the high efficacy of the preparation method. The small charge capacity in the charge curve of the Na/FePO_4 cell shown in **Figure 3-3** also indicates that lithium is adequately extracted and the remaining lithium has a very limited impact on the electrochemical performance of the SIB.

The SEM images and the EDX mappings of the obtained FePO_4/C and the pristine LiFePO_4/C are shown in **Figure 3-4**. The SEM images reveal that the present delithiation process does not damage the morphology of the pristine particles. The EDX analysis of the obtained FePO_4/C and the pristine LiFePO_4/C identifies that the carbon contents of both materials are almost the same, indicating that this Cl_2 gas treatment did not damage the carbon coating of the pristine LiFePO_4 . The EDX mapping images, obtained at the same magnification level, display an even distribution of all the elements across the obtained FePO_4/C particles. Additionally, the EDX results show that only 0.1% of Cl is present on the FePO_4/C surface, confirming that the byproduct was adequately removed from the product (**Table 3-4**).

The electrochemical performance of the Na/NaFePO₄ cell is highlighted in **Figure 3-5**. The current densities are expressed as C-rates of NaFePO₄ (theoretical capacity of 154 mAh g⁻¹). Prior to the electrochemical performance tests, the FePO₄ electrode was discharged at 0.05C for sodiation. The preliminary discharge curve of the Na/FePO₄ cell is displayed in **Figure 3-6**. The electrode achieved a discharge capacity of 127 mAh (g-FePO₄)⁻¹, comparable performance with chemically or electrochemically prepared NaFePO₄ in previous works [23, 25, 26, 40]. The preliminary discharge curve also exhibited a slightly larger overpotential that was attributed to the reconstruction of the surface layer between electrode and electrolyte [25]. After the preliminary discharge, charge–discharge curves were obtained at 0.05C. **Figure 3-5a** shows the charge process entails a single-phase reaction ranging from NaFePO₄ to Na_{2/3}FePO₄, followed by a two-phase reaction ranging from Na_{2/3}FePO₄ to FePO₄ [15, 25, 41, 42]. However, these reaction ranges cannot be clearly discerned from the discharge curves (see the ex-situ XRD results below for the assignments of the plateaus). These results are attributed to the kinetics of (de)sodiation process, wherein Na⁺ mobility during the phase transformation between FePO₄ and Na_{2/3}FePO₄ is slower than in the solid-solution region between Na_{2/3}FePO₄ and NaFePO₄ [25]. **Figure 3-5b** shows the rate capability at varied C-rates. The measurements performed at 0.1C, 0.2C, 0.5C, 1C, and 2C provided discharge capacities of 100, 88, 71, 60, and 50 mAh (g-FePO₄)⁻¹, respectively. The charge–discharge curves obtained during the rate capability tests (**Figure 3-7**) demonstrate increased polarization at higher current densities, evincing that the poor

kinetics during the desodiation/sodiation reactions resulted from the low diffusivity of Na^+ and/or the high phase transformation barrier in Na_xFePO_4 . The low diffusivity of Na^+ is ascribed to the rigid $\cdots\text{PO}_4\text{--Fe--PO}_4\cdots$ framework, which impedes the movement of the larger-sized Na^+ compared to Li^+ [40]. As shown in **Figure 3-5c**, the cycle performance at 0.2C yielded an initial discharge capacity of $72 \text{ mAh (g-FePO}_4\text{)}^{-1}$ and an average coulombic efficiency of 99.9% for 150 cycles. During cycling, the discharge capacity was observed to increase gradually, reaching $88 \text{ mAh (g-FePO}_4\text{)}^{-1}$ at the 150th cycle. One possible reason for the increase is the increase in active sites because of the deagglomeration of particles during the cycle. On the other hand, the cycle performance at 1C (**Figure 3-5d**) achieved an initial discharge capacity of $69 \text{ mAh (g-FePO}_4\text{)}^{-1}$ and remarkably maintained an average coulombic efficiency of 98.9% for 1000 cycles. Additionally, the electrode exhibited excellent capacity retentions of 98.5%, 97.1%, and 88.6% after the 250th, 500th, and 1000th cycles, respectively. The corresponding charge–discharge curves in **Figures 3-8** and **3-9** appear to overlap each other throughout the cycles, evidencing the high reversibility of the mechanisms. The excellent cycle performance observed indicates that delithiation using Cl_2 does not damage the host framework of the pristine LiFePO_4 . In addition, this electrochemical performance indicates Cl_2 gas treatment can preserve the carbon coating of the pristine LiFePO_4 and keep good electronic conductivity of the material.

An XRD pattern of the discharged electrode after 1000 cycles (**Figure 3-10a**) shows the triphylite NaFePO_4 structure (space group: *Pnma*) [15] was maintained

throughout cycling. The absence of a phase transition to maricite validates the high structural stability of this framework. The SEM image obtained after the electrode was carefully washed demonstrates that the distinct shape of particles was preserved with no sign of cracks or deposits from electrolyte decomposition. Although EDX analysis (**Figure 3-10b** and **Table 3-5**) can only approximate the elemental composition, the obtained Na/Fe ratio of 1.06 suggests that the sodiation process has high reversibility throughout the 1000 cycles.

The phase transition mechanism during charge–discharge was determined through ex-situ XRD analyses of FePO₄/C electrodes at different states of charge, as shown in **Figure 3-11**. Before the charge–discharge test, the electrode manifests peaks belonging to the heterosite FePO₄ [23] (Pattern (1)). After discharge to 2.0 V, the diffraction pattern shows that a triphylite NaFePO₄ [15] (Pattern (2)) is formed. This suggests that Na-ion insertion into the heterosite FePO₄ involves a Fe³⁺/Fe²⁺ reaction accompanied by a structural transformation to the triphylite NaFePO₄. However, this pattern retains some FePO₄ peaks since the discharge capacity obtained is lower than the theoretical capacity. The XRD pattern obtained at the state of charge of 32% during charging confirms the existence of a Na_{2/3}FePO₄ intermediate phase (space group: *Pnma*) [15, 25, 41, 42] with diffraction peaks at higher angles than those of NaFePO₄ (Pattern (3)). This structural change validates the single-phase reactions exhibited by the charge curves in **Figure 3-5a**. After charging the electrode to 3.8 V, majority of the peaks displayed were ascribed to the FePO₄ (Pattern (4)), demonstrating the high reversibility

of the two-phase sodiation/desodiation reaction between heterosite FePO_4 and triphylite $\text{Na}_{2/3}\text{FePO}_4$. Even so, peaks ascribed to residual $\text{Na}_{2/3}\text{FePO}_4$ were also noted, signifying incomplete charging due to the low diffusion coefficient of Na^+ [40].

3.4 Conclusions

In summary, this chapter reported a novel preparation method for a heterosite FePO_4 positive electrode for SIBs through the delithiation of LiFePO_4/C using Cl_2 gas. The heterosite framework of the obtained FePO_4/C electrode is ascertained through a combination of XRD analyses and the Rietveld refinement. Charge–discharge tests demonstrate a high reversible capacity of $127 \text{ mAh (g-FePO}_4\text{)}^{-1}$ at 0.05C, indicating comparable performance with previously reported NaFePO_4 . Additionally, the electrode exhibits excellent cycling performance at 1C with high capacity retentions of 98.5%, 97.1%, and 88.6% after 250, 500, and 1000 cycles, respectively. Ex-situ XRD analyses confirm the sodiation/desodiation mechanisms involve highly reversible phase transitions between the heterosite FePO_4 and triphylite NaFePO_4 via an intermediate $\text{Na}_{2/3}\text{FePO}_4$ phase. This study establishes delithiation using Cl_2 gas as an effective technique for the mass production of highly stable triphylite structures.

Table 3-1. Previously reported preparation methods for triphylite NaFePO₄ from triphylite LiFePO₄.

Delithiation Process (from LiFePO ₄ to FePO ₄)	Sodiation Process (from FePO ₄ to NaFePO ₄)	Ref.
Electrochemical in aqueous electrolyte	Electrochemical in aqueous electrolyte	[25]
Electrochemical in organic electrolyte	Electrochemical in organic electrolyte	[23]
Chemical by NO ₂ BF ₄ in CH ₃ CN	Electrochemical in organic electrolyte	[15]
Chemical by NO ₂ BF ₄ in CH ₃ CN	Electrochemical in ionic liquid or organic electrolyte	[26]
Chemical by NO ₂ BF ₄ in CH ₃ CN	Chemical by NaI in CH ₃ CN	[27]
Chemical by NO ₂ BF ₄ in CH ₃ CN	Chemical by NaI in CH ₃ CN	[28]
Chemical by Na ₂ S ₂ O ₈ in water	Chemical by Na ₂ S ₂ O ₃ in water	[29]

Table 3-2. Crystallographic data of LiFePO₄/C by the Rietveld refinement.

LiFePO ₄ (Space group: <i>Pnma</i>)						
$R_p = 20.7\%$, $R_{wp} = 15.4\%$						
		a (Å)	b (Å)	c (Å)	V (Å ³)	
		10.32606(10)	6.00515(5)	4.69085(5)	290.877(5)	
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Li	4 <i>a</i>	0	0	0	0.5	1.000
Fe	4 <i>c</i>	0.28239(16)	0.2500	0.9728(5)	0.5	1.000
P	4 <i>c</i>	0.0953(4)	0.2500	0.4239(8)	0.5	1.000
O1	4 <i>c</i>	0.0982(8)	0.2500	0.7473(14)	0.5	1.000
O2	4 <i>c</i>	0.4555(11)	0.2500	0.2174(11)	0.5	1.000
O3	8 <i>d</i>	0.1637(6)	0.0483(9)	0.2819(9)	0.5	1.000

The starting parameters were taken from a previous report [39], and the B factor and Occupancy were fixed at 0.5 and 1.0, respectively.

Table 3-3. Crystallographic data of FePO₄/C by the Rietveld refinement.

FePO ₄ (Space group: <i>Pnma</i>)						
$R_p = 20.2\%$, $R_{wp} = 15.1\%$, Weight fraction = 98.0%						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	9.81363(10)	5.78686(5)	4.78166(6)	271.551(5)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Fe	4c	0.27396(19)	0.2500	0.9512(4)	0.5	1.000
P	4c	0.0954(3)	0.2500	0.4046(9)	0.5	1.000
O1	4c	0.1217(6)	0.2500	0.7120(15)	0.5	1.000
O2	4c	0.4446(9)	0.2500	0.1650(10)	0.5	1.000
O3	8d	0.1707(5)	0.0450(7)	0.2473(8)	0.5	1.000

The starting parameters were taken from a previous report [39], and the B factor and Occupancy were fixed at 0.5 and 1.0, respectively. The triphylite LiFePO₄ is considered to be an impurity phase. Crystallographic data in **Table 3-2** were used for the impurity LiFePO₄ phase (weight fraction of 2.0 %) in this refinement without any change.

Table 3-4. EDX analysis results of the pristine LiFePO_4/C and the FePO_4/C obtained by delithiation of LiFePO_4/C using Cl_2 gas. The theoretical amount of each element in LiFePO_4 and FePO_4 is also described.

Element	LiFePO_4 (at%)		FePO_4 (at%)	
	Obs.	Calc.	Obs.	Calc.
O	69.3	66.6	70.2	66.6
P	16.0	16.7	15.8	16.7
Cl	—	—	0.1	—
Fe	14.7	16.7	13.9	16.7

The amount of carbon was omitted from the calculation of elemental composition.

Table 3-5. EDX analysis result of the NaFePO₄ electrode after 1000 cycles of charge–discharge at 1C. The theoretical amount of each element in NaFePO₄ is also escribed.

Element	NaFePO ₄ (at%)	
	Obs.	Calc.
O	48.9	57.1
F	3.8	—
Na	15.8	14.3
P	16.6	14.3
Fe	14.9	14.3

The amount of carbon was omitted from the calculation of elemental composition.

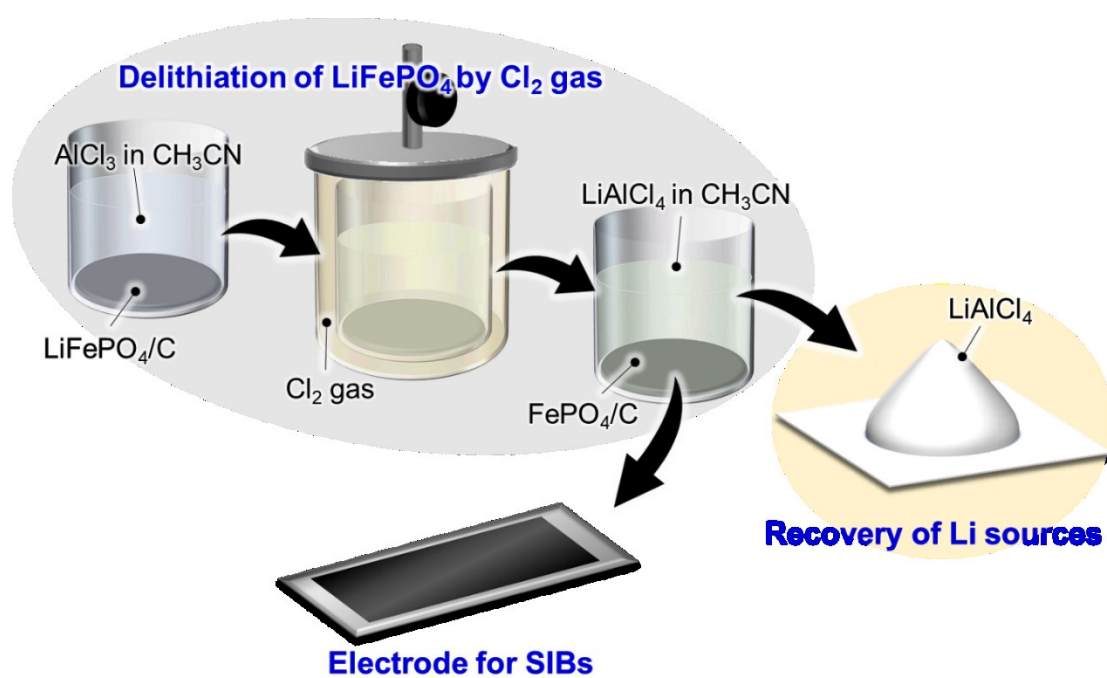


Figure 3-1. Schematic illustration of the synthetic route of FePO_4/C by delithiation using Cl_2 gas and the recovery route of the Li sources.

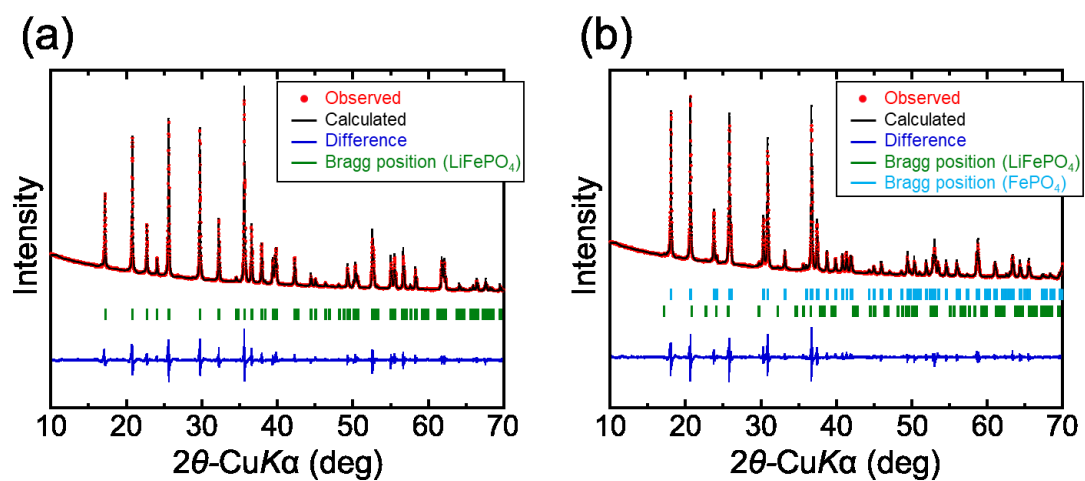


Figure 3-2. XRD patterns with Rietveld refinement results of (a) the pristine LiFePO₄/C and (b) the FePO₄/C obtained by delithiation of LiFePO₄/C using Cl₂ gas.

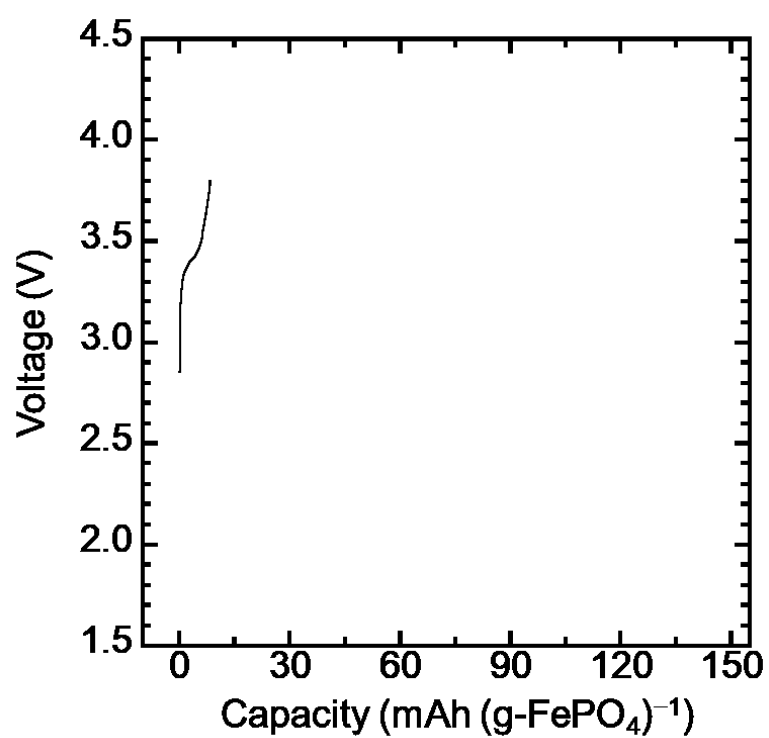


Figure 3-3. Charge curve of the Na/FePO₄ cell with the 1 mol dm⁻³ Na[PF₆]-EC/DMC (1:1 v/v) with 3wt% of FEC addition at 0.1C up to 3.8 V.

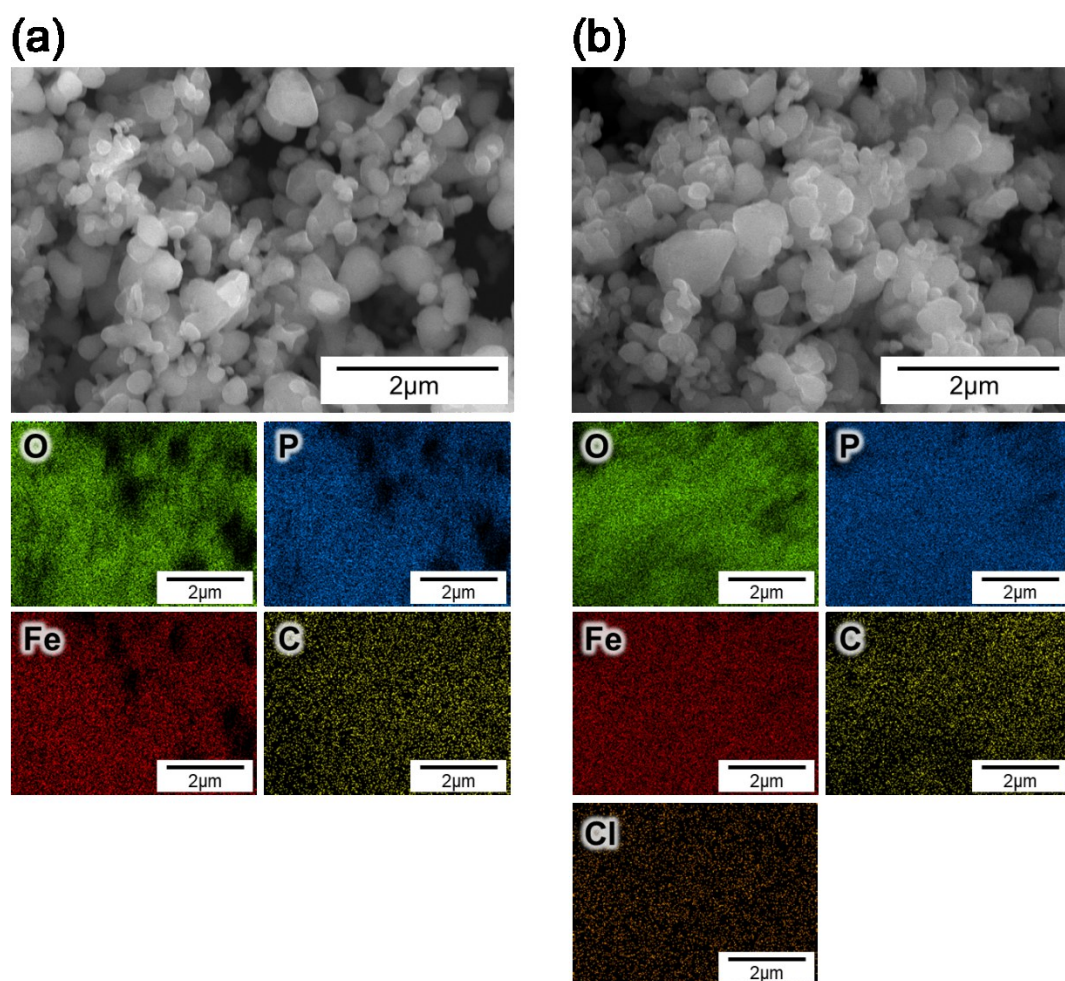


Figure 3-4. SEM images and EDX mappings of (a) the pristine LiFePO_4/C and (b) the FePO_4/C obtained by delithiation of LiFePO_4/C using Cl_2 gas.

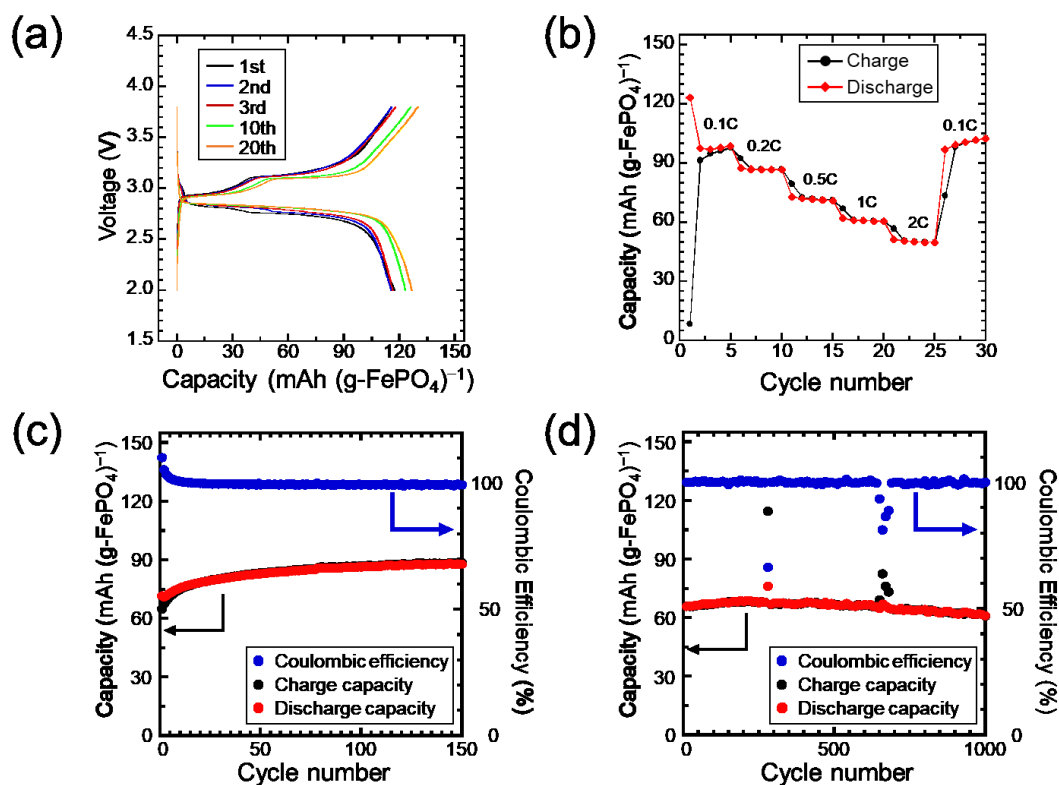


Figure 3-5. Electrochemical performance of the Na/NaFePO₄ cell with the 1 mol dm⁻³ Na[PF₆]-EC/DMC (1:1 v/v) with 3wt% of FEC addition. The FePO₄ obtained by chemical oxidation was preliminarily discharged at 0.05C prior to these tests. (a) Charge–discharge curves at 0.05C, (b) rate capability test, (c) cycle performance at 0.2C, and (d) cycle performance at 1C. Fluctuation observed during the cycle performance test over 1000 cycles is caused by physical shocks to the test cells.

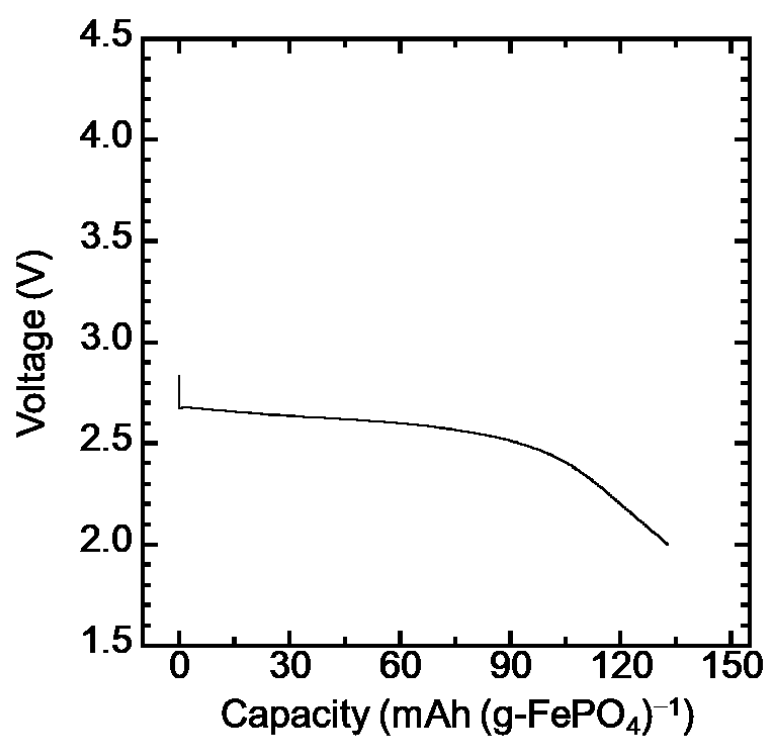


Figure 3-6. Preliminary discharge curve of the Na/FePO₄ cell before the charge–discharge test in **Figure 3-5a** at 0.05C.

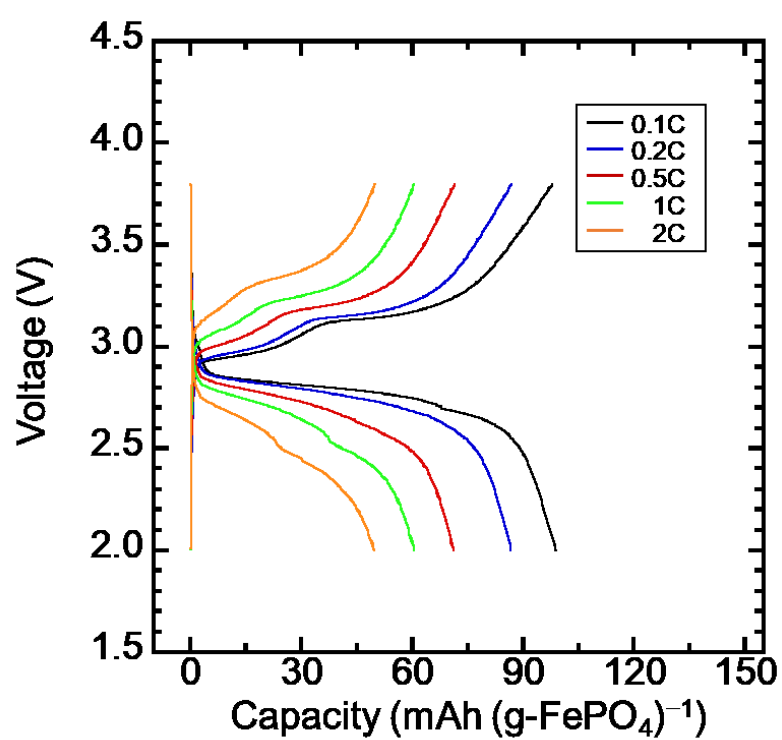


Figure 3-7. Charge–discharge curves of the Na/FePO₄ cell during the rate capability test in Figure 3-5b.

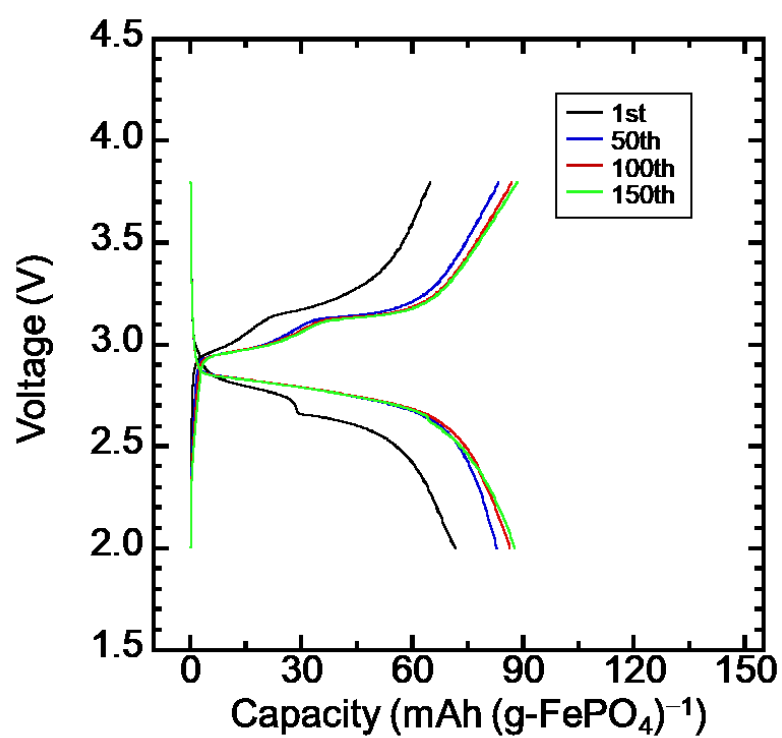


Figure 3-8. Charge–discharge curves of the Na/FePO₄ cell during cycle performance test at 0.2C in Figure 3-5c.

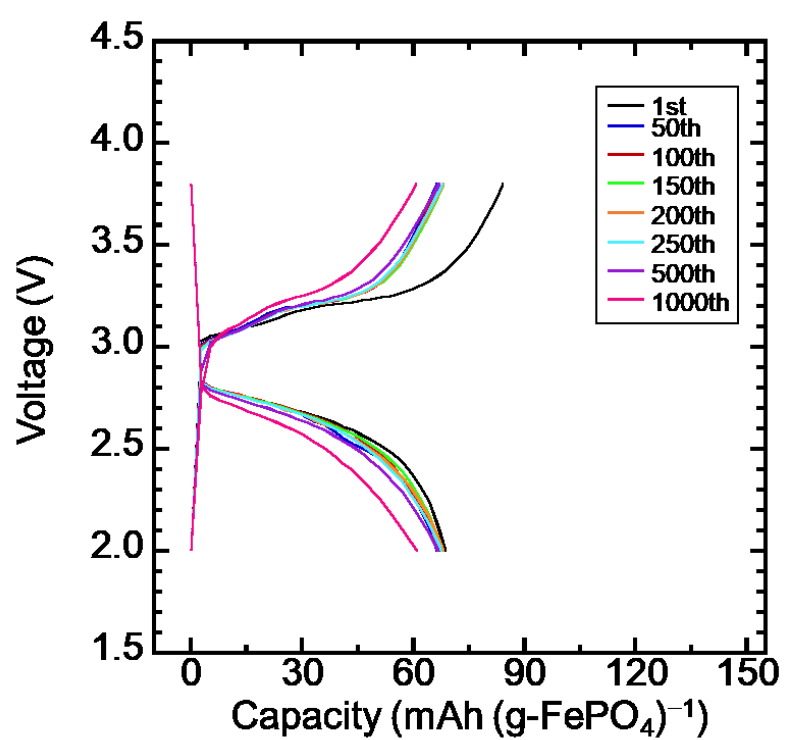


Figure 3-9. Charge–discharge curves of the Na/FePO₄ cell during cycle performance test at 1C in **Figure 3-5d**.

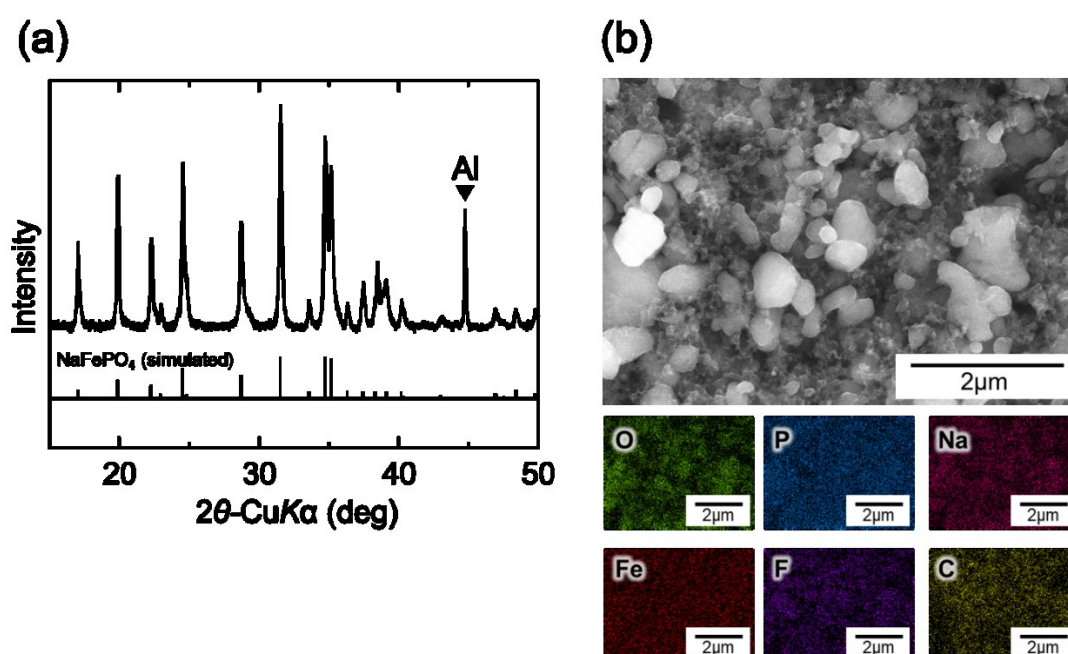


Figure 3-10. (a) XRD pattern and (b) SEM image and EDX mappings of the NaFePO_4 electrode after 1000 cycles of charge-discharge at 1C. The simulated pattern was calculated based on crystallographic data in previous reports [15] using VESTA software. The peak at 44.7° in the XRD pattern is assigned to Al metal [43].

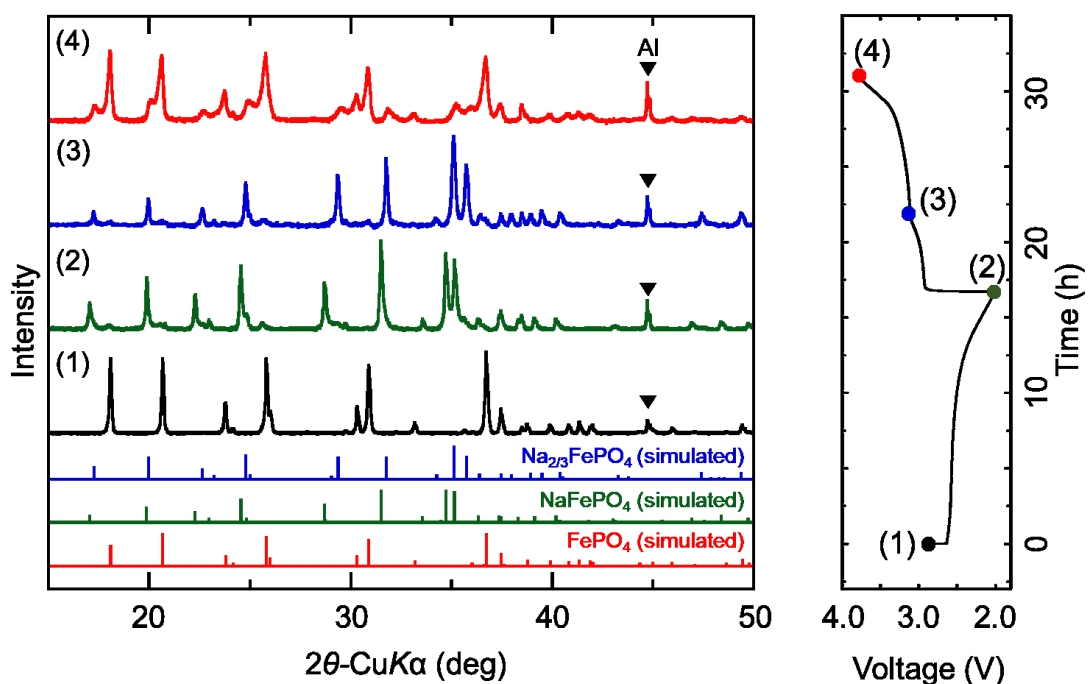


Figure 3-11. Ex-situ XRD patterns of the FePO_4/C electrodes at different states of charge. (1) Before preliminary discharge (pristine heterosite FePO_4), (2) after preliminary discharge (mainly assigned to NaFePO_4), (3) after charge to 32% SOC (mainly assigned to $\text{Na}_{2/3}\text{FePO}_4$), and (4) after full charge (mainly assigned to FePO_4). The simulated patterns are calculated based on crystallographic data in previous reports [15, 39] using VESTA software. The peak at 44.7° is assigned to Al metal [43].

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Chapter 4

Oxygen-Powered Sustainable FePO₄ Preparation for Sodium Metal Batteries with Li Acetate Recovery

4.1 Introduction

Sodium-ion batteries (SIBs) are regarded as alternatives to lithium-ion batteries (LIBs) due to the abundance and wide distribution of sodium resources [1]. However, one downside of SIBs is their low gravimetric energy density because of the heavier weight of Na [2]. The use of sodium metal as a negative electrode is gaining attention for improving the specific energy density because sodium metal possesses a high specific capacity (1166 mAh g⁻¹) and low redox potential (-2.71 V vs. SHE) [3]. Na metal-free (so-called anode-free) batteries are the ideal sodium metal batteries (SMBs) configuration since all the sodium sources originate from the positive active material and get deposited on the negative current collector during charging [4]. Such configuration eliminates the burdensome production of the sodium metal negative electrode and contributes to safer cell production [5]. Despite these anticipated characteristics, metal-free batteries suffer from low cycle stability and coulombic efficiency because of unstable dissolution/deposition of sodium metal and the formation and growth of dendrites when sodium metal is deposited onto the current collector [5-7]. Various groups have made modifications to current collectors and intermediate layers to address such challenges [3, 5, 7-11]. However, such modifications often

require tedious processes and cause a decrease in the gravimetric energy density. As another alternative solution, a recent study proved the practical energy density of lean metal batteries is higher than that of metal-free batteries [12], which can provide significant insight into improving the energy density of metal batteries.

As discussed in the previous chapters, triphylite NaFePO_4 is one of the promising positive electrode materials for SIBs due to its structural stability with a polyanionic frame and a relatively high theoretical capacity (154 mAh g^{-1}) [13-15]. It is also worth noting that this material is composed only of relatively abundant elements and does not contain expensive elements such as cobalt and nickel, which benefits resource security. However, due to its metastable nature, triphylite NaFePO_4 must be synthesized using triphylite LiFePO_4 as the starting material.

To deal with the above-mentioned two issues (Na-metal-free SMB and synthesis of triphylite NaFePO_4) simultaneously, this chapter offers a sustainable oxygen-powered heterosite FePO_4 production method and its application as a positive electrode for SMBs. Here, heterosite FePO_4 is obtained from triphylite LiFePO_4 through the chemical delithiation technique using O_2 in acetic acid aqueous solution. While the obtained heterosite FePO_4 is utilized as a positive electrode for SMBs, the extracted lithium during the delithiation process is recovered as lithium acetate (CH_3COOLi) that can be used to further synthesize LiFePO_4 . This process enables closed-loop lithium recycling and a more cost-effective heterosite FePO_4 production. Furthermore, it is important to highlight that the full-cell configuration in this work demonstrates a

gravimetric energy level closely approaching that of Na-metal-free SMB with excellent cyclability.

4.2 Experimental

Purchased LiFePO_4/C (7.98 g, 50.0 mmol), acetic acid (CH_3COOH , 3.60 g, 60.0 mmol), and distilled water (200 cm^3) were added into an air-tight glass reaction vessel before introducing 1.5 atm of O_2 gas. After the reaction, the delithiated product (FePO_4/C , 7.49 g, 49.6 mmol) was obtained. The solution separated by centrifugation was vacuum-dried at $100\text{ }^\circ\text{C}$, resulting in the white lithium acetate powder (3.2 g, 44.8 mmol). Hereafter, the purchased LiFePO_4/C and the FePO_4/C prepared from it are denoted as P-LFP and PO-FP, respectively.

The LiFePO_4/C powder was synthesized from the recovered lithium acetate via a solid-state reaction. The purchased $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$ was also provided as the lithium source to confirm the synthesis route. The precursor powder (mixture of lithium acetate, $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, and glucose in molar ratio of 1:1:1:0.1) was sintered at $300\text{ }^\circ\text{C}$ for 3h and then at $700\text{ }^\circ\text{C}$ for 6 h under the Ar atmosphere. The resulting LiFePO_4/C powder was delithiated to prepare FePO_4/C using O_2 gas in the acetic acid solution in the same procedure. Hereafter, the resynthesized LiFePO_4/C and the FePO_4/C prepared from it are denoted as R-LFP and RO-FP, respectively.

The samples were subjected to XRD for structure identification, SEM for surface observation, and EDX for elemental composition analysis. The Rietveld refinement of

the obtained XRD patterns was performed to determine lattice parameters. AAS and ICP-AES were also conducted to quantitatively determine the composition of the samples. The specific surface area of the samples was analyzed with the BET method. The recovered lithium acetate was analyzed by FT-IR and an organic elemental analyzer. The SEI components on the Na metal electrode were analyzed using XPS. The Na metal electrode after cycling tests of the Na/FePO₄ cell was washed with DME (the electrolyte solvent), dried under vacuum at room temperature, and transferred into an XPS chamber using an airtight vessel.

For the half-cell and full-cell tests, 2032-type coin cells were assembled under a dry Ar atmosphere. The composition of the positive electrodes were PO-FP (or RO-FP) : Super C65 : SWCNT : PVDF = 91:3:2:4 wt%. The mass loadings of the electrodes for half cells and full cells were 2–3 and 8–10 mg-FePO₄ cm⁻², respectively. Sodium metal negative electrodes in 13 mm diameter and 10 mm diameter were for the half-cell and full-cell tests, respectively. Sodium metal was weighed accurately with a restricted amount for the full cell tests to control the N/P ratio. The 40mol% Na[FSA]-[C₂C₁im][FSA] ionic liquid (IL) electrolyte was prepared by adding the dried Na[FSA] and [C₂C₁im][FSA] in the molar ratio of Na[FSA]:[C₂C₁im][FSA] = 40:60 and stirring the mixture in a bottle at 60 °C. This IL was served as an electrolyte for the half-cell and full-cell tests at 90 °C. For the half-cell and full-cell tests at 25 °C, 1 mol dm⁻³ Na[PF₆]-EC/DMC (1:1 v/v) with 3wt% of FEC and 1 mol dm⁻³ Na[PF₆]-DME electrolytes were selected, respectively. A glass fiber was used as the standard in half-

cell tests and full-cell tests operated at 90 °C using ionic liquid electrolyte, considering the wettability of the ionic liquid electrolyte and to secure thermal stability at 90 °C. In full-cell tests conducted at 25 °C using DME electrolyte, a polypropylene (PP) separator was used from a practicality aspect.

Charge–discharge properties, rate capabilities, and cycle performance were evaluated at 25 and 90 °C. The capacity was calculated based on the weight of the FePO₄ active material. The cutoff voltage was set in the 2.0 V–3.8 V range for the half-cell tests and the full-cell tests at 25 °C and the 2.0–3.6 V range for the full-cell tests at 90 °C. After the charge–discharge tests, some coin cells were disassembled, and the electrodes were washed with EC/DMC and ethanol. The washed electrodes were dried at 60 °C for a few hours, then characterized by XRD and EDX. The GITT measurements were conducted in the manner described in Chapter 2. The in-situ EIS was conducted at 25 °C with a three-electrode cell, wherein the RO-FP electrode was used as the working electrode and sodium metal was used as the reference and counter electrode with 1 mol dm⁻³ Na[PF₆]-EC/DMC (1:1 v/v) with 3wt% of FEC electrolyte. A glass fiber was used as a separator.

To evaluate the electrochemical performances of the P-LFP and R-LFP at 25 °C, Li/P-LFP and Li/R-LFP half cells were also prepared. Here, the mixture of P-LFP (or R-LFP), conductive carbon, and PVDF in the weight ratio of 80:15:5 was served as the positive electrode. Li metal was used as the negative electrode. As the electrolyte, 1 mol dm⁻³ Li[PF₆]-EC/DMC (1:1 v/v) was selected. A glass fiber was used as a separator.

The cutoff voltage and C-rate were set in the 2.0 V–4.2 V range and 0.05C (1C = 170 mA g⁻¹), respectively. The capacity was calculated based on the weight of the LiFePO₄ active material.

The NEB calculations were started with the unit cells of NaFePO₄, LiFePO₄, Na_{2/3}FePO₄, and FePO₄ taken from references [16-18]. These unit cell structures are shown in **Figure 4-1**. To ensure the consistency of the NEB calculations across different stoichiometries, the 1 × 2 × 1 supercell for Na_{2/3}FePO₄ and 1 × 3 × 2 supercell for NaFePO₄, LiFePO₄, and FePO₄ were simulated to have similar size and number of atoms. The experimental cell parameter was kept constant during the ionic relaxation and NEB calculations. A Na/Li atom was added to the FePO₄ while the respective atom was removed from LiFePO₄ and NaFePO₄ to model Na⁺ and Li⁺ diffusion.

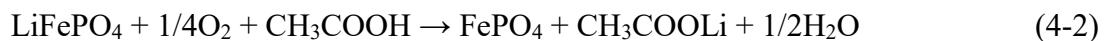
4.3 Results and discussion

Figure 4-2 schematically shows the redox potentials of oxidizing agents for chemical delithiation of positive electrode materials. Because the redox potential of LiFePO₄ is estimated to be around 0.4 V vs. SHE based on the redox potentials of Li (−3.04 V vs. SHE) [19] and LiFePO₄ (3.4 V vs. Li⁺/Li) [20], LiFePO₄ can be chemically oxidized (delithiated) by oxidizing agents with redox potentials higher than 0.4 V vs. SHE such as Br₂ (1.07 V vs. SHE) [21], O₂ (1.23 V vs. SHE) [22], Cl₂ (1.36 V vs. SHE) [23], Na₂S₂O₈ (2.01 V vs. SHE) [24], and NO₂BF₄ (2.1 V vs. SHE) [25]. To facilitate the oxidation reaction and design a sustainable route, it is necessary to separate the Li

source from FePO₄. Here, O₂ and water, which are ubiquitous around us, are used as an oxidizing agent and a solvent, respectively. The pH control of the aqueous solution during the reaction is especially important for the oxidation process with O₂, since the reaction of active materials with O₂ in water entails H⁺ consumption as shown in the following equation (4-1), where the redox potential decreases by 0.059 V per the increase of pH unit [22].



In this study, acetic acid (CH₃COOH, pK_a = 4.76) was added to water to maintain the solution in a weakly acidic condition and recover the Li source as lithium acetate (CH₃COOLi) in the subsequent procedure. The delithiation reaction of LiFePO₄ with O₂ in an acetic acid solution is described in accordance with the following reaction (4-2).



Without acetic acid, the reaction is expected to proceed as indicated by the following reaction (4-3), where LiOH is generated and therefore the pH of the solution increases.



The increase in pH is not preferred because FePO_4 can dissolve in the basic solution [26], and the redox potential of $\text{O}_2/\text{H}_2\text{O}$ decreases with the increase of pH (e.g., 0.40 V vs. SHE at pH = 14).

A sustainable FePO_4 production scheme in this study is illustrated in **Figure 4-3**. Herein, LiFePO_4/C is delithiated by O_2 in an acetic acid solution to produce FePO_4/C in accordance with Equation (2). The extracted lithium source can be easily separated from FePO_4 in the form of lithium acetate solution by filtration or centrifugation. The recovered lithium acetate powder from the solution is used to repetitively synthesize LiFePO_4 , which enables closed-loop lithium recycling. Of note, this delithiation process using O_2 and acetic acid ensures high lithium source recovery in the form of lithium acetate. The yield of FePO_4 in this study is 99.2% based on the weight change, which is comparable to those obtained when using other oxidizing agents such as $\text{Na}_2\text{S}_2\text{O}_8$ (91% from LiFePO_4 to NaFePO_4 via FePO_4) [27] or Cl_2 (97.4%) as discussed in Chapter 3.

XRD patterns of the P-LFP and PO-FP are shown in **Figure 4-4a**. Successful delithiation of LiFePO_4/C using O_2 and acetic acid is confirmed by Rietveld refinement (lattice parameters of the P-LFP, space group = $Pnma$, $a = 10.32279(8)$ Å, $b = 6.00338(4)$ Å, and $c = 4.68896(4)$ Å and PO-FP, space group = $Pnma$, $a = 9.81209(12)$ Å, $b = 5.78685(6)$ Å, and $c = 4.78223(6)$ Å) [17]. Detailed crystallographic data are shown in **Figures 4-5, 4-6, Tables 4-1, and 4-2**. The SEM images of the P-LFP and PO-FP (**Figure 4-4b**) show identical particle morphologies, revealing the present

delithiation process does not damage the morphology of the pristine particles. The EDX mappings of the PO-FP in **Figure 4-4c** indicate an even distribution of P, O, and Fe across the PO-FP particles. The AAS and the ICP-AES analyses of the PO-FP verify that 97.6% of Li was extracted from the P-LFP, which can be considered to be the lithium resource recovery ratio since it is a closed system. The lithium acetate powder recovered from the reacted solution was amorphous and identified by the FT-IR as shown in **Figure 4-7**. The FT-IR spectra and the organic elemental analysis using the combustion method in **Table 4-3** indicate lithium acetate hydrate ($\text{CH}_3\text{COOLi} \cdot 0.3\text{H}_2\text{O}$) was recovered [28]. The recovered lithium acetate was reused as a precursor for the LiFePO_4/C (R-LFP) synthesis via a solid-state method, followed by the preparation of FePO_4/C (RO-FP) from the R-LFP using O_2 and acetic acid. XRD patterns of the R-LFP and RO-FP are shown in **Figure 4-4a**. Rietveld refinement revealed the successful reproduction of LiFePO_4/C (triphylite structure) and FePO_4/C (heterosite structure), confirming a closed-loop lithium recycling and a sustainable FePO_4 preparation route illustrated in **Figure 4-3** (lattice parameters of R-LFP, space group = $Pnma$, $a = 10.3146(3) \text{ \AA}$, $b = 6.00458(14) \text{ \AA}$, and $c = 4.69769(13) \text{ \AA}$ and RO-FP, space group = $Pnma$, $a = 9.8196(3) \text{ \AA}$, $b = 5.79774(17) \text{ \AA}$, and $c = 4.77120(17) \text{ \AA}$), respectively. Detailed results are shown in **Figures 4-8** and **4-9** for Rietveld refinement and **Tables 4-4** and **4-5** for detailed crystallographic data.

As shown in **Figure 4-10**, SEM observation found that the particle size of R-LFP (100 nm) is smaller than that of P-LFP (1 μm) (**Figure 4-4b**). The smaller particle size

of R-LFP is also manifested in the charge–discharge curves shown in **Figure 4-11**, where the slope regions expand at the beginning and end of the charge–discharge curves compared to P-LFP, indicating the expansion of solid-solution region of Li_xFePO_4 ($x \approx 0$ and 1) due to the downsized particles [29]. The particle size difference is also revealed by the specific surface area analysis using BET method, where the specific surface areas of P-LFP and R-LFP are $7.2 \text{ m}^2 \text{ g}^{-1}$ and $34.2 \text{ m}^2 \text{ g}^{-1}$, respectively.

The electrochemical performances of the Na/FePO₄ half cells are highlighted in **Figure 4-12**. Here, three types of cells are tested to compare the data in different conditions. The PO-FP electrode is evaluated with two different electrolytes, 1 mol dm⁻³ Na[PF₆]-EC/DMC (1:1 v/v) with 3wt% of FEC organic electrolyte (denoted as OE hereafter) at 25 °C and 40mol% Na[FSA]-[C₂C₁im][FSA] ionic liquid electrolyte (denoted as IL hereafter) at 90 °C. The RO-FP electrode is evaluated with OE at 25 °C. The charge–discharge curves at 10 mA (g-FePO₄)⁻¹ in **Figure 4-12a** demonstrate the particle downsizing and temperature rise contribute to the increase in capacity due to the improved Na ion diffusion. The downsized FePO₄ particle resulted in the discharge capacity evolution from 104 mAh (g-FePO₄)⁻¹ to 129 mAh (g-FePO₄)⁻¹ at 25 °C. Notably, the discharge capacity of a cell operated at 90 °C achieved 171 mAh (g-FePO₄)⁻¹, which is close to the theoretical capacity (178 mAh (g-FePO₄)⁻¹). **Table 4-6** summarizes the electrochemical properties of FePO₄ or NaFePO₄ prepared using various delithiation methods. In this study, FePO₄ prepared using oxygen as an oxidizing agent exhibits performance comparable to those obtained through other

oxidation methods. The rate capability tests in **Figure 4-12b** also show the significant improvement of Na ion diffusivity resulting from the particle downsizing and temperature rise. The improved Na ion diffusion is verified by the GITT in **Figures 4-12c** and **4-12d**. Whereas the larger overpotentials in the PO-FP cell at 25 °C indicate the poor Na ion diffusivity, the downsized RO-FP cell at 25 °C and the PO-FP cell at 90 °C show the smaller overpotentials, revealing the improved diffusivity of Na ions. Interestingly, the two distinct regions are observed for overpotentials during both discharge and charge processes at 90 °C, where the overpotential in the Na_xFePO_4 solid-solution region ($2/3 \leq x \leq 1$) is much smaller than that in the two-phase region between FePO_4 and $\text{Na}_{2/3}\text{FePO}_4$. In-situ EIS of the RO-FP electrode in a three-electrode cell was performed at 25 °C during charge–discharge cycles (CV mode, intervals 0.1 V or 0.05 V until the current dropped below $3 \mu\text{A cm}^{-2}$, **Figure 4-13**. The results reveal that the open-circuit voltage (OCV) state exhibits the highest charge transfer resistance (R_{ct}). As sodium ions are inserted into FePO_4 , R_{ct} decreases until it reaches a plateau region. The R_{ct} is maintained throughout the discharge process. Interestingly, during the charging process, R_{ct} further decreases in the solid-solution region (2.0 V–2.9 V), reaching its minimum value. This suggests that the intermediate phase transition is not the rate-determining step. After this region, R_{ct} begins to increase again in the two-phase region (2.9 V–3.8 V), indicating that the desodiation process becomes progressively more difficult. This increase in R_{ct} during the desodiation step highlights the limitations of capacity at RO-FP at 25 °C. However, these limitations are mitigated at 90 °C, where

the performance improves, suggesting that temperature elevation facilitates charge transfer reaction and overall kinetics in the RO-FP. These results support the different Na ion diffusivity between the solid-solution region and the two-phase region [14]. It is also found that the overpotentials at the end of charging are large regardless of the particle size and temperature. This implies that other factors than the Na ion diffusion such as the charge transfer influence the overpotentials [30]. The kinetic behavior of Na^+ ion is investigated further using a set of NEB calculations. The resulting diffusion energy barriers and diffusion path are shown in **Figure 4-14** at all the considered compositions ($x = 0, 2/3$, and 1 for Na_xFePO_4). The composition of $x = 2/3$ exhibits the lowest diffusion barrier of the Na^+ ion, which demonstrates that the Na^+ ion diffusion in the $\text{Na}_{2/3}\text{FePO}_4$ phase is not the rate-determining step for reaching the thermodynamic equilibrium. These results are consistent with the results observed in in-situ EIS in **Figure 4-13**. The simulation results thus support that the slow phase transformation from FePO_4 to $\text{Na}_{2/3}\text{FePO}_4$ accounts for the single plateau observed during the discharge. Considering the NEB calculations and electrochemical properties, an increase of capacity by reducing particle size and increasing operational temperature can effectively overcome the higher diffusion barrier at the edges of the FePO_4 and NaFePO_4 states as shown in **Figure 4-15**.

Ex-situ XRD of the electrodes after initial discharging shows Na ions are inserted into FePO_4 and only the peaks assigned to NaFePO_4 are observed for PO-FP at 90 °C and RO-FP at 25 °C at the end of discharge (**Figure 4-16**). On the other hand, the pattern

of the discharged PO-FP electrode at 25 °C retains the FePO₄ peaks. This difference also indicates a significant impact on particle size and Na⁺ ion diffusion in the FePO₄ phase is the biggest limitation for charge–discharge capacity. The two flat voltage regions observed during charging in **Figure 4-12a** imply the Na_xFePO₄ solid-solution phase ($2/3 \leq x \leq 1$) followed by the two-phase between FePO₄ and Na_{2/3}FePO₄, which agrees with the previous literature [31]. On the other hand, only one plateau appears during discharging because the Na ion diffusivity in the Na_xFePO₄ solid-solution phase ($2/3 \leq x \leq 1$) is faster than that during the phase transformation between FePO₄ and Na_{2/3}FePO₄ [14]. This phase transition behavior is confirmed by the in-situ XRD of the electrode during charge–discharge at 90 °C (**Figure 4-17**).

Na metal full-cell performance is investigated to demonstrate the effective use of heterosite FePO₄. **Figure 4-18a** explains the comparison between the typical Na-metal-free (anode-free) SMB cell configuration and the charged state of the SMB configuration suggested in this study. For the Na-metal-free cell, the discharged (sodiated) active material is usually applied for the positive electrode without any Na metal at the negative electrode, wherein all the sodium inventory of positive active material can be plated onto a current collector on the negative electrode side and the N/P ratio is considered to be one [6], although some studies define it as zero [32]. In the present study, on the other hand, the charged (desodiated) active material (FePO₄) and the sodium metal are applied for the positive and negative electrodes, respectively. Herein, the N/P ratio ($r_{N/P}$) is calculated on the basis of the capacity of the charged state

of FePO₄ (Q_P) and the additional Na metal (Q_N) as defined in the following Equation (4-4):

$$r_{N/P} = Q_N / Q_P \quad (4-4)$$

The Q_N and Q_P values are determined from the theoretical capacities of the negative and positive electrodes, respectively. Here, the term “capacity” refers to the ability to store or release sodium. The only difference between the discharged- and charged-state SMBs lies in whether the sodium is initially located on the positive side or the negative side.

Figure 4-18b presents the cycle performance of the Na/RO-FP full cell with 1 mol dm⁻³ Na[PF₆]-DME (the N/P ratio of 2.44) at 25 °C. Over 300 cycles, stable cycle performance is achieved with the average coulombic efficiency of 99.9% at 100 mA (g-FePO₄)⁻¹. Charge–discharge curves during this test are shown in **Figure 4-19**. The voltage drops during discharging are probably because of the polarization of the Na metal counter electrode [33]. Rate capability of the Na/RO-FP cell with 1 mol dm⁻³ Na[PF₆]-DME electrolyte at 25 °C shown in **Figure 4-20** is consistent with that obtained in the half-cell configuration (**Figure 4-12b**). The stable cycling performance is attributed to the rigid framework of FePO₄ and the mild oxidation process that does not damage FePO₄. Additionally, the high Na deposition/dissolution properties of the Na[PF₆]-DME electrolyte, as reported in previous reports [34-36]. When using 1 mol

dm^{-3} $\text{Na}[\text{PF}_6]$ -DME electrolyte, high Na plating/stripping reversibility can be achieved due to the formation of a uniform inorganic solid electrolyte interphase (SEI) made of Na_2O and NaF on Na metal, which is highly impermeable to electrolyte and conducive to nondendritic growth [34]. XPS measurements of the Na metal electrode of the cycled Na/ FePO_4 cell confirmed that the surface of the SEI contained both organic and inorganic components, including Na_2O and NaF as shown in **Figure 4-21**, which is consistent with previous reports [34-36]. All the spectra were recorded without Ar-etching to avoid chemical degradation or artifacts in the SEI [37, 38]. The organic ethereal-oligomers, ether sodium-salts, and carbonate species SEI compounds, such as $\text{O}=\text{C}-\text{O}$, $\text{C}-\text{O}-\text{C}$ in C 1s, and $\text{C}-\text{O}-\text{Na}$ in O 1s, are primarily attributed to the reduction of DME molecules [35]. Fluorine- and phosphorus-containing species were also analyzed to identify the components of the SEI. The Na-F species were found to originate mainly from the direct decomposition of $\text{Na}[\text{PF}_6]$ salt, while the P-F species (~ 688 eV) is associated with residual $\text{Na}-\text{PO}_x\text{F}_y$, likely formed via solvent decomposition and hydrolysis of $\text{Na}[\text{PF}_6]$ due to water residues during cycling. Two close peaks located around ~ 1072 eV in the Na 1s spectrum are assigned to Na-O and Na-F [34].

The highly stable cycling is also attributed to the additional sodium source on the negative electrode, which compensates for irreversible sodium consumption during cycles [39]. This is verified by the galvanostatic sodium deposition/dissolution tests of the Al/Na and Na/Na half cells using 1 mol dm^{-3} $\text{Na}[\text{PF}_6]$ -DME electrolyte at 0.5 mA

cm^{-2} as shown in **Figure 4-22**. The dissolution/deposition efficiency is lower in the Al/Na cell, particularly in the first cycle, because of the SEI formation [40, 41]. On the other hand, the Coulombic efficiency remains at almost 100% in the Na/Na cell, indicating that the excess sodium can compensate for the sodium loss during cycle [39]. Moreover, the intrinsic dissolution/deposition performance, including efficiency, nucleation process, and SEI formation, may differ between Al/Na (metal-free cell configuration) and Na/Na (metal cell configuration); however, this requires further investigation.

This configuration cell exhibits a high gravimetric energy of 270 Wh ($\text{kg-Na} + \text{FePO}_4$)⁻¹ at 10 mA (g-FePO_4)⁻¹, and lowering the N/P ratio to 1.56 achieves 300 Wh ($\text{kg-Na} + \text{FePO}_4$)⁻¹. The further high gravimetric energy density of 364 Wh ($\text{kg-Na} + \text{FePO}_4$)⁻¹ is attained to the Na/IL/PO-FP full cell (the N/P ratio of 2.20) at 90 °C. Within the realm of SMB batteries employing phosphate-based active materials [10, 11, 33, 42], this configuration operating at 90 °C showcases the highest gravimetric energy density (**Figure 4-18c**). **Tables 4-7** and **4-8** summarize the capacity, average voltage, and gravimetric energy density in this study and several phosphate SMB full-cell systems shown in **Figure 4-18c**. Charge–discharge curves corresponding to the data in **Table 4-8** are displayed in **Figures 4-23–4-27**. Remarkably, even at 25 °C, the gravimetric energy density of the FePO₄ cell is competitive with the cells with other phosphates like Na₃V₂(PO₄)₃ and Na₃V₂(PO₄)₂F₃, although some NASICON-type materials with high energy densities such as Na₃MnTi(PO₄)₃ [43, 44] which enable a

three-electron reaction by lowering the cutoff voltage are not included as a comparison due to the lack of sufficient data on their performance in SMBs. These findings underscore the capability of the charged-state SMB configuration to achieve both high gravimetric energy density and cycle performance.

4.4 Conclusions

This chapter provided a concept of sustainable heretosite FePO_4 production using O_2 and the FePO_4 potential for a positive electrode for SMBs. The mechanism of chemical oxidation (delithiation) of LiFePO_4 with oxidative agents of O_2 was demonstrated, and the FePO_4/C active material was obtained from LiFePO_4/C through the delithiation method using O_2 in acetic acid solution without any surface morphology degradations. The lithium source was recovered after chemical oxidation in the form of lithium acetate and used as a precursor of LiFePO_4/C repetitive production, validating the closed-loop lithium recycling route. Electrochemical and computational investigations revealed that particle size reduction and temperature increase improved the Na^+ diffusivity in Na_xFePO_4 , resulting in a capacity increase. The charged state of SMB configuration in this chapter (Na/FePO_4) showed a gravimetric energy density comparable to the conventional Na-metal-free SMBs in the discharged state. Notably, the Na/FePO_4 full cell at 25 °C achieved stable cycle performance with the average coulombic efficiency of 99.9% at 100 mA (g- FePO_4)⁻¹ over 700 cycles as well as the energy density of 300 Wh (kg-Na + FePO_4)⁻¹ at 10 mA (g- FePO_4)⁻¹. In addition, the

Na/FePO₄ full cell at 90 °C accomplished the gravimetric energy of 364 Wh (kg-Na + FePO₄)⁻¹ at 10 mA (g-FePO₄)⁻¹, which is one of the highest energy densities among the phosphate system SMBs. The charged-state SMB using FePO₄ exhibited excellent cycle performance and high gravimetric energy, but there is still room to improve its performance by considering the capacity achieved at 25 °C in this study (70% based on the theoretical capacity of FePO₄). Moreover, the preparation process of thin Na metal electrodes is required to be developed for practical applications.

LiFePO ₄ (Space group: <i>Pnma</i>)						
$R_p = 1.19\%$, $R_{wp} = 2.12\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	10.32365(18)	6.00369(10)	4.68888(9)	290.617(9)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Li	$4a$	0	0	0	0.5	1.000
Fe	$4c$	0.2804(1)	0.2500	0.9806(5)	0.5	1.000
P	$4c$	0.1015(3)	0.2500	0.4256(7)	0.5	1.000
O1	$4c$	0.0977(8)	0.2500	0.7395(11)	0.5	1.000
O2	$4c$	0.4450(9)	0.2500	0.2087(10)	0.5	1.000
O3	$8d$	0.1862(13)	0.0424(19)	0.2864(17)	0.5	1.000

The starting parameters were taken from a previous report [17], and the B factor and Occupancy were fixed at 0.5 and 1.0, respectively.

Table 4-2. Crystallographic data of the PO-FP by the Rietveld refinement.

FePO₄ (Space group: *Pnma*)
$$R_p = 14.9\%, R_{wp} = 9.9\%$$

	a (Å)	b (Å)	c (Å)	V (Å ³)		
	9.81209(12)	5.78685(6)	4.78223(6)	271.540(5)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Fe	4 <i>c</i>	0.27329(10)	0.2500	0.9498(2)	0.5	1.000
P	4 <i>c</i>	0.09449(18)	0.2500	0.4010(4)	0.5	1.000
O1	4 <i>c</i>	0.1222(3)	0.2500	0.7028(8)	0.5	1.000
O2	4 <i>c</i>	0.4410(4)	0.2500	0.1619(6)	0.5	1.000
O3	8 <i>d</i>	0.1705(3)	0.0413(4)	0.2552(4)	0.5	1.000

The starting parameters were taken from a previous report [17], and the B factor and Occupancy were fixed at 0.5 and 1.0, respectively.

Table 4-3. Organic elemental analysis of the recovered lithium acetate.

Element	Composition (wt%)
H	5.0
C	33.9

LiFePO ₄ (Space group: <i>Pnma</i>)						
$R_p = 12.1\%$, $R_{wp} = 8.3\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	10.3146(3)	6.00458(14)	4.69769(13)	290.952(13)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Li	$4a$	0	0	0	0.5	1.000
Fe	$4c$	0.28317(11)	0.2500	0.9736(4)	0.5	1.000
P	$4c$	0.0977(3)	0.2500	0.4199(6)	0.5	1.000
O1	$4c$	0.1025(6)	0.2500	0.7297(10)	0.5	1.000
O2	$4c$	0.4599(7)	0.2500	0.2089(9)	0.5	1.000
O3	$8d$	0.1595(4)	0.0472(7)	0.2750(6)	0.5	1.000

The starting parameters were taken from a previous report [17], and the B factor and Occupancy were fixed at 0.5 and 1.0, respectively.

FePO ₄ (Space group: <i>Pnma</i>)						
$R_p = 16.3\%$, $R_{wp} = 10.6\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	9.8196(3)	5.79774(17)	4.77120(17)	271.632(16)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Fe	4 <i>c</i>	0.27397(18)	0.2500	0.9511(4)	0.5	1.000
P	4 <i>c</i>	0.0940(3)	0.2500	0.3908(7)	0.5	1.000
O1	4 <i>c</i>	0.1309(6)	0.2500	0.6895(14)	0.5	1.000
O2	4 <i>c</i>	0.4501(8)	0.2500	0.1436(11)	0.5	1.000
O3	8 <i>d</i>	0.1734(5)	0.0549(7)	0.2453(7)	0.5	1.000

The starting parameters were taken from a previous report[17], and the B factor and Occupancy were fixed at 0.5 and 1.0, respectively.

Table 4-6. Comparison of the electrochemical properties of FePO₄ or NaFePO₄ prepared using various delithiation methods.

Delithiation method	Sodiation method	Capacity	Electrolyte	Current density	Cutoff voltage	Temp. (°C)	Ref.
Electrochemical	Electrochemical	125 mAh (g-NaFePO ₄) ⁻¹	1 mol dm ⁻³ NaClO ₄ -PC/FEC (98:2 v/v)	7.5 mA g ⁻¹	2.2 V–4.3 V	25	[13]
Chemical (NO ₂ BF ₄)	Electrochemical	120 mAh (g-NaFePO ₄) ⁻¹	1 mol dm ⁻³ NaClO ₄ -EC/DEC (1:1 v/v)	7.7 mA g ⁻¹	2 V–3.8 V	25	[45]
Chemical (Na ₂ S ₂ O ₈)	Chemical (NaI)	132 mAh (g-NaFePO ₄) ⁻¹	1 mol dm ⁻³ Na[PF ₆]-PC	7.7 mA g ⁻¹	1.5 V–4 V	25	[27]
Chemical (Cl ₂)	Electrochemical	127 mAh (g-FePO ₄) ⁻¹ (110 mAh (g-NaFePO ₄) ⁻¹)	1 mol dm ⁻³ Na[PF ₆]-EC/DMC (1:1 v/v) + 3wt% FEC	7.7 mA (g-FePO ₄) ⁻¹	2 V–3.8 V	25	Chapter 3
Chemical (O ₂)	Electrochemical	129 mAh (g-FePO ₄) ⁻¹ (112 mAh (g-NaFePO ₄) ⁻¹)	1 mol dm ⁻³ Na[PF ₆]-EC/DMC (1:1 v/v) + 3wt% FEC	10 mA (g-FePO ₄) ⁻¹	2 V–3.8 V	25	This chapter

PC: Propylene carbonate, DEC: Diethyl carbonate.

Table 4-7. Comparison of the capacity, average voltage, and energy density calculated based on the total mass of positive and negative active materials in this study and several phosphate full-cell systems [10, 11, 33, 42]. The N/P ratio in the references was revised according to the definition used in this study.

Full-cell system	N/P ratio	Capacity (mAh g ⁻¹)	Average voltage (V)	Energy density (Wh kg ⁻¹)	Temperature (°C)	Rate or current density	Ref.
Na/FePO ₄	2.20	128	2.86	364	90	10 mA (g-FePO ₄) ⁻¹	This work
Na/FePO ₄	1.56	108	2.78	300	25	10 mA (g-FePO ₄) ⁻¹	This work
O-CCF/Na ₃ V ₂ (PO ₄) ₃	1	74.3	3.4	252	Room temp.	1 mA cm ⁻²	[42]
Na/Na ₃ V ₂ (PO ₄) ₃	2.97	83.8	3.34	268	25	0.2C	[33]
Na/Na ₃ V ₂ (PO ₄) ₃	2.81	80.6	3.34	280	90	0.2C	[33]
Na/Na ₃ V ₂ (PO ₄) ₂ F ₃	5	83.4	3.54	295	25	1C	[11]
Graphite-Na/Na ₄ Fe ₃ (PO ₄) ₂ (P ₂ O ₇)	-	81.7	3.0	245	25	0.75 mA cm ⁻²	[10]

Table 4-8. Comparison of the capacity, average voltage, and energy density calculated based on the total mass of positive and negative active materials in this study.

FePO ₄ source	FePO ₄ mass loading (mg cm ⁻²)	N/P ratio	Capacity (mAh g ⁻¹)	Average voltage (V)	Energy density (Wh kg ⁻¹)	Temperature (°C)	Rate (mA (g-FePO ₄) ⁻¹)
PO-FP	9.9	2.20	128	2.85	364	90	10
RO-FP	8.4	1.56	108	2.78	300	25	10
RO-FP	8.4	1.56	94	2.65	248	25	100
RO-FP	8.1	2.44	97	2.79	270	25	10
RO-FP	8.1	2.44	80	2.65	213	25	100

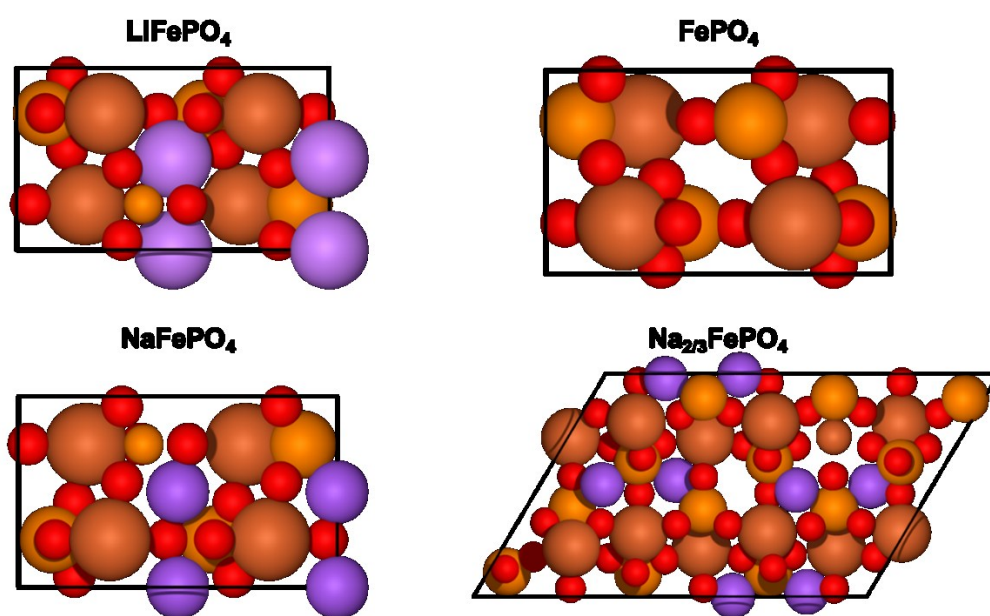


Figure 4-1. Unit cell structures of NEB calculations.

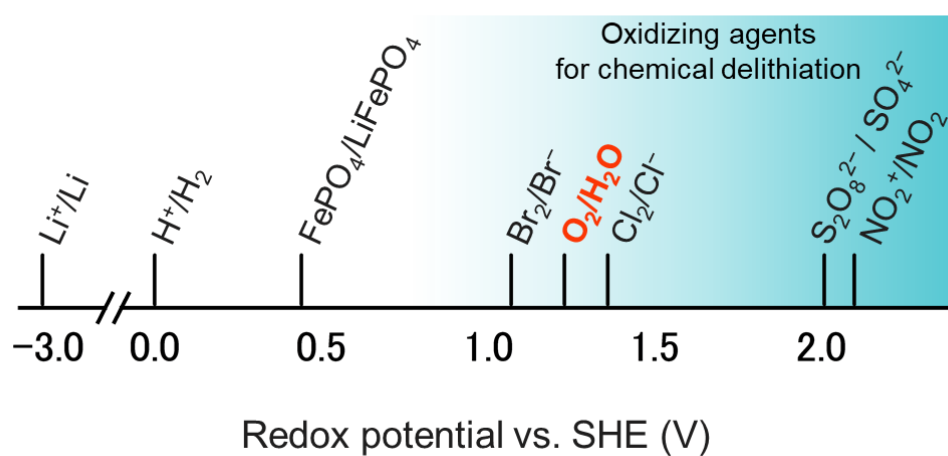


Figure 4-2. Redox potentials of oxidation agents for chemical delithiation of LiFePO_4 .

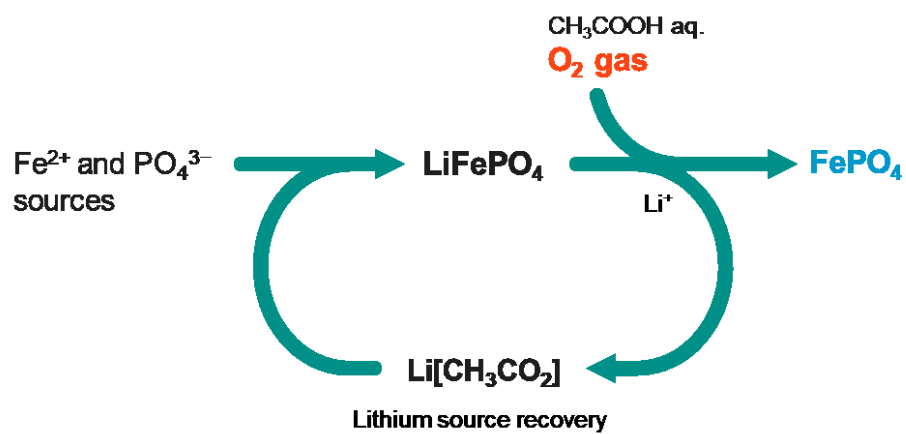


Figure 4-3. A schematic illustration of the sustainable FePO_4 preparation route using O_2 .

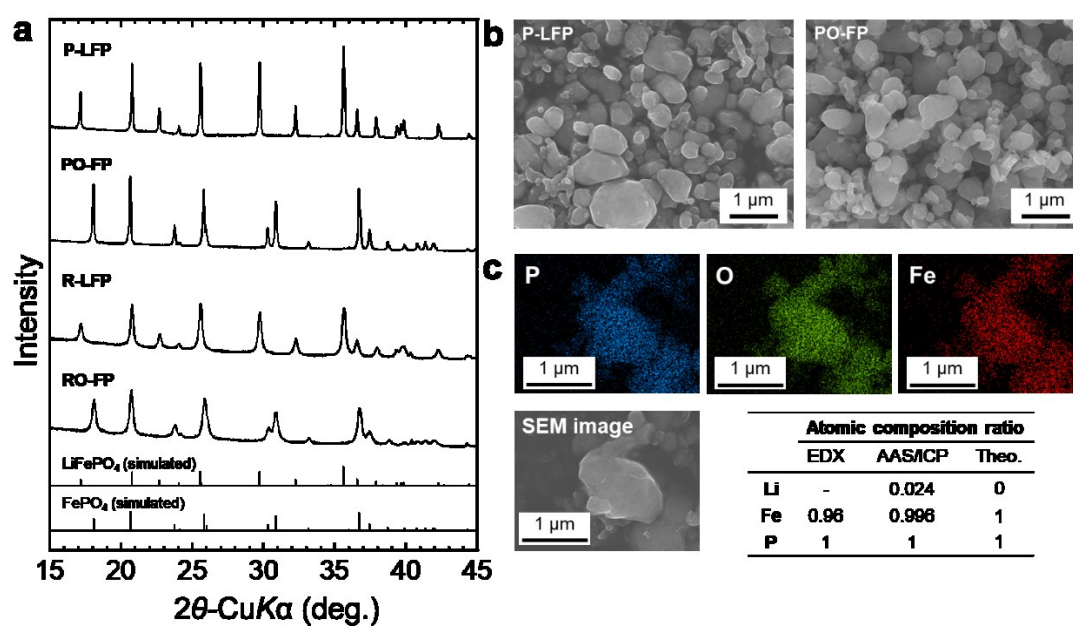


Figure 4-4. Characterizations of the LiFePO_4/C and FePO_4/C . (a) XRD patterns of the P-LFP and R-LFP along with delithiated samples (PO-FP and RO-FP) achieved through O_2 gas delithiation. (b) SEM images of the P-LFP and PO-FP. (c) EDX mapping images of the PO-FP and the comparison of atomic composition ratio between EDX and AAS/ICP-AES.

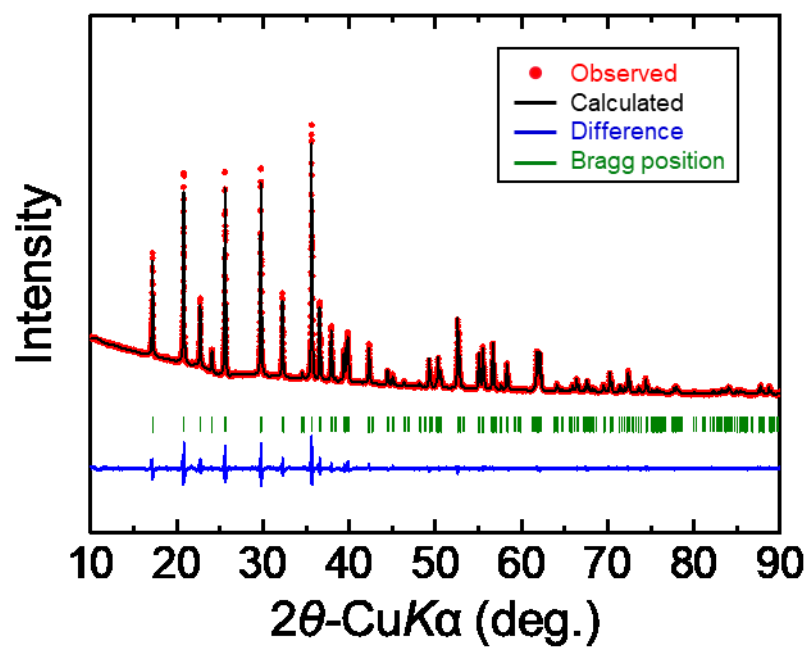


Figure 4-5. Rietveld refinement result of the P-LFP.

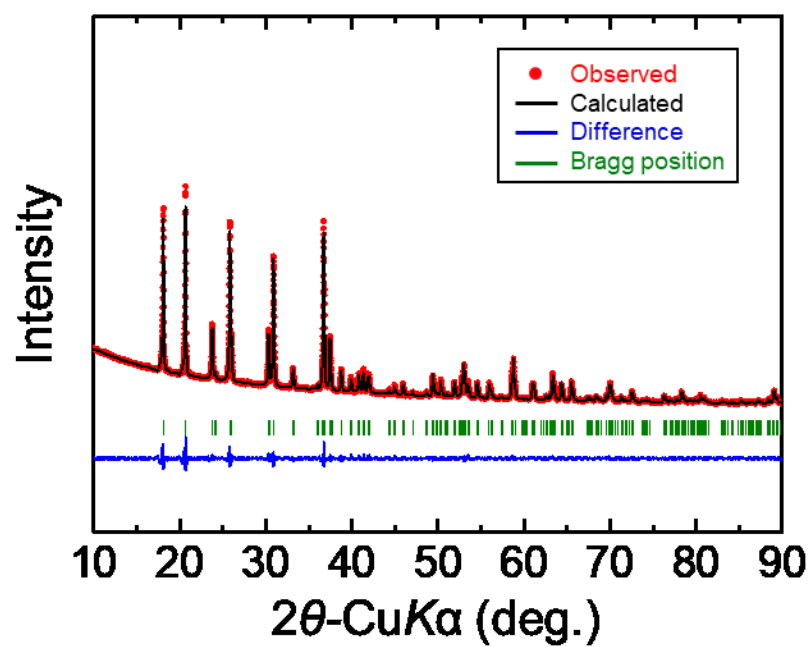


Figure 4-6. Rietveld refinement result of the PO-FP.

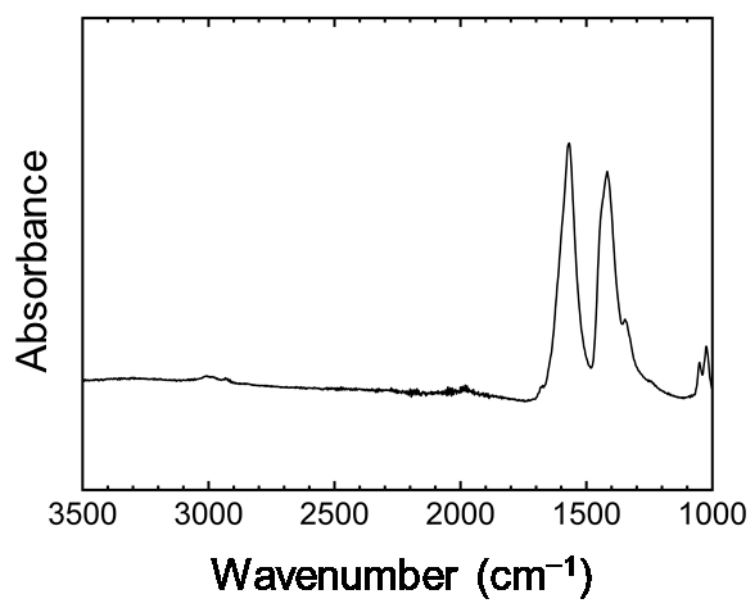


Figure 4-7. FT-IR spectra of the recovered lithium acetate.

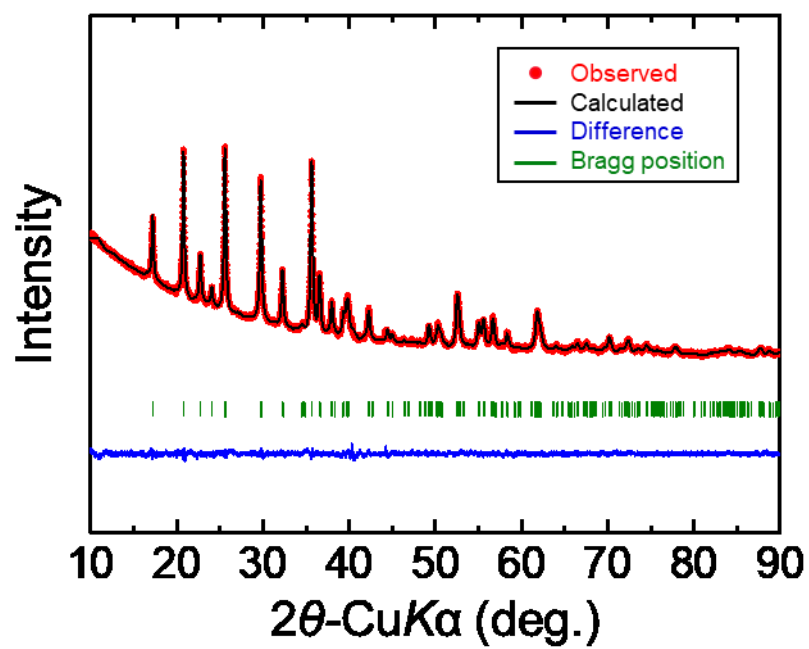


Figure 4-8. Rietveld refinement result of the R-LFP.

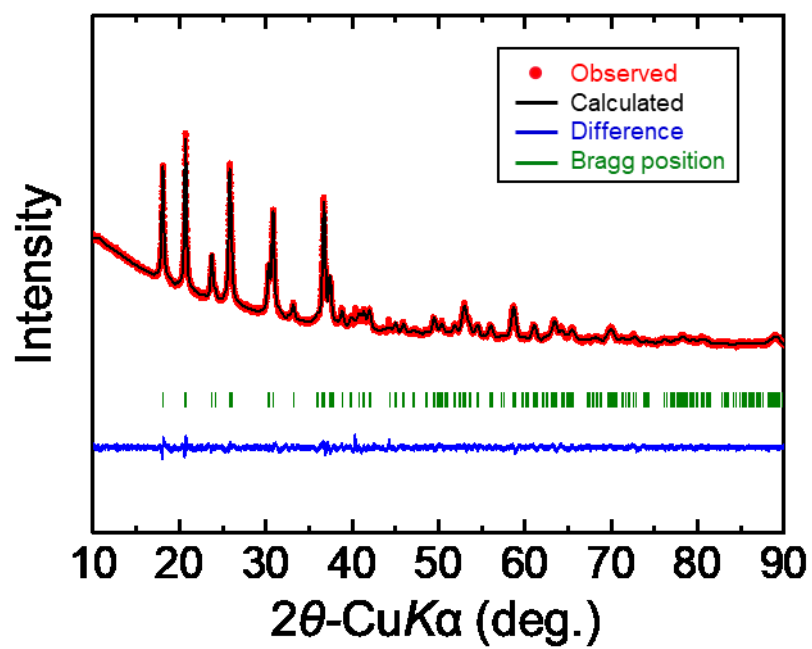


Figure 4-9. Rietveld refinement result of the RO-FP.

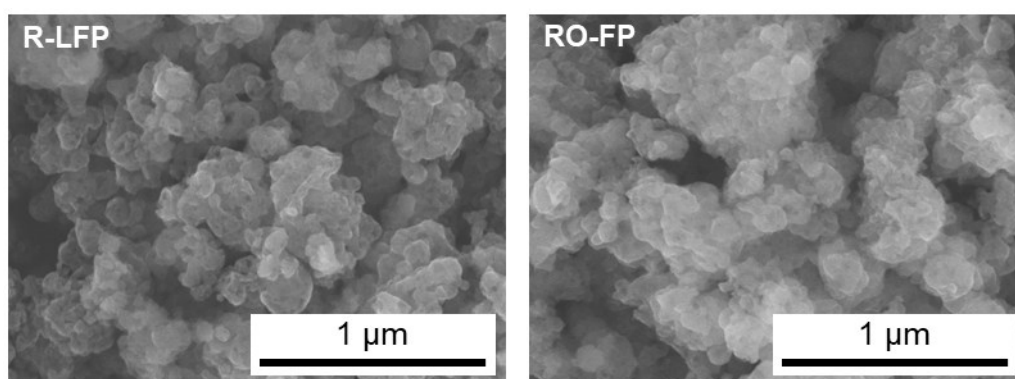


Figure 4-10. SEM images of R-LFP and RO-FP.

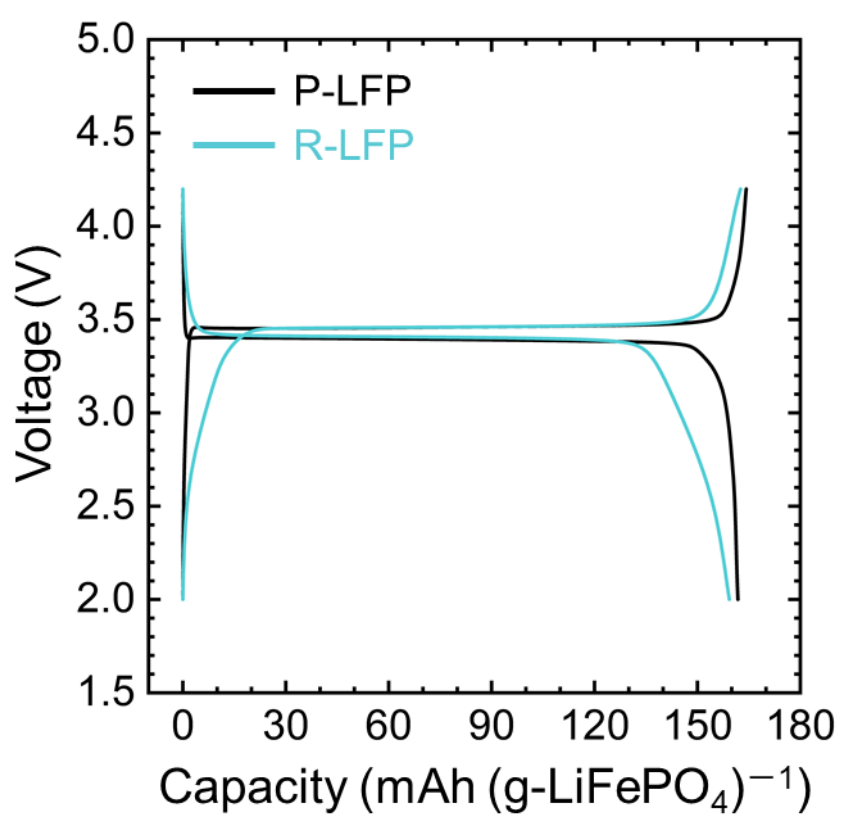


Figure 4-11. Charge–discharge curves of the Li/P-LFP and Li/R-LFP half cells at 25 °C. C-rate: 0.05C (1C = 170 mA g⁻¹).

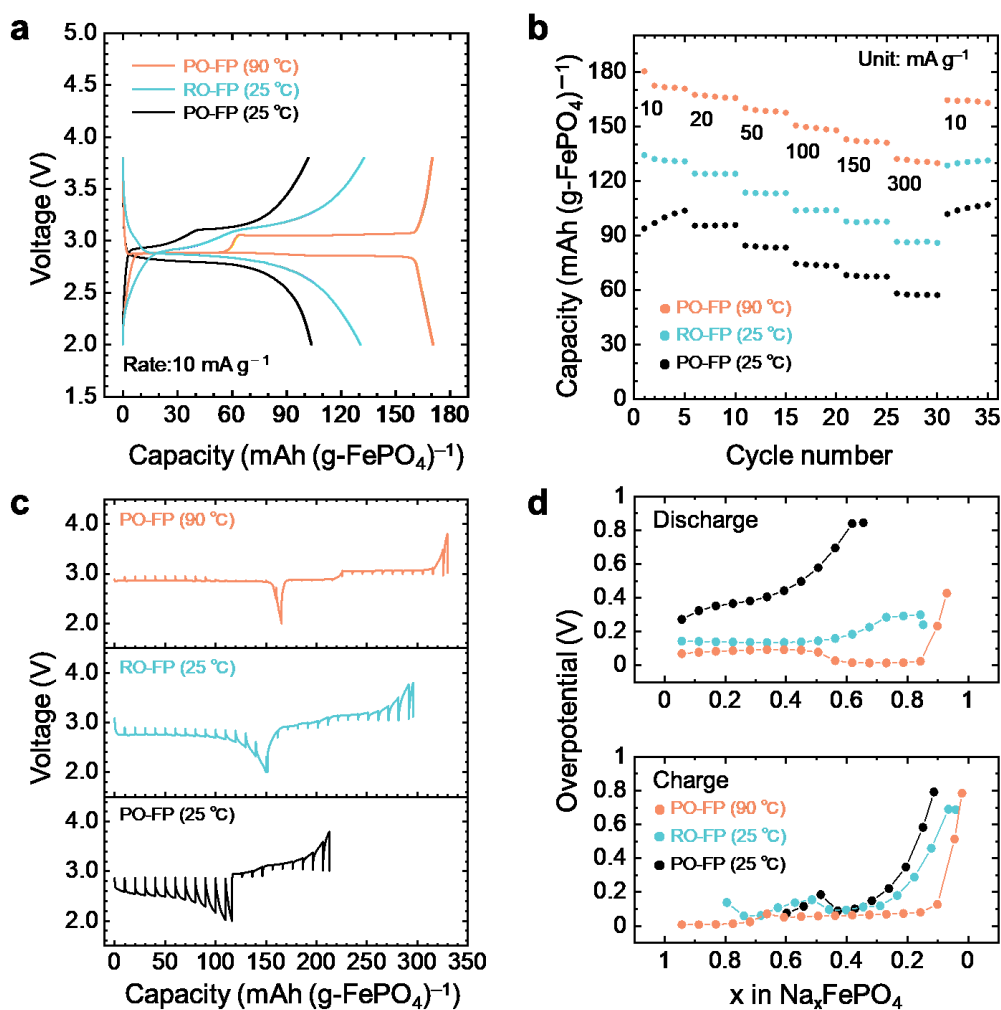


Figure 4-12. Electrochemical performances of the FePO₄/C in Na/FePO₄ half cells prepared from the commercial LiFePO₄ and resynthesized LiFePO₄ from lithium acetate. (a) Charge-discharge curves at 10 mA g⁻¹ based on the weight of FePO₄. (b) Rate capabilities. (c) GITT curves at 10 mA g⁻¹ with a relaxation time of 5 h. (d) Overpotential of GITT during charge and discharge.

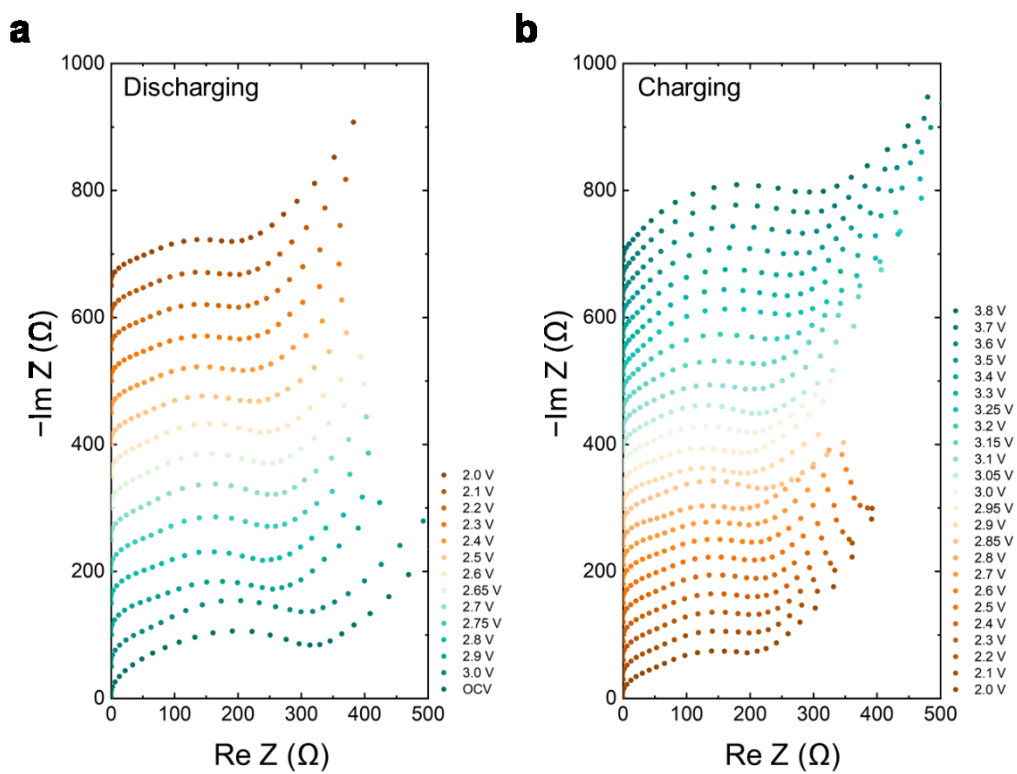


Figure 4-13. In-situ EIS results of the RO-FP electrode at 25 °C (a) obtained after constant voltage discharging from open circuit voltage (OCV) to 2.0 V, and (b) obtained after constant voltage charging from 2.0 V to 3.8 V.

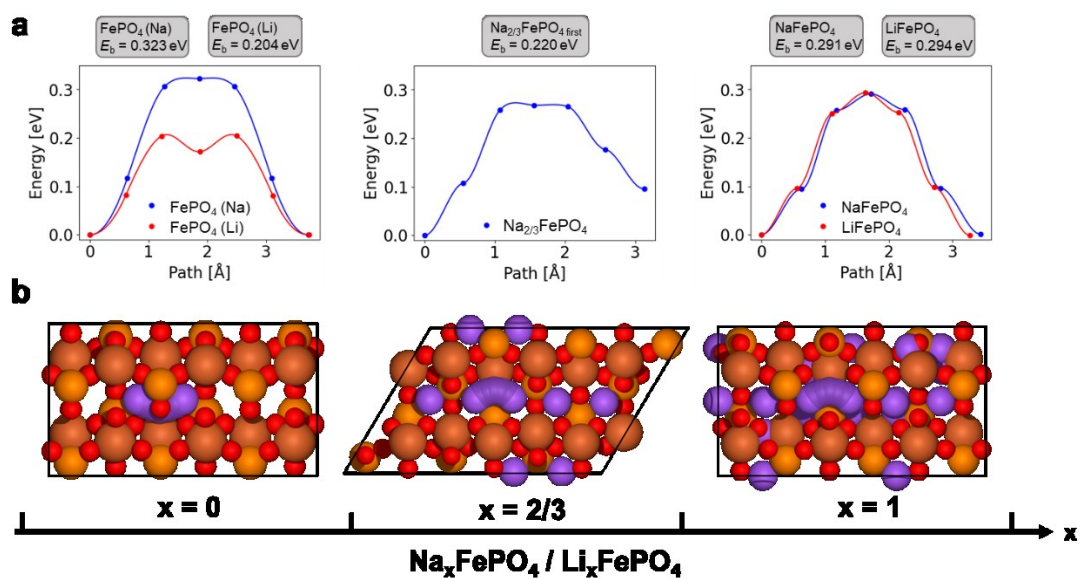


Figure 4-14. NEB calculations for Na^+ and Li^+ diffusion in FePO_4 , LiFePO_4 and NaFePO_4 . (a) Computed diffusion energy barriers at different concentrations of Na and Li. The kinetic average barrier (E_b) is given for each of the 5 systems. (b) Visualization of Na^+ diffusion paths. The diffusion paths of the Li^+ ions are not shown but are similar to those of the Na^+ ions.

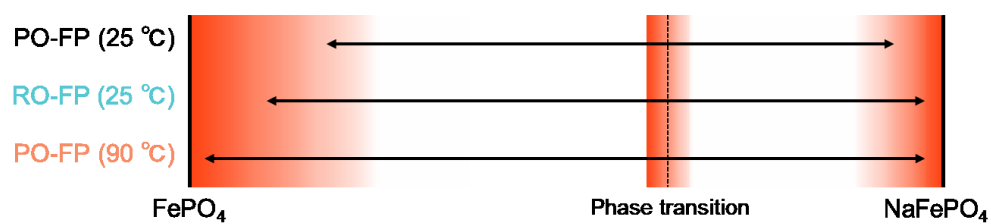


Figure 4-15. An illustration of kinetic barriers for PO-FP (25 °C), RO-FP (25 °C), and PO-FP (90 °C) during charge–discharge. Darker red shading indicates higher kinetic barriers. Black arrows show the range within which the reversible sodium insertion/extraction reaction can occur.

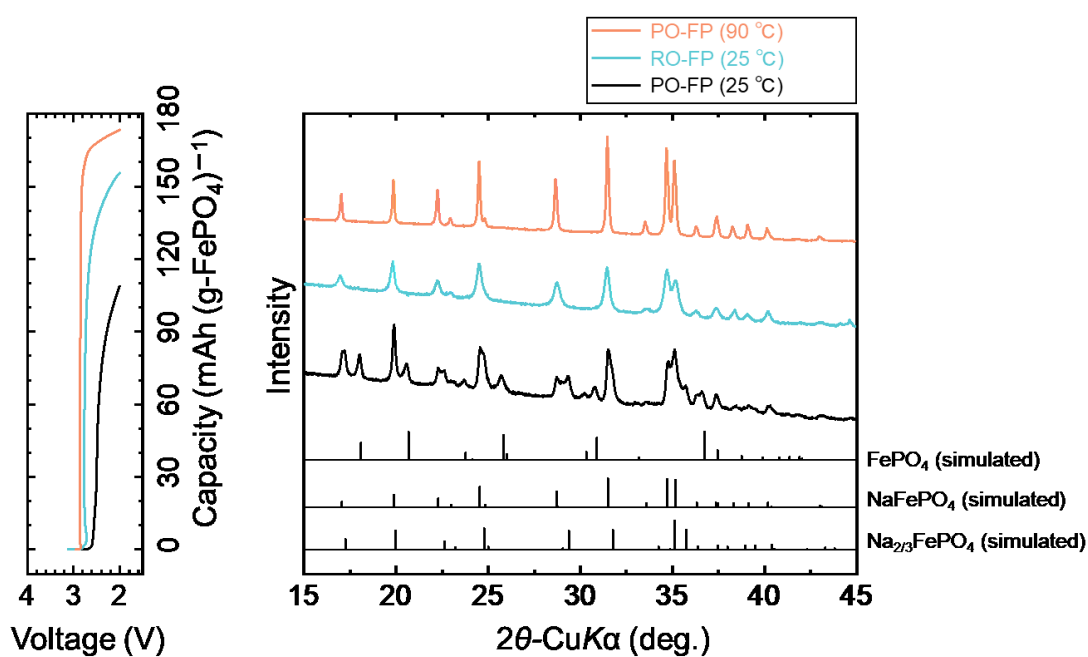


Figure 4-16. Ex-situ XRD patterns of the FePO₄ electrodes after the first discharge. Rate: 10 mA (g-FePO₄)⁻¹. The simulated patterns of FePO₄, NaFePO₄, and Na_{2/3}FePO₄ are calculated using VESTA software based on crystallographic data in previous reports [16, 17].

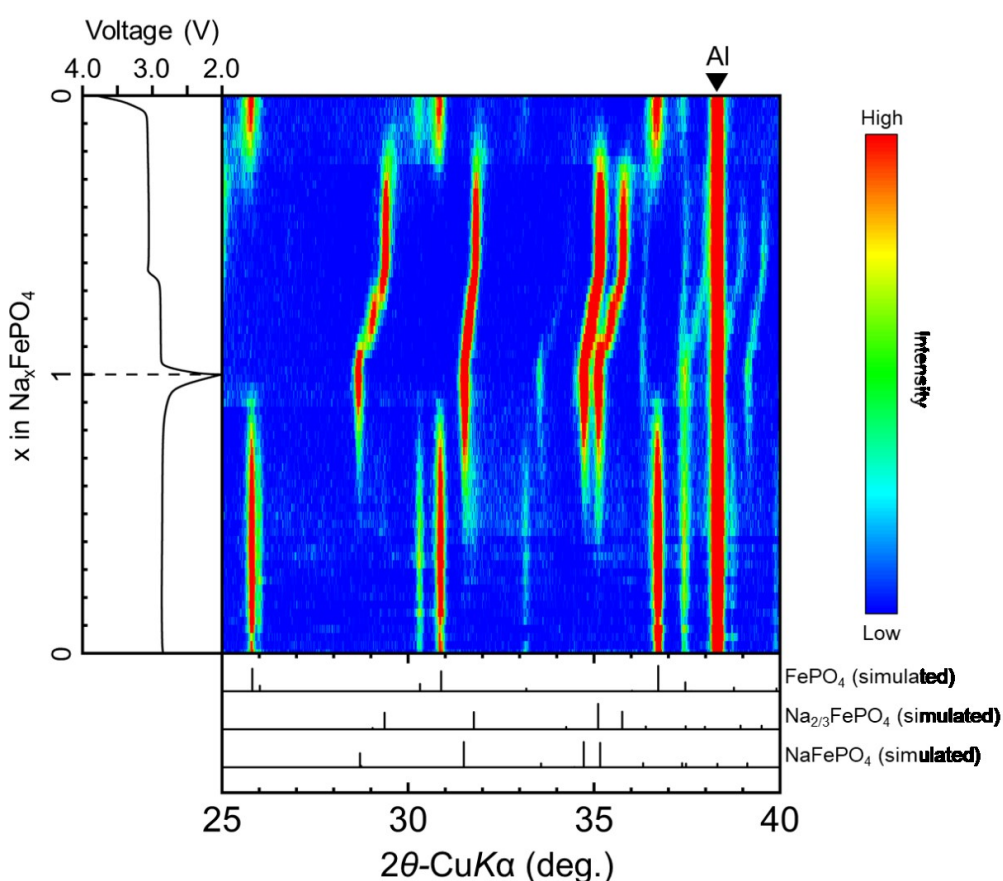


Figure 4-17. In-situ XRD of the PO-FP electrode during charge–discharge at 90 °C. Rate: 10 mA (g-FePO₄)⁻¹. The simulated patterns of FePO₄, NaFePO₄, and Na_{2/3}FePO₄ are calculated using VESTA software based on crystallographic data in previous reports [16, 17]. The peak at 38.47° is assigned to Al current collector [46].

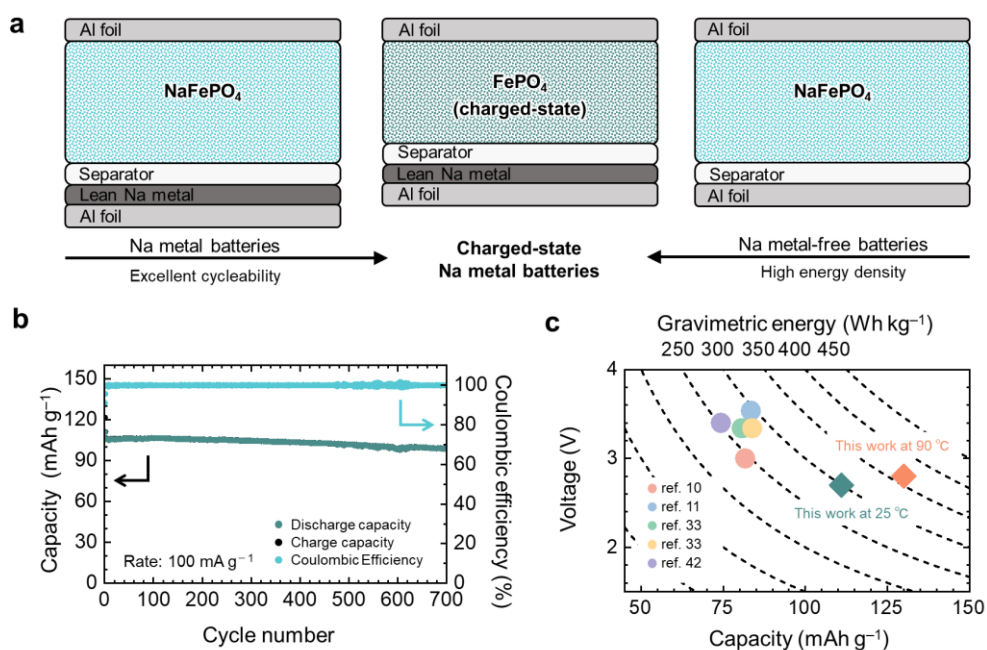


Figure 4-18. Stable cycling ability and high energy density of the Na/FePO₄ full cell. (a) Schematic illustration of the typical Na metal batteries (restricted the amount of Na), Na metal-free batteries (so-called anode-free cell), and charged-state Na metal batteries (positive electrode without Na sources) configurations. (b) Cycle performance of the charged-state Na/RO-FP full cell at 25 °C (N/P = 2.44). (c) Comparative gravimetric energy density of Na metal batteries using phosphate positive electrodes [10, 11, 33, 42]. The gravimetric energy is calculated based on the total mass of positive and negative active materials.

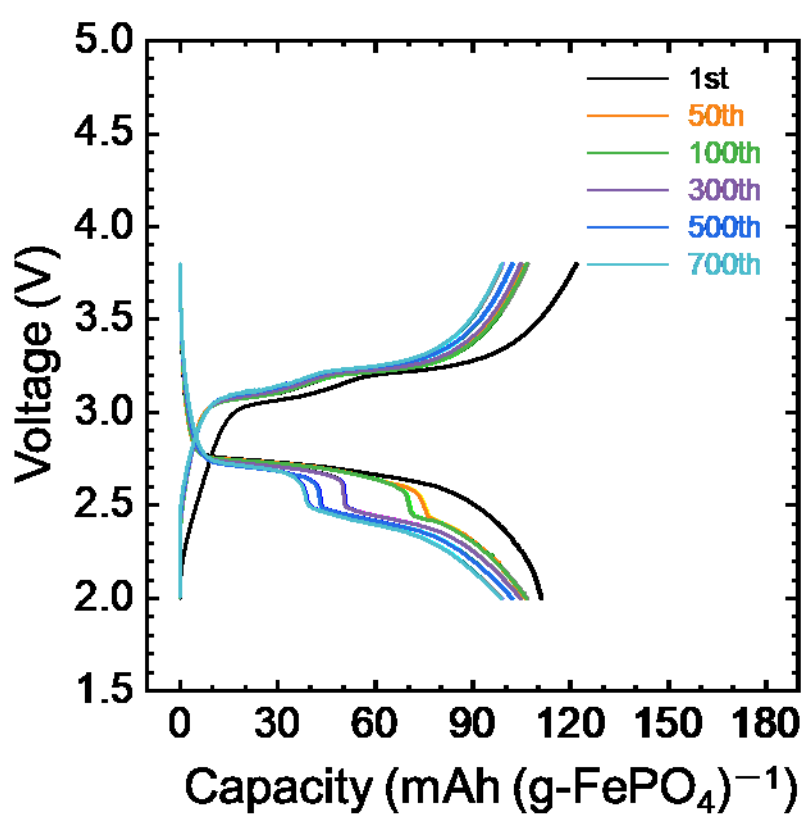


Figure 4-19. Charge–discharge curves during cycle performance test of the Na/RO-FP full cell shown in **Figure 4-18b** at 25 °C (N/P = 2.44). Rate: 100 mA (g-FePO₄)⁻¹.

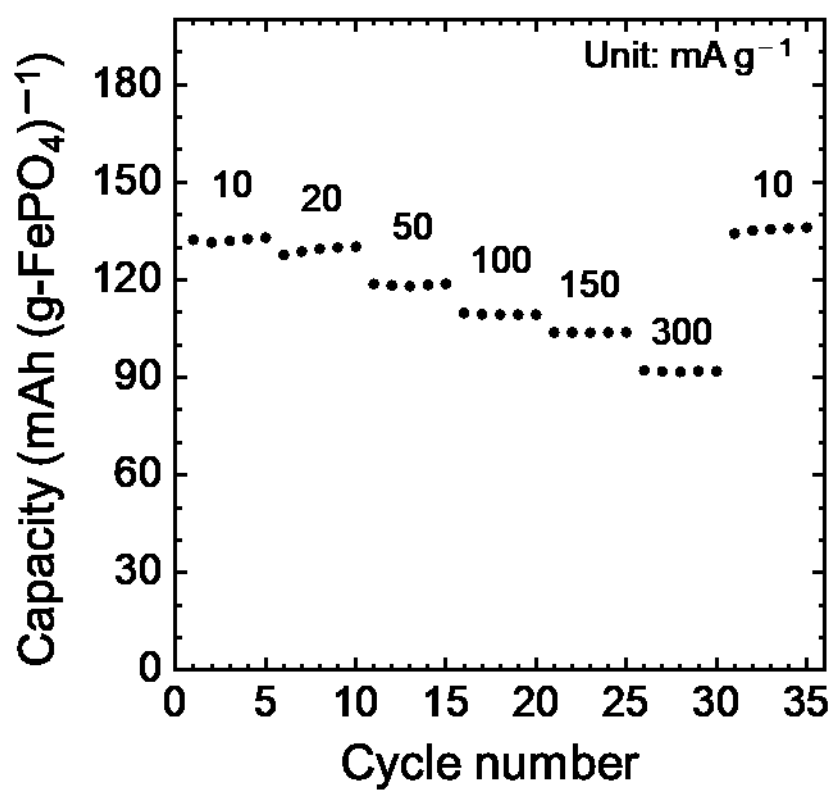


Figure 4-20. Rate capability of the Na/RO-FP cell with 1 mol dm⁻³ Na[PF₆]-DME at 25 °C.

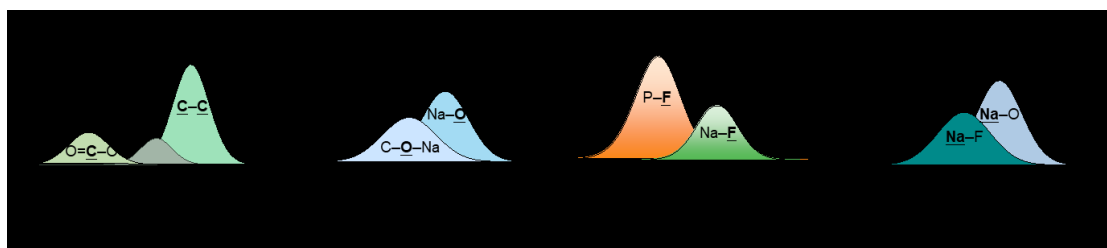


Figure 4-21. XPS spectra of (a) C 1s, (b) O 1s, (c) F 1s, and (d) Na 1s regions for characterization of the SEI layer on the metallic sodium in Na/FePO₄ cell after 100 cycles at 100 mA (g-FePO₄)⁻¹. Electrolyte: 1 mol dm⁻³ Na[PF₆]-DME.

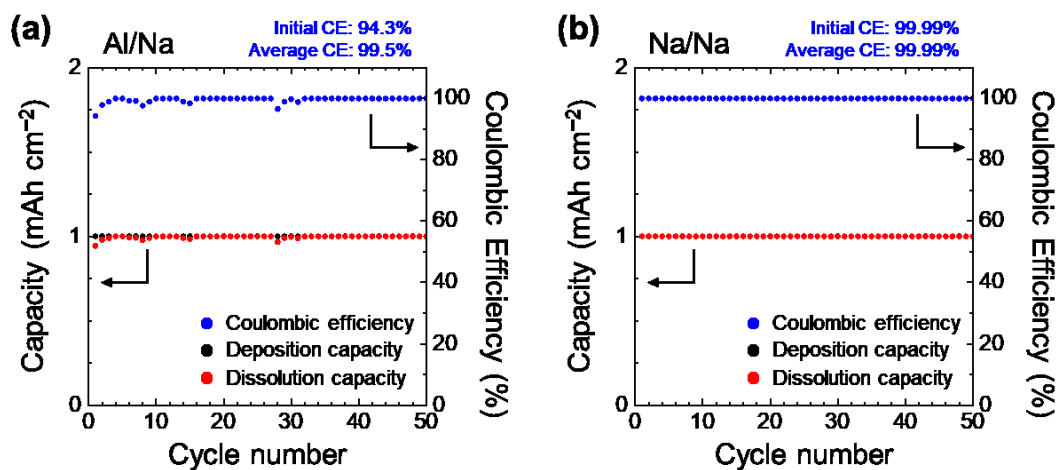


Figure 4-22. Galvanostatic sodium deposition/dissolution test results of (a) Al/Na and (b) Na/Na cells at 0.5 mA cm^{-2} (1 mAh cm^{-2}). Cutoff voltage: -1 V – 1 V .

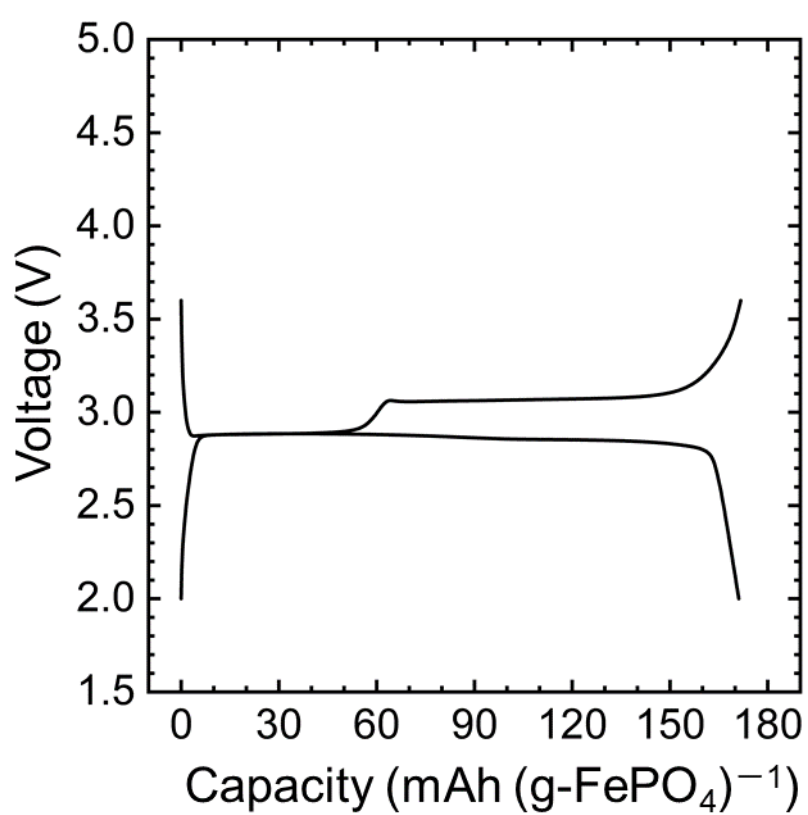


Figure 4-23. Charge–discharge curves of the Na/PO-FP full cell at 90 °C (N/P = 2.20). Rate: 10 mA (g-FePO₄)⁻¹.

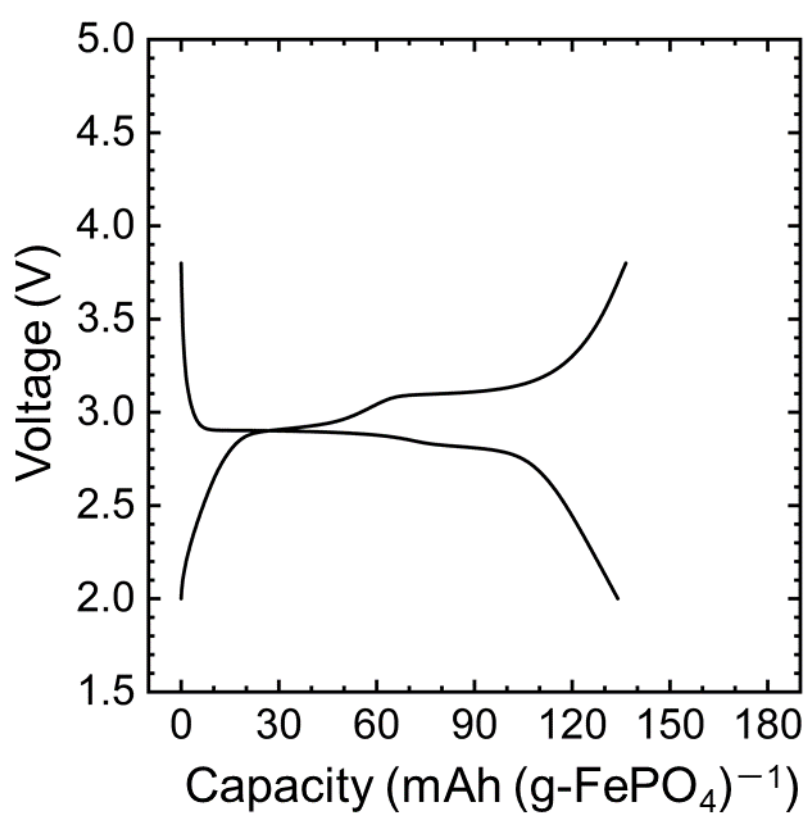


Figure 4-24. Charge–discharge curves of the Na/RO-FP full cell at 25 °C (N/P = 1.56). Rate: 10 mA (g-FePO₄)⁻¹.

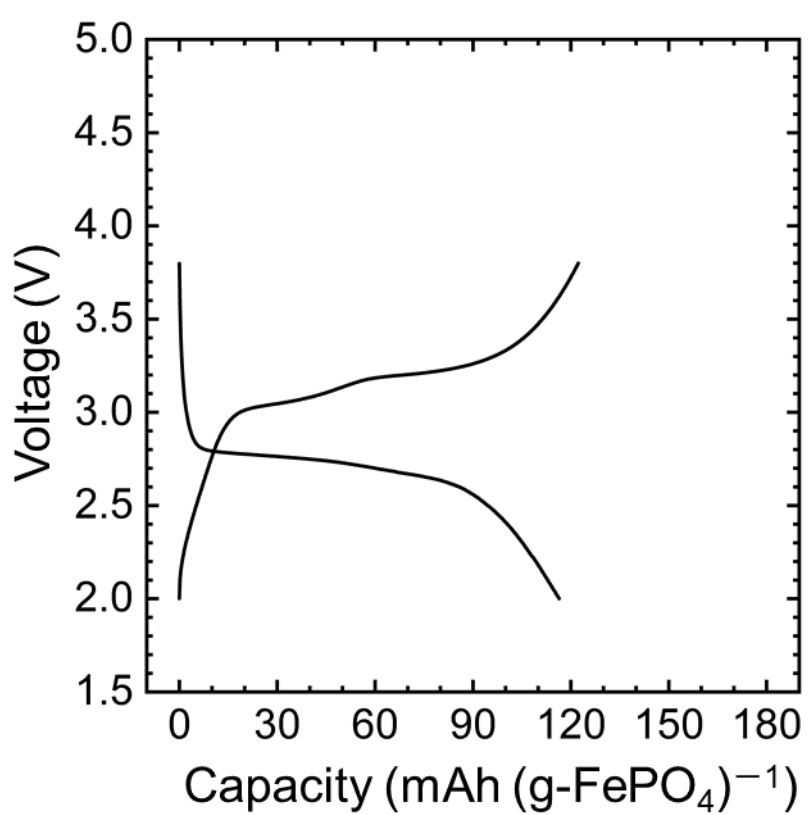


Figure 4-25. Charge–discharge curves of the Na/RO-FP full cell at 25 °C (N/P = 1.56). Rate: 100 mA (g-FePO₄)⁻¹.

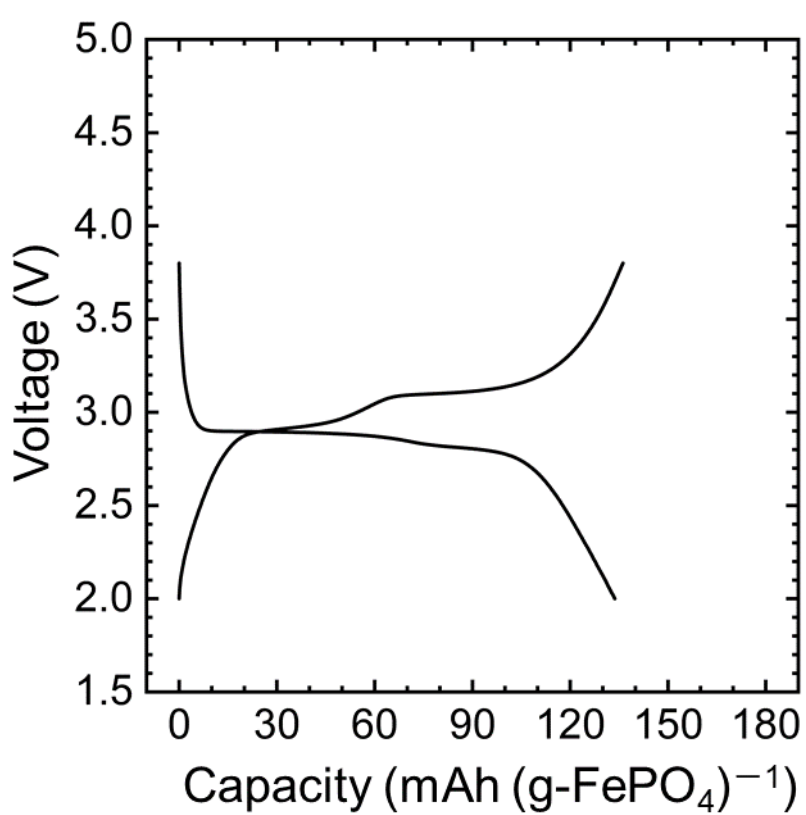


Figure 4-26. Charge–discharge curves of the Na/RO-FP full cell at 25 °C (N/P = 2.44). Rate: 10 mA (g-FePO₄)⁻¹.

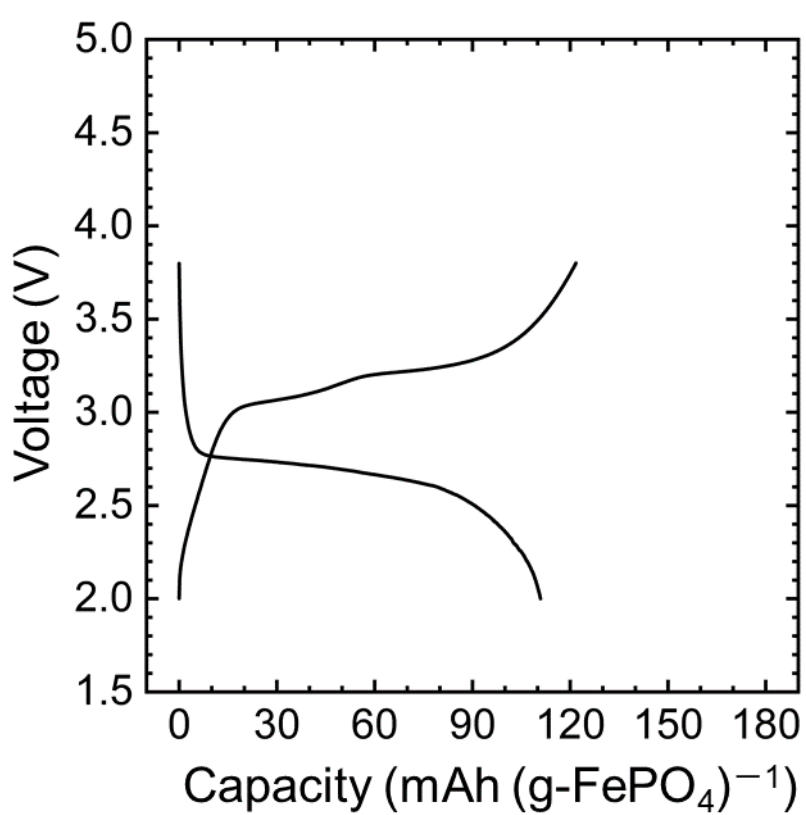


Figure 4-27. Charge–discharge curves of the Na/RO-FP full cell at 25 °C (N/P = 2.44). Rate: 100 mA (g-FePO₄)⁻¹.

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Chapter 5

Sustainable Reuse of FePO₄ for Charged-State Lithium Metal Battery with High Energy Density and Stable Cycle Performance

5.1 Introduction

Lithium metal batteries (LMBs) have been one of the promising candidates to achieve high-energy-density rechargeable batteries because of the lowest redox potential (-3.04 V vs. SHE) and the high theoretical capacity (3860 mAh g^{-1}) of lithium metal [1, 2]. The ideal LMB configuration is lithium metal-free batteries (LMFBs, so-called anode-free batteries), where all the lithium is located in the positive material and lithium metal deposits on the negative current collector during charging [2, 3]. As a result, LMFBs can theoretically achieve the highest energy density because they eliminate the need for excess material on the negative electrode side, thereby reducing the overall weight and volume of the cells [2, 4, 5]. Additionally, LMFBs can reduce manufacturing costs related to the negative electrode and alleviate safety concerns associated with excess lithium metal in typical LMBs [3, 4]. However, achieving stable cycling performance of LMFBs remains a challenge due to the loss of Li inventory during the initial charging and the limited reversibility of Li deposition/dissolution during cycling [2, 5]. To tackle these issues, many research groups have made modifications to current collectors and electrolytes [6-10]. Besides such modifications, lean lithium metal batteries (LLMBs)

have been proposed to simultaneously enhance both the cycling performance and energy density of LMBs [11-14]. The results claim that a small amount of lithium metal is employed on the negative electrode, maintaining the energy density comparable to that of LMFBs while improving the cycling performance beyond that of LMFBs.

LiFePO₄ is gaining renewed attention due to its resource advantages, compared to layered oxide materials containing cobalt and nickel, long-term cycle stability, and high thermal stability. Recently, its application has expanded to electric vehicles (EVs) [15]. Along with the increasing use of LiFePO₄ batteries, research into recycling LiFePO₄ is also advancing [16]. In the hydrometallurgical method, lithium is often extracted from LiFePO₄ by oxidation in an acidic solution and separated from the resulting FePO₄. Lithium is a highly valuable element for recycling, whereas iron phosphate has limited applications for recycling. Therefore, the separated FePO₄ is often used as a raw material for reproducing LiFePO₄ [17-19]. However, due to the rigid structure and outstanding cycle stability of olivine-group materials [20-23], the reuse of FePO₄ is a plausible and sustainable method.

This chapter proposes charged-state lithium metal batteries (CSLMBs) which are composed of a charged-state positive electrode material and a lithium metal negative electrode, achieving both the high energy density comparable to LMFBs and the relatively high cycle stability characteristic of LLMBs. Chemically delithiated FePO₄ is used as a charged-state positive electrode, and the cycling performance and energy density of CSLMBs (Li/FePO₄ configuration) are evaluated in comparison to Li-

free/LiFePO₄ cell configuration. This process is intended to recover lithium from used LiFePO₄ electrodes while simultaneously reusing the resulting FePO₄ electrodes for CSLMBs.

5.2 Experimental

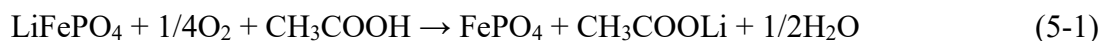
FePO₄/C power (3.73 g, 24.4 mmol) was produced from commercial LiFePO₄/C (4.00 g, 25.1 mmol) using O₂ gas in acetic acid solution as described in Chapter 4. XRD and XPS measurements were conducted for the characterizations of LiFePO₄/C and FePO₄/C.

All the half cells were assembled using 2032-type coin cells under a dry Ar atmosphere. Li[FSA] and DME were mixed to prepare 2 mol dm⁻³ Li[FSA]-DME electrolyte. The positive electrodes were prepared by mixing the active materials (LiFePO₄/C or FePO₄/C) with a conductive carbon and the SWCNT dispersion in NMP with PVDF in the weight ratio of LiFePO₄/C (or FePO₄/C) : carbon : SWCNT : PVDF = 91:3:2:4. The mixture was pasted onto an Al foil and dried to completely remove NMP. The mass loading of the active material was 11–13 mg cm⁻². Lithium metal was used as negative electrodes in the CSLMB configuration, whereas no lithium metal was crimped on a Cu current collector in the LMFB configuration. Electrochemically deposited lithium metal was used to make the CSLMB with the N/P ratio of one. Lithium metal was also served to prepare Cu/Li and Li/Li half cells for the lithium deposition/dissolution tests. A polypropylene (PP) separator was used as a separator.

The galvanostatic lithium deposition/dissolution tests of the Cu/Li and Li/Li half cells and charge–discharge tests of the CSLMB and LMFB full cells were evaluated at 25 °C. In the lithium deposition/dissolution tests, lithium deposition and dissolution were alternated every 2 hours at 1 mA cm⁻² in the cutoff range of –1.0 V and 1.0 V. In the CSLMB and LMFB full-cell tests, the capacity was calculated based on the total weight of the FePO₄ and Li on the positive and negative electrodes. The cutoff voltage was set in the range of 2.0 V and 4.0 V. The C-rate was set to 1C = 170 mAh (g-LiFePO₄)⁻¹ for Cu/LiFePO₄ cells and 1C = 178 mA (g-FePO₄)⁻¹ for Li/FePO₄ cells to ensure equivalent conditions based on each material's theoretical capacity.

5.3 Results and discussion

A schematic illustration of the preparation route of FePO₄ is displayed in **Figure 5-1**. In this work, FePO₄/C is obtained from LiFePO₄/C, which is supposed to be recovered from spent batteries, through the chemical delithiation method using O₂ gas in acetic acid aqueous solution by the following reaction (5-1), as discussed in Chapter 4.



Here, O₂ acts as an oxidizing agent to oxidize (delithiate) LiFePO₄, and acetic acid is added to keep the solution weakly acidic condition and to extract Li source as lithium acetate (CH₃COOLi). While the obtained FePO₄/C is used as a positive electrode for

CSLMBs, the extracted lithium source during the delithiation process is supplied again for the synthesis of LiFePO_4 , enabling closed-loop lithium recycling and a more sustainable FePO_4 preparation

Successful delithiation of LiFePO_4 using O_2 and acetic acid was verified by XRD and XPS. XRD patterns of the pristine LiFePO_4/C and obtained FePO_4/C powder shown in **Figure 5-2** match that of triphylite LiFePO_4 (*Pnma*) and heterosite FePO_4 (*Pnma*), respectively [24]. XPS spectra of the pristine LiFePO_4/C and obtained FePO_4/C in **Figure 5-3** suggests that the oxidation state of FePO_4/C shifts from Fe(II) to Fe (III), confirming the oxidation of LiFePO_4 [25]. The delithiation process was successfully achieved not only for LiFePO_4 powder but also for LiFePO_4 electrode (**Figure 5-4**), demonstrating the potential applicability of this method to spent LiFePO_4 electrodes.

Figure 5-5a shows the schematic comparison between LMFB using LiFePO_4 and CSLMB using FePO_4 . In the initial configuration of LMFB, LiFePO_4 in a discharged state is employed for the positive electrode without lithium metal (only a Cu current collector is placed). On the other hand, CSLMB consists of a charged-state FePO_4 on the positive electrode with lean lithium metal on the negative electrode.

One advantage of the CSLMBs is their excellent cycle performance, which arises from the dependency of deposited lithium states on the current collectors. In other words, the deposition of lithium metal on copper and lithium metal exhibit differences in nucleation, solid electrolyte interphase (SEI) formation, and efficiency [26]. The Li deposition/dissolution properties on the Cu and Li electrodes will be discussed later.

Another advantage of CSLMBs is the ability to load more metal, thus thicker metal, on the negative electrode compared to LMBs, because extremely thin lithium metal increases production complexities and material processing requirements. This is particularly advantageous in the cases with low N/P ratios (the ratio of negative to positive electrode capacities as explained below). For instance, assuming a positive electrode capacity of 2 mAh cm^{-2} , assembling a discharged-state LMB with N/P ratio of two would require $10 \text{ }\mu\text{m}$ of lithium metal in thickness. In contrast, creating an equivalent CSLMB to the LMB would require $20 \text{ }\mu\text{m}$ of lithium (**Figure 5-6**), which has significantly different burdens for the commercial production of lithium metal foil. Considering that $20 \text{ }\mu\text{m}$ lithium metal is recently commercially available [13], CSLMBs have the potential to facilitate the fabrication of cells with lower N/P ratios more readily compared to conventional LMBs in a discharged state.

When discussing LMBs, the N/P ratio is an important factor. For instance, cells with a high N/P ratio can essentially function as half cells, leading to an exaggeration of the electrochemical performance of LMBs [27]. Moreover, the definition of the N/P ratio for LMBs varies across studies. In a typical LMB cell configuration, the N/P ratio is often calculated using the following Equation (5-2).

$$r_{\text{N/P}} = Q_{\text{N}} / Q_{\text{P}} \quad (5-2)$$

Here, $r_{N/P}$, Q_N , and Q_P are the N/P ratio, the capacity of the negative electrode, and the capacity of the positive active material. The term “capacity” refers to the ability to store or release lithium. For LMFBs, the N/P ratio is defined as one in this study [2], although some studies define it as zero [5, 8]. Similarly, the N/P ratio of CSLMBs that is equivalent to LMFBs (N/P = 1) is one. There is no difference in the theoretical N/P ratio between LMBs and CSLMBs, since the only difference lies in whether the lithium is initially located on the positive side or the negative side.

The gravimetric energy densities (GEDs) of LMFB and CSLMB after n th cycle were estimated. The capacity and GED of a LMFB after n th cycle ($Q_{LMFB,n}$ and $E_{LMFB,n}$) can be estimated by using the Equations (5-3) and (5-4), with an assumption that the positive electrode degradation is negligible compared with the Li loss on the negative electrode during cycling [2].

$$Q_{LMFB,n} = Q_{LFP} \prod_{i=1}^n CE_{neg,i} \quad (5-3)$$

$$E_{LMFB,n} = Q_{LMFB,n} U_{cell} \quad (5-4)$$

Here, Q_{LFP} is the theoretical capacity of $LiFePO_4$, $CE_{neg,i}$ is the Coulombic efficiency (CE) of the Li deposition/dissolution in the i th cycle, and U_{cell} is the cell voltage. It is generally the case that the initial Li deposition/dissolution efficiency is lower than in subsequent cycles [28, 29], however, for simplicity in this calculation, $CE_{neg,i}$ was assumed to be the same.

Similarly, the capacity and GED of a CSLMB after n th cycle ($Q_{\text{CSLMB},n}$ and $E_{\text{CSLMB},n}$) can be estimated by using the Equations (5-5) and (5-6), with an assumption that the CE of the cell after n th cycle is determined by that of the positive electrode when lithium metal remains and by that of the negative electrode after lithium metal is depleted.

$$Q_{\text{CSLMB},n} = \frac{m_{\text{FP}}}{m_{\text{FP}} + m_{\text{Li}}} Q_{\text{FP}} \prod_{i=1}^m \text{CE}_{\text{pos},i} \prod_{i=m+1}^n \text{CE}_{\text{neg},i} \quad (5-5)$$

$$E_{\text{CSLMB},n} = Q_{\text{CSLMB},n} U_{\text{cell}} \quad (5-6)$$

Here, Q_{FP} is the theoretical capacity of FePO_4 . $\text{CE}_{\text{pos},i}$ and $\text{CE}_{\text{neg},i}$ are the CE of the positive electrode and the Li deposition/dissolution in the i th cycle, respectively. The remaining amount of Li can be estimated from the initial Li quantity and the total Li consumption per cycle. The relationship between the weight of FePO_4 (m_{FP}) and Li metal (m_{Li}) is determined by the N/P ratio (Equation (5-7)), and thus $Q_{\text{CSLMB},n}$ is described as Equation (5-8).

$$r_{\text{N/P}} = \frac{m_{\text{Li}} Q_{\text{Li}}}{m_{\text{FP}} Q_{\text{FP}}} \quad (5-7)$$

$$Q_{\text{CSLMB},n} = \frac{1}{1 + r_{\text{N/P}} \frac{Q_{\text{FP}}}{Q_{\text{Li}}}} Q_{\text{FP}} \prod_{i=1}^m \text{CE}_{\text{pos},i} \prod_{i=m+1}^n \text{CE}_{\text{neg},i} \quad (5-8)$$

Here, Q_{Li} is the theoretical capacity of lithium metal. The parameters used for the calculations are listed in **Table 5-1**.

As shown in **Figure 5-5b**, the GEDs of LMFB and CSLMB with $N/P = 1$ (the state of both systems is without excess lithium.) significantly drop because of the irreversible lithium consumption during cycling [30], while the cycle life of CSLMB with $N/P \geq 2$ greatly improves because the additional lithium metal compensates for the irreversible depletion of lithium [31]. After the lithium metal is depleted, the cycling performance of CSLMB shows similar behavior to that of LMFB. As the N/P ratio increases, the total electrode weight also increases due to the additional lithium content, leading to a decrease in the maximum GED. However, the surplus lithium enhances cycling performance, indicating a trade-off between GED and cycle stability.

The above-mentioned evaluation was experimentally verified. **Figure 5-7** shows the galvanostatic lithium deposition/dissolution curves and cycling performances of the Cu/Li and Li/Li half cells using 2 mol dm^{-3} Li[FSA]-DME electrolyte at 1 mA cm^{-2} . The dissolution capacity is lower than the deposition capacity in the Cu/Li cell, particularly in the first cycle (**Figure 5-7a**). The initial CE of the Cu/Li cell is 94.3% because of irreversible capacity during the initial SEI formation [28, 29] and the average CE over 100 cycles reaches 98.8%, showing a trend consistent with previous reports (**Figure 5-7c**) [14, 29, 30]. Conversely, the initial CE reaches 99.99%, and the average CE remains at 99.99% over 100 cycles in the Li/Li cell (**Figures 5-7b and 5-7d**). This stability is attributed to the additional lithium, which compensated for lithium consumption during cycles and SEI formation [31]. Additionally, the intrinsic deposition/dissolution performance, including efficiency, nucleation process, and SEI

formation, may differ between Al/Li (metal-free cell configuration) and Li/Li (metal cell configuration); further investigation is required to draw clear factors on this point. This demonstrates the benefit of surplus lithium in maintaining high initial and cycle-averaged CEs, effectively mitigating efficiency loss due to SEI formation.

Moreover, to evaluate the electrochemical performances of CSLMBs, full cells were assembled using the FePO_4/C positive electrode, lithium metal negative electrode, and 2 mol dm^{-3} Li[FSA]-DME electrolyte. The FePO_4/C positive electrode is used here under the prospect of its reuse from spent LiFePO_4 as mentioned above. Additionally, lithium metal-free full cells were also fabricated using LiFePO_4/C as the positive electrode and Cu foil as the negative current collector to compare the CSLMB with a conventional LMFB. Here, three activation cycles at 0.1C ($1\text{C} = 170 \text{ mA (g-LiFePO}_4)^{-1}$ or $178 \text{ mA (g-FePO}_4)^{-1}$) were conducted before cycling tests. In the CSLMB, predischarging at 0.1C was also performed prior to activation cycles. The gravimetric values are calculated based on the total weight of positive and negative active materials.

Figures 5-8a and 5-9 show the cycle performances and charge–discharge curves of the CSLMB ($\text{N/P} = 2.50$) and LMFB at 0.3C including initial three activation cycles at 0.1C . In the LMFB, while the initial charge capacity was close to the theoretical value, the initial discharge capacity was just 115 mAh g^{-1} . The discharge capacity continued to decrease after the second cycle, and the average CE over 100 cycles was 98.5%. This capacity decrease is related to lithium consumption due to side reactions including the SEI formation as mentioned in the lithium deposition/dissolution tests (**Figure 5-7**). On

the other hand, the CSLMB shows highly stable cycling performance, benefiting from the compensatory lithium metal to mitigate lithium loss during cycling [31]. The discharge capacity of CSLMB (N/P = 2.50) at the 100th cycle is 140 mAh g⁻¹, while that of LMFB at the 100th cycle is 42 mAh g⁻¹. The high overpotential observed during preliminary discharge of the CSLMB shown in **Figure 5-9b** could be due to the formation of a surface layer such as LiFePO₄(OH) resulting from side reactions with water during delithiation process or washing [32, 33]. However, as cycling progresses, this layer dissipates, eliminating the overvoltage.

The longer cycling performance was also evaluated. **Figures 5-8b** and **5-10** demonstrate the cycle performances and charge–discharge curves of the CSLMB (N/P = 4.16) and LMFB at 1C including the initial three activation cycles at 0.1C. In the LMFB cell, the capacity drops to nearly zero after 300 cycles, whereas the CSLMB cell demonstrates stable cycling performance up to around 300 cycles. Beyond 300 cycles, the CSLMB cell experiences a rapid decline similar to that observed in the LMFB cell. This sharp decrease is attributed to the depletion of lithium at the negative electrode, resulting in irreversible lithium consumption and the deterioration of capacity retention.

The GEDs corresponding to **Figure 5-8** and the CSLMB (N/P = 1) are shown in **Figure 5-11**. As suggested by the calculations (**Figure 5-5b**), the GEDs of LMFB and CSLMB (N/P = 1) significantly decrease with each cycle, while the CSLMB (N/P ≥ 2) maintains a relatively high GED. Even after the first cycle, the GEDs of LMFB and CSLMB (N/P = 1) fall below 400 Wh kg⁻¹, which is smaller than that of the CSLMB

($N/P \geq 2$). The CSLMB ($N/P = 2.50$) achieves a stable GED of more than 450 Wh kg^{-1} over 100 cycles at $0.3C$ (**Figure 5-11a**), whereas the GED of CSLMB with a higher N/P ratio of 4.16 operated at $1C$ is below 400 Wh kg^{-1} (**Figure 5-11b**). The decrease is explained by the increase in N/P ratio and current density, resulting in the heavier total mass of active materials and the lower specific capacity, respectively. The GED of CSLMB ($N/P = 4.16$) demonstrates stable values over 300 cycles and then drops significantly. This aligns well with the result from the calculation (**Figure 5-5b**).

5.4 Conclusions

This chapter demonstrated the concept of CSLMB, where the initial cell configuration consists of a charged-state positive electrode (FePO_4) with a lean lithium metal negative electrode. Compared with LMFBs, CSLMBs showcase superior cycle stability and higher energy density owing to the additional lithium metal compensating for the irreversible loss of Li inventory during cycling. In addition, a Li source extracted during the delithiation process of LiFePO_4 can be recovered and then used to resynthesize LiFePO_4 , realizing the closed-loop Li recycling. This potential approach could involve the reuse of LiFePO_4 electrodes to recover Li source while utilizing the remaining FePO_4 for CSLMB applications.

Although the production of thin lithium metal is still challenging, since all the lithium inventory stems from lithium metal, CSLMBs require thicker lithium metal than LMBs in a discharged state with the same N/P ratio, providing an advantage in lithium

metal film production. CSLMBs could be promising as a means of enhancing cycle stability and GED in LMBs.

Table 5-1. Parameters used for the GED calculation.

Symbol	Parameter	Value
Q_{LFP}	Theoretical capacity of LiFePO_4	170 mAh g^{-1}
Q_{FP}	Theoretical capacity of FePO_4	178 mAh g^{-1}
Q_{Li}	Theoretical capacity of Li	3860 mAh g^{-1}
$\text{CE}_{\text{pos},i}$	Coulombic efficiency of positive electrode in the i th cycle	99.98%
$\text{CE}_{\text{neg},i}$	Coulombic efficiency of Li deposition/dissolution in the i th cycle	99%
U_{cell}	Cell voltage	3.4 V
$r_{\text{N/P}}$	N/P ratio	1–4

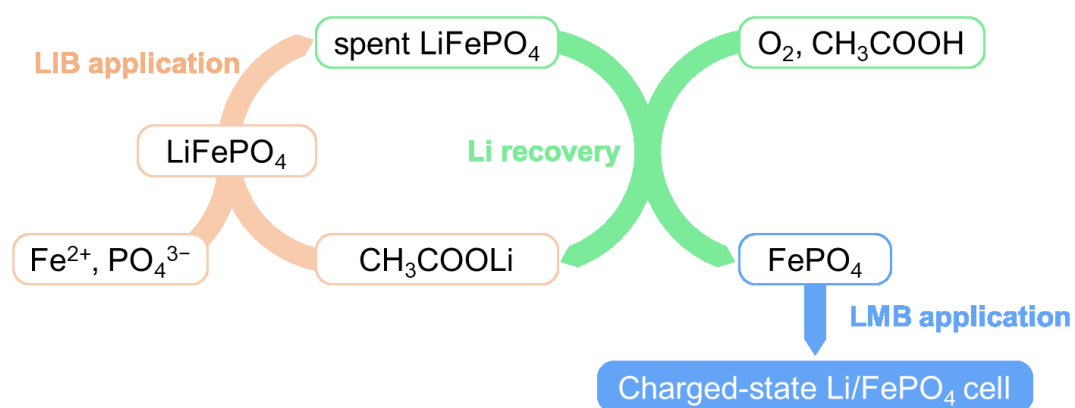


Figure 5-1. Schematic illustration of the production route of FePO_4 for CSLMBs and Li recovery using O_2 gas as an oxidizing agent.

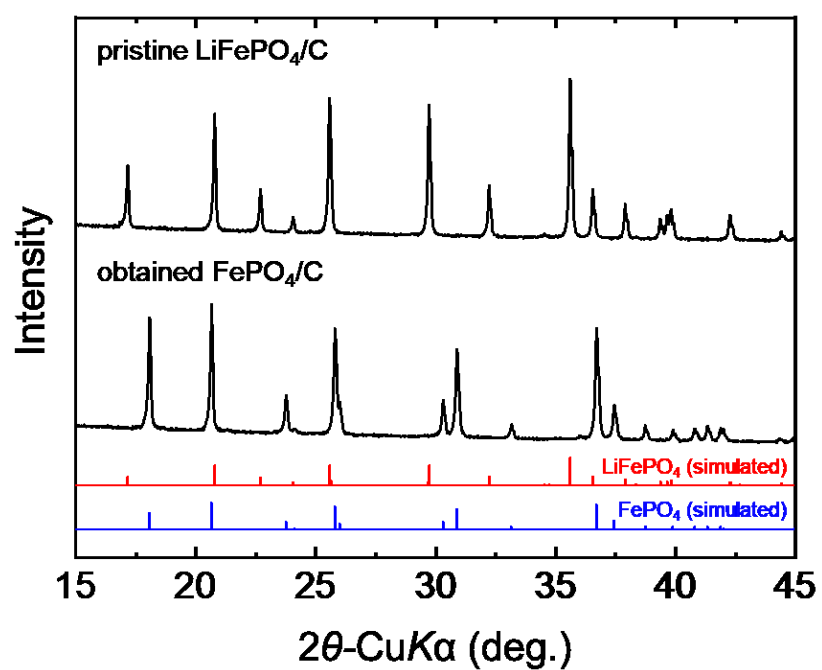


Figure 5-2. XRD patterns of the pristine LiFePO₄/C and obtained FePO₄/C. The simulated patterns are calculated based on crystallographic data in a previous report [24] using VESTA software.

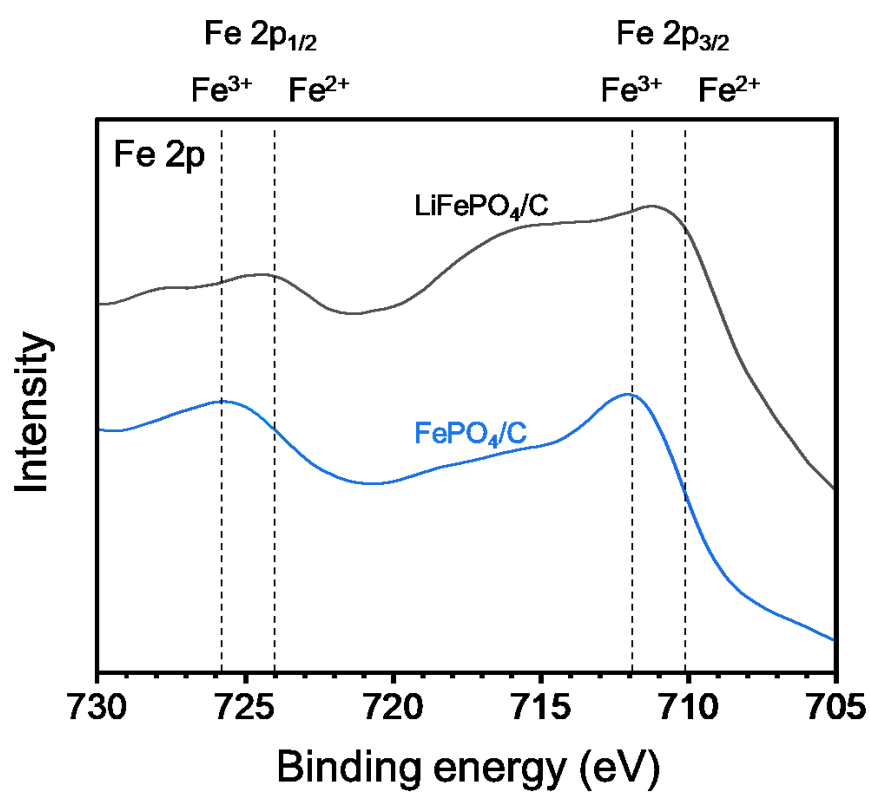


Figure 5-3. XPS spectra of the LiFePO₄ and FePO₄ electrodes.

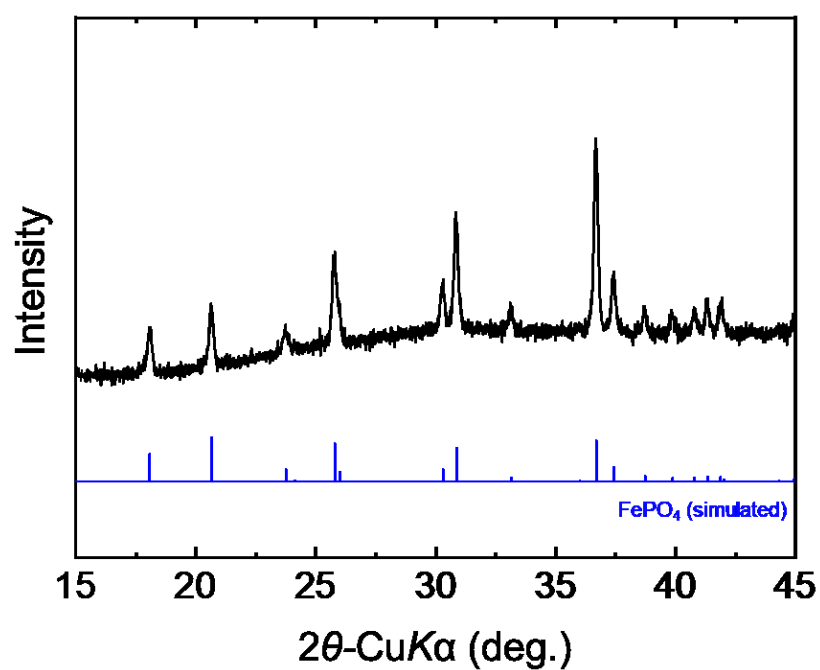


Figure 5-4. XRD pattern of the FePO₄ electrode produced by the chemical delithiation of the LiFePO₄ electrode using O₂ gas. The simulated patterns are calculated based on crystallographic data in a previous report [24] using VESTA software.

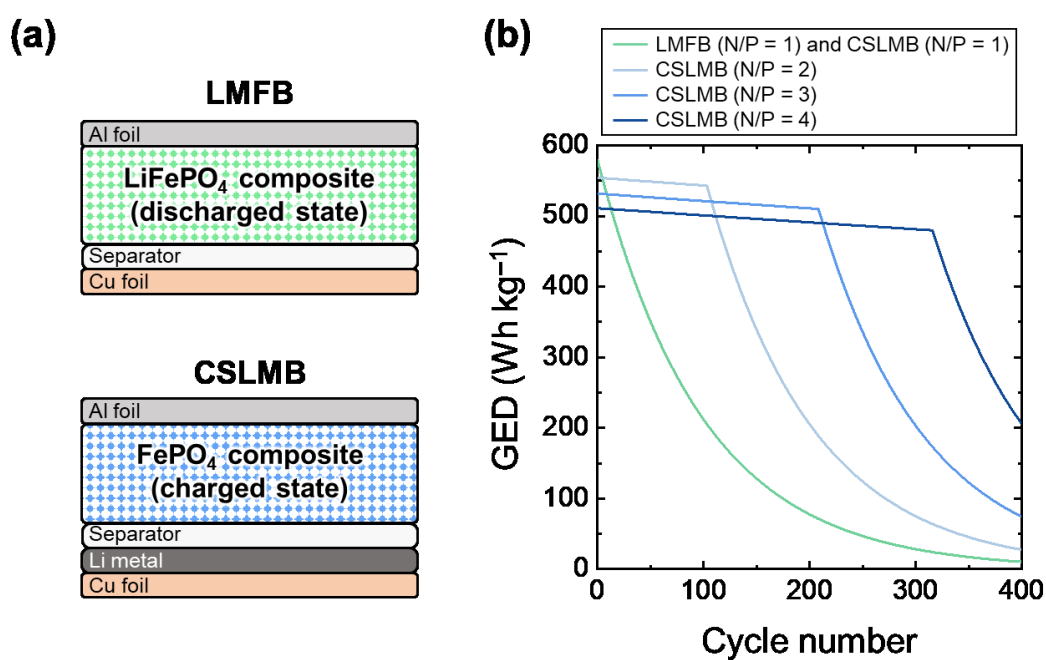


Figure 5-5. (a) Schematic comparison between LMFB and CSLMB. (b) Calculated GEDs of LMFB (N/P = 1) and CSLMB (N/P = 1, 2, 3, and 4).

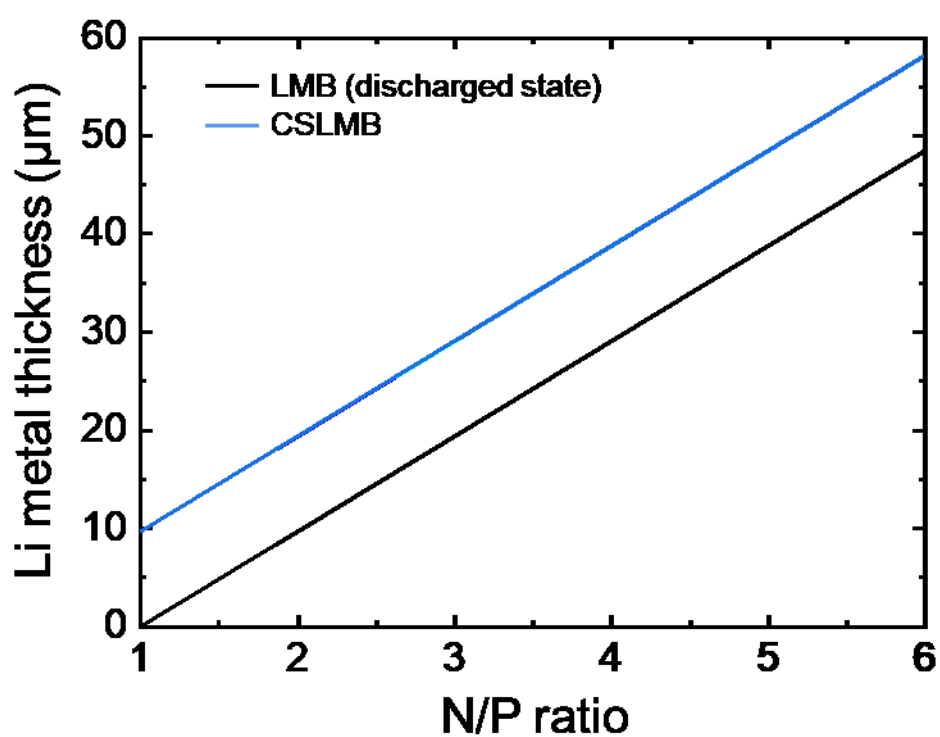


Figure 5-6. Relationship between the lithium metal thickness and the N/P ratio, assuming that the areal capacity of positive electrode is 2 mAh cm^{-2} . The thickness is estimated from the theoretical capacity and density of lithium metal.

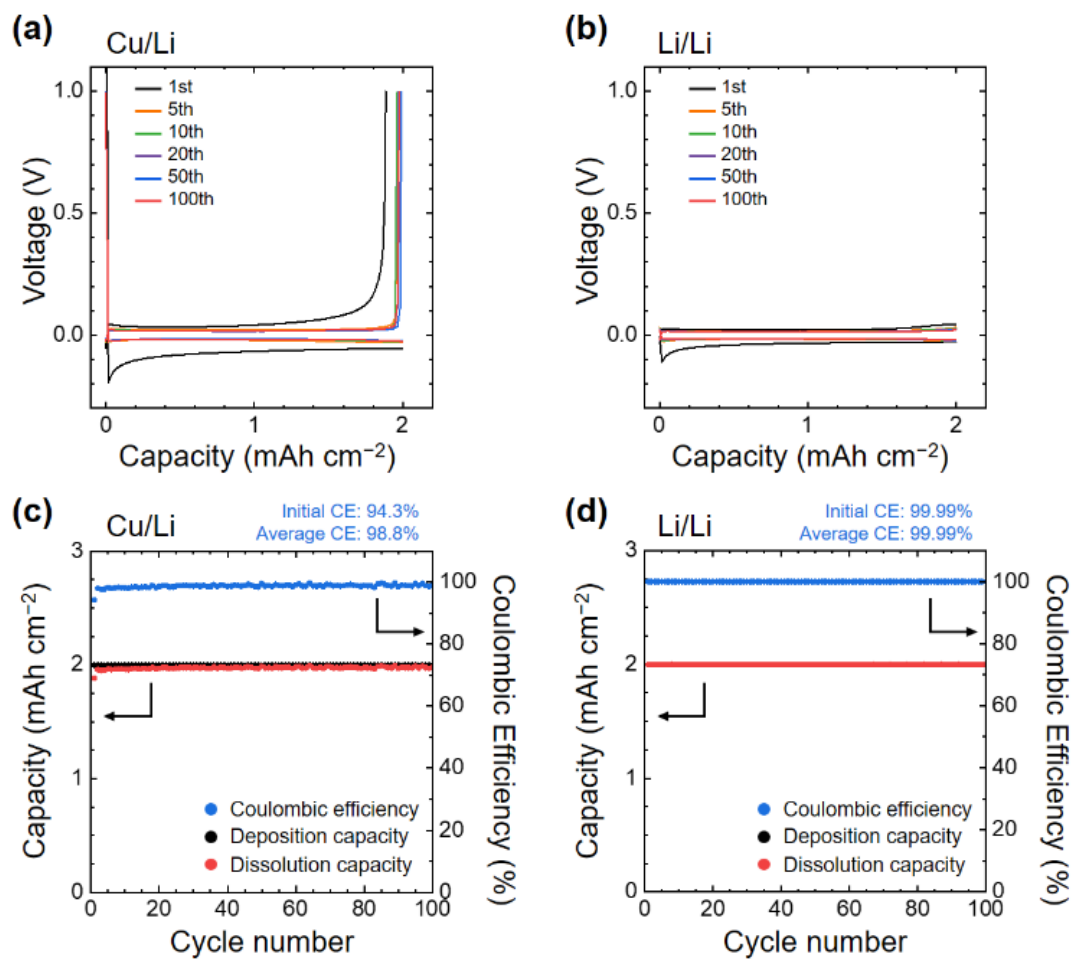


Figure 5-7. Galvanostatic lithium deposition/dissolution curves of (a) Cu/Li and (b) Li/Li cells at 1 mA cm⁻² (2 mAh cm⁻²). Corresponding cycle plots of the (c) Cu/Li and (d) Li/Li cells.

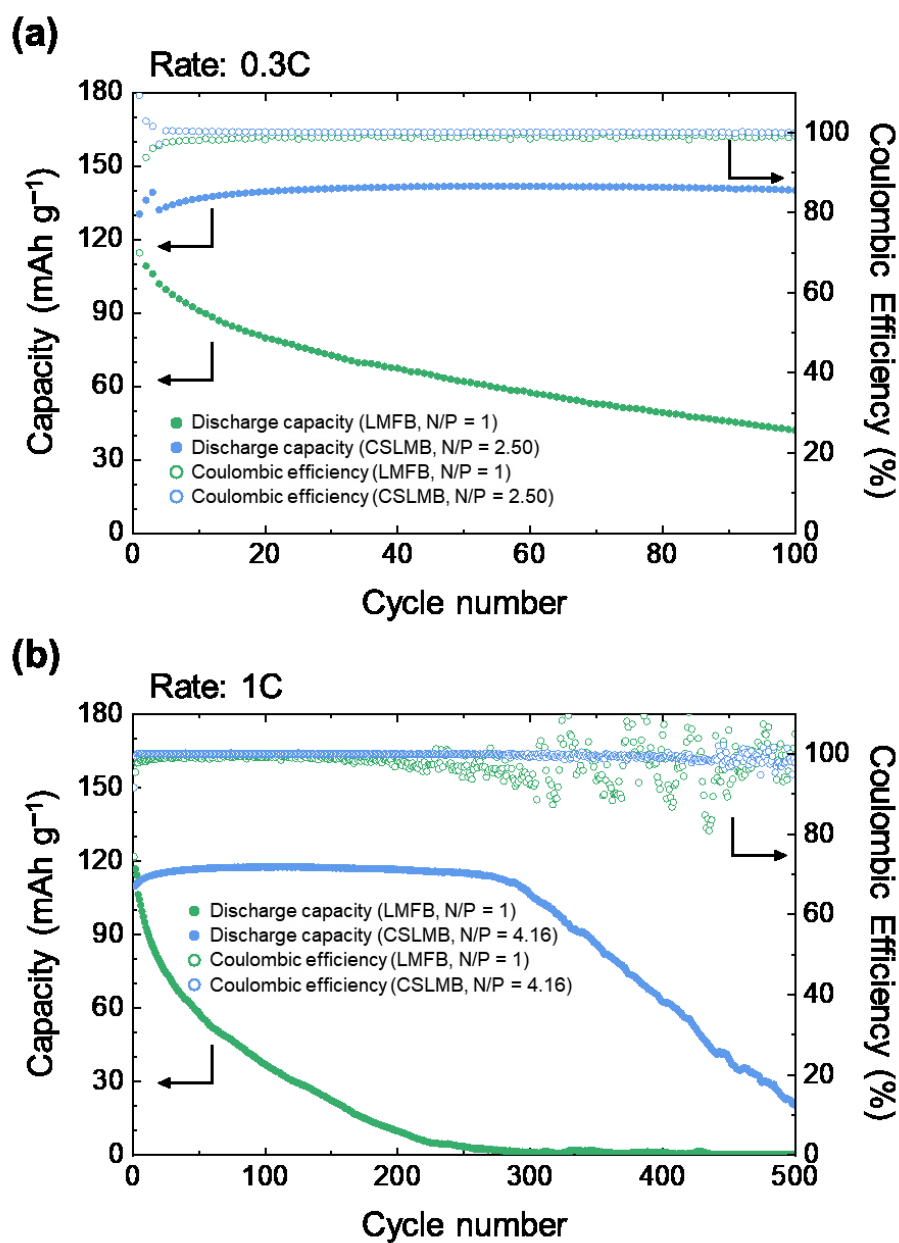


Figure 5-8. Cycle performances of (a) LMFB and CSLMB (N/P = 2.50) at 0.3C including initial three activation cycles at 0.1C and (b) LMFB and CSLMB (N/P = 4.16) at 1C including initial three activation cycles at 0.1C. Capacity is calculated based on the total weight of positive and negative active materials.

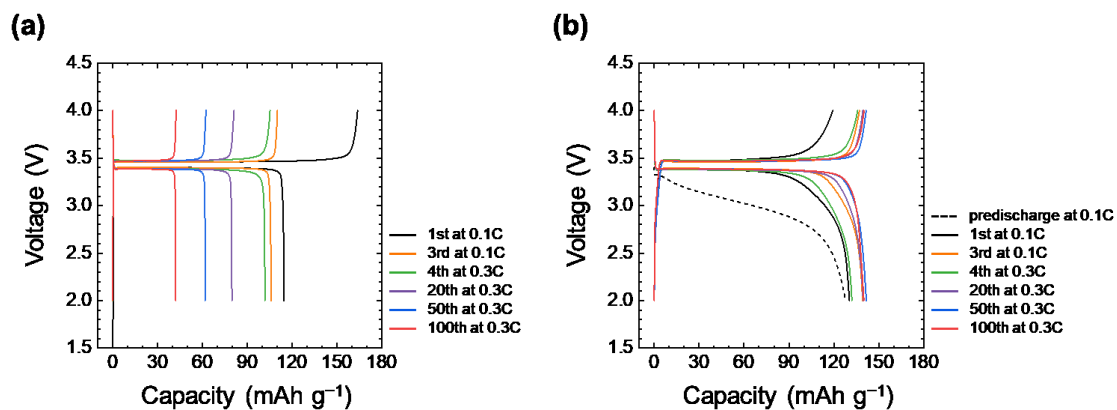


Figure 5-9. Charge–discharge curves of (a) LMFB and (b) CSLMB (N/P = 2.50) at 0.3C including initial three activation cycles at 0.1C.

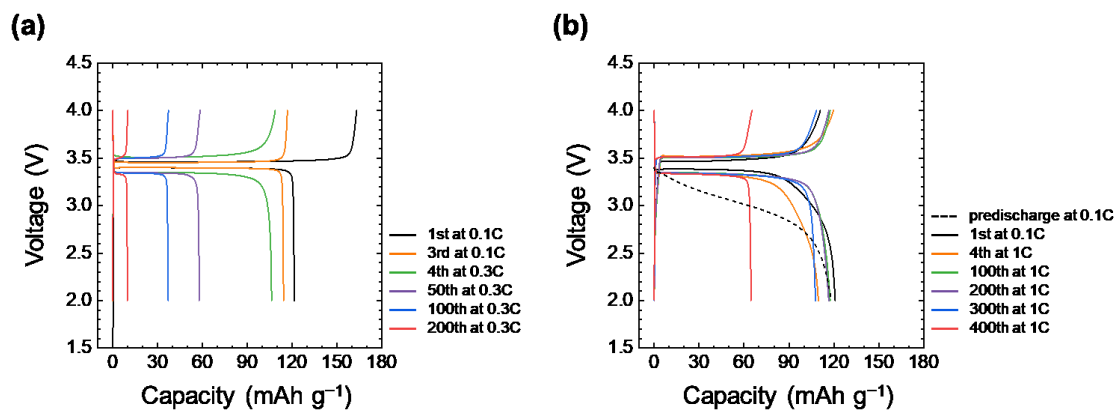


Figure 5-10. Charge–discharge curves of (a) LMFB and (b) CSLMB (N/P = 4.16) at 1C including initial three activation cycles at 0.1C.

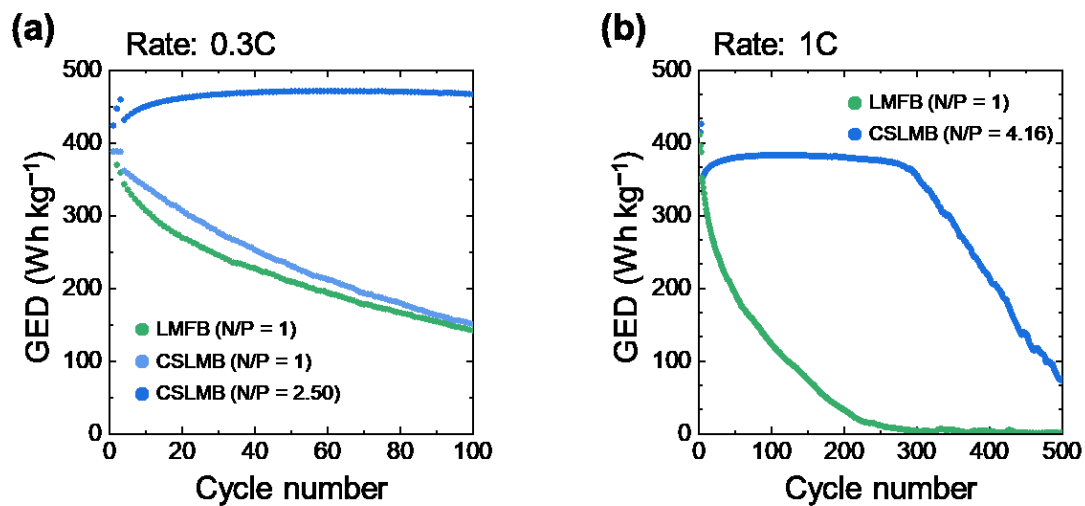


Figure 5-11. GEDs of (a) LMFB and CSLMB (N/P = 2.50 and 1) at 0.3C including initial three activation cycles at 0.1C and (b) LMFB and CSLMB (N/P = 4.16) at 1C including initial three activation cycles at 0.1C. GED is calculated based on the total weight of positive and negative active materials.

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Chapter 6

Mg-doped Heterosite FePO₄ for Sodium-Ion Batteries

6.1 Introduction

Triphylite NaFePO₄ needs to overcome the limited electrochemical performance mainly because of its low electronic and ionic conductivity. Although there are reports of enhanced capacity values close to the theoretical capacity at elevated temperatures [1-3], limited reversible capacities below the theoretical value at room temperature and low rate capability by the sluggish kinetics of Na⁺ remain a challenge [4-6]. To improve the electrochemical performance of materials, doping is one of the effective strategies for positive electrodes [7]. Doping of LiFePO₄ has been investigated extensively so far and many studies indicate doping leads to the improvement of electronic and ionic conductivity of LiFePO₄ [8-13]. Therefore, a similar strategy of doping triphylite NaFePO₄ (or heterosite FePO₄) can be a possible solution to enhance its electrochemical properties, and a recent study has demonstrated Mn and Ni co-substitution into heterosite FePO₄ improves electronic conductivity, contributing to the enhanced rate performance of Na/FePO₄ cells [14]. Mg doping has been extensively reported for LiFePO₄ [8, 15, 16], however, there have been no reports of its application to triphylite NaFePO₄.

Aiming to enhance the electrochemical performance of triphylite NaFePO₄ and heretosite FePO₄ as SIBs, this chapter applies Mg-doped heterosite FePO₄ as a positive

electrode for SIBs. Here, Mg-doped LiFePO_4 is delithiated using O_2 gas in acetic acid aqueous solution to obtain Mg-doped heterosite FePO_4 , and then structural and electrochemical properties of Mg-doped heterosite FePO_4 as SIBs are evaluated.

6.2 Experimental

Mg-doped LiFePO_4/C powder was synthesized through a solid-state reaction as described in Chapter 2. The obtained samples ($\text{LiFe}_{1-x}\text{Mg}_x\text{PO}_4/\text{C}$, ($x = 0, 0.01, 0.02, 0.03$, and 0.04)) are denoted as Mgy-LFP ($y = 0, 1, 2, 3$, and 4), respectively. They were subjected to the delithiation process using O_2 gas in an acetic acid solution. The resulting delithiated samples ($\text{Fe}_{1-x}\text{Mg}_x\text{PO}_4/\text{C}$, ($x = 0, 0.01, 0.02, 0.03$, and 0.04)) are denoted as Mgy-FP ($y = 0, 1, 2, 3$, and 4), respectively. XRD, SEM, and EDX measurements were conducted for the characterizations of Mgy-LFP and Mgy-FP. The Rietveld refinement of the obtained XRD patterns was performed to determine lattice parameters.

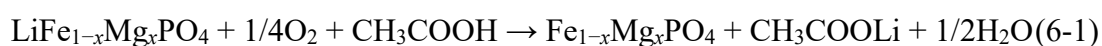
All the half cells were assembled using 2032-type coin cells under a dry Ar atmosphere. The positive electrodes were prepared by mixing the Mgy-FP with conductive carbon and the SWCNT dispersion in NMP with PVDF in the weight ratio of Mgy-FP : carbon : SWCNT : PVDF = 91:3:2:4, pasting onto an Al foil, and then drying. Sodium metal was used as a negative electrode. The electrolyte was 1 mol dm^{-3} $\text{Na}[\text{PF}_6]\text{-EC/DMC}$ (1:1 v/v) with 3wt% of FEC. A glass fiber and a polypropylene (PP)

separator were used as a separator for rate capability tests and cycle stability tests, respectively.

Charge–discharge properties, rate capabilities, and cycle performances were evaluated at 25 °C. The capacity was calculated based on the weight of the Mg-doped FePO₄ active material. The cutoff voltage was set in the 2.0 V–3.8 V range. Cycle tests were conducted at 100 mA (g-FePO₄)⁻¹ after initial discharging at 10 mA (g-FePO₄)⁻¹. The GITT measurements were also conducted in the manner described in Chapter 2.

6.3 Results and discussion

Mg_y-FP ($y = 0, 1, 2, 3$, and 4) are prepared through the delithiation of Mg_y-LFP ($y = 0, 1, 2, 3$, and 4) using O₂ in acetic acid aqueous solution in accordance with the following reaction (6-1).



Herein, O₂ acts as an oxidizing agent to oxidize/delithiate LiFePO₄, and acetic acid is added in water to keep the solution weak acidic condition and to extract Li source as lithium acetate (CH₃COOLi). The delithiated Mg-doped FePO₄ is separated from lithium acetate solution by filtration or centrifugation and the recovered lithium acetate can be used to synthesize LiFePO₄ again. More detailed delithiation principle has been discussed in Chapter 4.

XRD patterns of Mgy-LFP exhibited in **Figure 6-1** match that of typical LiFePO₄ (triphylite, space group: *Pnma*) [17], indicating Mg-doped LiFePO₄ keeps triphylite structure and Mg ions are successfully doped into the LiFePO₄ lattice. An enlarged view around $2\theta = 35.6^\circ$ in **Figure 6-2** shows that the peak gradually shifts towards higher angles with increasing the Mg concentration. This trend is consistent with previous reports [16, 18], suggesting lattice shrinkage due to doping. To determine the lattice parameters, the Rietveld refinement was conducted based on a previous computational report arguing that Mg ions occupy Fe sites [19]. The refinement results reveal that Mg doping monotonously decreases the lattice constants as shown in **Figure 6-3**. Detailed results of the refinement are displayed in **Figure 6-4** and **Tables 6-1–6-5**. The decrease in lattice parameters can be explained by the difference in ionic radii between Fe^{II} (0.78 Å) and Mg^{II} (0.72 Å) [20]. XRD patterns of Mgy-FP (heterosite, space group: *Pnma*) in **Figure 6-5** demonstrate successful delithiation of LiFePO₄ using O₂ and acetic acid, and the peak around $2\theta = 36.6^\circ$ shifts towards lower angles as the Mg concentration increases as shown in **Figure 6-6**. The increase in lattice parameters with higher Mg concentration, which is because of the difference in ionic radii between Fe^{III} (0.645 Å) and Mg^{II} (0.72 Å) [20], is revealed through the Rietveld refinement shown in **Figure 6-7**. Detailed results of the refined results are displayed in **Figure 6-8** and **Tables 6-6–6-10**. SEM images of Mgy-LFP and Mgy-FP are shown in **Figures 6-9** and **6-10**. The images exhibit similar surface morphologies compared to Mgy-LFP and Mgy-FP, which indicates the delithiation method using O₂ in acetic acid aqueous solution does not

damage the morphology of the pristine particles. Increasing Mg incorporation into LiFePO₄ is confirmed by the EDX analyses shown in **Table 6-11**.

The electrochemical performances of the Na/Mg-doped FePO₄ half cells are evaluated. Here, current densities are calculated based on the weight of Mgy-FP. **Figure 6-11** shows the rate capability at varied current rates (10, 20, 50, 100, 150, and 300 mA (g-FePO₄)⁻¹). The Mg1-FP and Mg2-FP electrodes demonstrate enhanced discharge capacity compared to the non-doped FePO₄ (Mg0-FP), whereas the capacities of Mg3 and Mg4-FP are lower than that of Mg0-FP. The case with minimum doping, Mg1-FP, shows the highest average capacities of 139, 133, 124, 115, 109, and 98 mAh (g-FePO₄)⁻¹ at 10, 20, 50, 100, 150, and 300 mA (g-FePO₄)⁻¹, respectively, which is around 10 mAh (g-FePO₄)⁻¹ higher than those of Mg0-FP. The capacity retention ratios based on the first discharge capacity shown in **Figure 6-12** reveal that Mg1-FP and Mg2-FP exhibit superior capacity retention compared to Mg0-FP, suggesting that Mg doping improves the rate capability. The charge–discharge curves of Mgy-FP at each current rate obtained during the rate capability tests shown in **Figure 6-13** demonstrate Mg1-FP and Mg2-FP reduce polarization, implying improved Na⁺ mobility. The reduced polarization is also verified by the GITT test in **Figure 6-14**, where Mg1-FP and Mg2-FP cells show smaller overpotentials. The two plateaus observed during charging in **Figure 6-13** imply the Na_xFePO₄ solid-solution region ($2/3 \leq x \leq 1$) followed by the two-phase region between FePO₄ and Na_{2/3}FePO₄ [21]. Meanwhile, only one plateau appearing during discharging is caused by the faster Na ion mobility in the Na_xFePO₄

solid-solution ($2/3 \leq x \leq 1$) than that during the phase transformation between FePO_4 and $\text{Na}_{2/3}\text{FePO}_4$ [22]. **Figure 6-15** exhibits the cycle test results of Na/Mg-doped FePO_4 half cells that were conducted at $100 \text{ mA (g-FePO}_4\text{)}^{-1}$ after initial discharging at $10 \text{ mA (g-FePO}_4\text{)}^{-1}$. Similar to the rate capability test results shown in **Figure 6-11**, FePO_4 with 1 and 2% Mg doping achieve a higher discharge capacity than the non-doped FePO_4 (Mg0-FP), though 3 and 4% Mg-doped FePO_4 demonstrate the lower capacity. During cycling, a gradual increase in the discharge capacity is observed at all Mg concentrations and this can be ascribed to the increase in active sites due to the deagglomeration of particles with cycling. The stable cycle performances suggest the delithiation method using O_2 gas does not damage the host framework of the pristine Mg-doped LiFePO_4 powder and Mg doping also does not affect the structure. Such improvement in electrochemical properties by Mg doping can be attributed to enhanced electronic conductivity resulting from the formation of impurity phases such as FeP_2 [16, 23]. Changes in lattice constants can also affect the electrochemical properties of Mg-doped FP. The decreased b parameter could facilitate Na^+ diffusion since the diffusion pathway aligns along the b axis. Conversely, a decrease in the a and c parameters may reduce the cross-sectional area of diffusion pathways, potentially hindering Na^+ diffusion.

6.4 Conclusions

In summary, this chapter investigated the Mg doping effects to heterosite FePO_4 as a positive electrode material for SIBs. Mg-doped FePO_4 was produced from Mg-doped LiFePO_4 by delithiation using O_2 as an oxidizing agent. The successful Mg doping was confirmed by the EDX analyses and peak shifts of XRD patterns. Electrochemical tests revealed that 1% and 2% Mg-doped FePO_4 showed improved discharge capacity and rate capability, benefiting from the enhanced electronic and ionic conductivity due to Mg doping. Although the electrochemical performance improvement through Mg doping was confirmed, it still has not reached values close to the theoretical capacity (139 mAh g^{-1} in this study vs. 178 mAh g^{-1} in theory), indicating that there remains room for further improvement.

Table 6-1. Crystallographic data of Mg0-LFP by the Rietveld refinement.

LiFePO ₄ (Space group: <i>Pnma</i>)						
$R_p = 12.5\%$, $R_{wp} = 8.2\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	10.3223(3)	6.00789(16)	4.69831(14)	291.367(14)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Li	4 <i>a</i>	0	0	0	0.5	1.000
Fe	4 <i>c</i>	0.28211(11)	0.2500	0.9765(5)	0.5	1.000
P	4 <i>c</i>	0.0938(3)	0.2500	0.4164(6)	0.5	1.000
O1	4 <i>c</i>	0.1007(6)	0.2500	0.7332(10)	0.5	1.000
O2	4 <i>c</i>	0.4552(8)	0.2500	0.2029(9)	0.5	1.000
O3	8 <i>d</i>	0.1599(5)	0.0419(8)	0.2843(6)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor and Occupancy were fixed at 0.5 and 1.0, respectively.

Table 6-2. Crystallographic data of Mg1-LFP by the Rietveld refinement.

LiFe _{0.99} Mg _{0.01} PO ₄ (Space group: <i>Pnma</i>)						
$R_p = 11.3\%$, $R_{wp} = 7.6\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	10.3121(3)	6.00400(15)	4.69775(14)	290.855(14)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Li	$4a$	0	0	0	0.5	1.000
Fe/Mg	$4c$	0.28236(11)	0.2500	0.9733(4)	0.5	0.990 /0.010
P	$4c$	0.0966(3)	0.2500	0.4216(6)	0.5	1.000
O1	$4c$	0.0923(7)	0.2500	0.7420(10)	0.5	1.000
O2	$4c$	0.4528(8)	0.2500	0.2028(9)	0.5	1.000
O3	$8d$	0.1618(5)	0.0551(7)	0.2826(6)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor was fixed at 0.5.

LiFe _{0.98} Mg _{0.02} PO ₄ (Space group: <i>Pnma</i>)						
$R_p = 12.8\%$, $R_{wp} = 8.4\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	10.3100(3)	6.00308(16)	4.69896(14)	290.826(14)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Li	4 <i>a</i>	0	0	0	0.5	1.000
Fe/Mg	4 <i>c</i>	0.28180(11)	0.2500	0.9758(5)	0.5	0.980 /0.020
P	4 <i>c</i>	0.0950(3)	0.2500	0.4171(6)	0.5	1.000
O1	4 <i>c</i>	0.0979(7)	0.2500	0.7335(11)	0.5	1.000
O2	4 <i>c</i>	0.4517(8)	0.2500	0.2028(9)	0.5	1.000
O3	8 <i>d</i>	0.1587(5)	0.0471(8)	0.2831(7)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor was fixed at 0.5.

Table 6-4. Crystallographic data of Mg3-LFP by the Rietveld refinement.

LiFe _{0.97} Mg _{0.03} PO ₄ (Space group: <i>Pnma</i>)						
$R_p = 14.3\%$, $R_{wp} = 9.9\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	10.3046(3)	5.99973(14)	4.69462(13)	290.243(13)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Li	$4a$	0	0	0	0.5	1.000
Fe/Mg	$4c$	0.28271(12)	0.2500	0.9753(5)	0.5	0.970 /0.030
P	$4c$	0.0976(3)	0.2500	0.4215(6)	0.5	1.000
O1	$4c$	0.0898(7)	0.2500	0.7347(11)	0.5	1.000
O2	$4c$	0.4566(8)	0.2500	0.2097(9)	0.5	1.000
O3	$8d$	0.1617(5)	0.0495(8)	0.2794(7)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor was fixed at 0.5.

Table 6-5. Crystallographic data of Mg4-LFP by the Rietveld refinement.

LiFe _{0.96} Mg _{0.04} PO ₄ (Space group: <i>Pnma</i>)						
$R_p = 16.5\%$, $R_{wp} = 10.3\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	10.2990(3)	5.99691(17)	4.69292(15)	289.846(15)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Li	$4a$	0	0	0	0.5	1.000
Fe/Mg	$4c$	0.28242(13)	0.2500	0.9766(5)	0.5	0.960 /0.040
P	$4c$	0.0945(3)	0.2500	0.4168(7)	0.5	1.000
O1	$4c$	0.1006(7)	0.2500	0.7351(12)	0.5	1.000
O2	$4c$	0.4585(8)	0.2500	0.2020(10)	0.5	1.000
O3	$8d$	0.1620(5)	0.0431(8)	0.2864(7)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor was fixed at 0.5.

Table 6-6. Crystallographic data of Mg0-FP by the Rietveld refinement.

FePO ₄ (Space group: <i>Pnma</i>)						
$R_p = 14.9\%$, $R_{wp} = 9.5\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	9.8368(4)	5.8059(2)	4.7815(2)	273.077(19)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Fe	4c	0.2746(2)	0.2500	0.9514(4)	0.5	1.000
P	4c	0.0901(4)	0.2500	0.3897(8)	0.5	1.000
O1	4c	0.1229(7)	0.2500	0.6924(16)	0.5	1.000
O2	4c	0.4438(9)	0.2500	0.1600(12)	0.5	1.000
O3	8d	0.1646(6)	0.0484(8)	0.2515(8)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor and Occupancy were fixed at 0.5 and 1.0, respectively.

Table 6-7. Crystallographic data of Mg1-FP by the Rietveld refinement.

Fe _{0.99} Mg _{0.01} PO ₄ (Space group: <i>Pnma</i>)						
$R_p = 10.6\%$, $R_{wp} = 7.4\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	9.8313(4)	5.8018(2)	4.77719(19)	272.489(18)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Fe/Mg	4 <i>c</i>	0.2744(3)	0.2500	0.9500(5)	0.5	0.990 /0.010
P	4 <i>c</i>	0.0951(5)	0.2500	0.3996(12)	0.5	1.000
O1	4 <i>c</i>	0.1197(9)	0.2500	0.704(2)	0.5	1.000
O2	4 <i>c</i>	0.4400(12)	0.2500	0.1523(17)	0.5	1.000
O3	8 <i>d</i>	0.1656(7)	0.0462(12)	0.2494(11)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor was fixed at 0.5.

Table 6-8. Crystallographic data of Mg₂-FP by the Rietveld refinement.

Fe _{0.98} Mg _{0.02} PO ₄ (Space group: <i>Pnma</i>)						
$R_p = 13.6\%$, $R_{wp} = 9.2\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	9.8476(4)	5.81029(19)	4.78374(19)	273.715(18)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Fe/Mg	4 <i>c</i>	0.2709(2)	0.2500	0.9477(4)	0.5	0.980 /0.020
P	4 <i>c</i>	0.0876(4)	0.2500	0.3884(8)	0.5	1.000
O1	4 <i>c</i>	0.1170(6)	0.2500	0.6839(15)	0.5	1.000
O2	4 <i>c</i>	0.4295(8)	0.2500	0.1455(12)	0.5	1.000
O3	8 <i>d</i>	0.1648(5)	0.0439(7)	0.2568(8)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor was fixed at 0.5.

Table 6-9. Crystallographic data of Mg3-FP by the Rietveld refinement.

Fe _{0.97} Mg _{0.03} PO ₄ (Space group: <i>Pnma</i>)						
$R_p = 18.6\%$, $R_{wp} = 12.9\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	9.8509(3)	5.81365(17)	4.78113(16)	273.815(15)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Fe/Mg	$4c$	0.2698(2)	0.2500	0.9457(4)	0.5	0.970 /0.030
P	$4c$	0.0888(4)	0.2500	0.3841(8)	0.5	1.000
O1	$4c$	0.1156(7)	0.2500	0.6602(17)	0.5	1.000
O2	$4c$	0.4199(8)	0.2500	0.1460(13)	0.5	1.000
O3	$8d$	0.1608(6)	0.0494(8)	0.2513(8)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor was fixed at 0.5.

Table 6-10. Crystallographic data of Mg4-FP by the Rietveld refinement.

Fe _{0.96} Mg _{0.04} PO ₄ (Space group: <i>Pnma</i>)						
$R_p = 12.1\%$, $R_{wp} = 8.7\%$						
	a (Å)	b (Å)	c (Å)	V (Å ³)		
	9.8643(4)	5.8189(2)	4.7825(2)	274.51(2)		
Atom	Wyckoff symbol	x	y	z	B (Å ²)	Occ.
Fe/Mg	$4c$	0.27393(19)	0.2500	0.9535(4)	0.5	0.960 /0.040
P	$4c$	0.0935(4)	0.2500	0.4007(8)	0.5	1.000
O1	$4c$	0.1211(6)	0.2500	0.6974(14)	0.5	1.000
O2	$4c$	0.4388(8)	0.2500	0.1643(11)	0.5	1.000
O3	$8d$	0.1621(6)	0.0489(7)	0.2481(8)	0.5	1.000

The starting parameters were taken from a previous report [15], and the B factor was fixed at 0.5.

Table 6-11. EDX analysis results of the $\text{Mg}_y\text{-LFP}$ ($y = 0, 1, 2, 3$, and 4).

Element (at%)	Mg0-LFP	Mg1-LFP	Mg2-LFP	Mg3-LFP	Mg4-LFP
O	65.75	67.92	58.53	61.73	65.86
Mg	-	0.27	0.49	0.63	0.80
P	16.89	15.89	20.03	19.61	18.14
Fe	17.36	15.93	20.95	18.03	15.20
Mg/P ratio	-	0.017	0.024	0.032	0.044

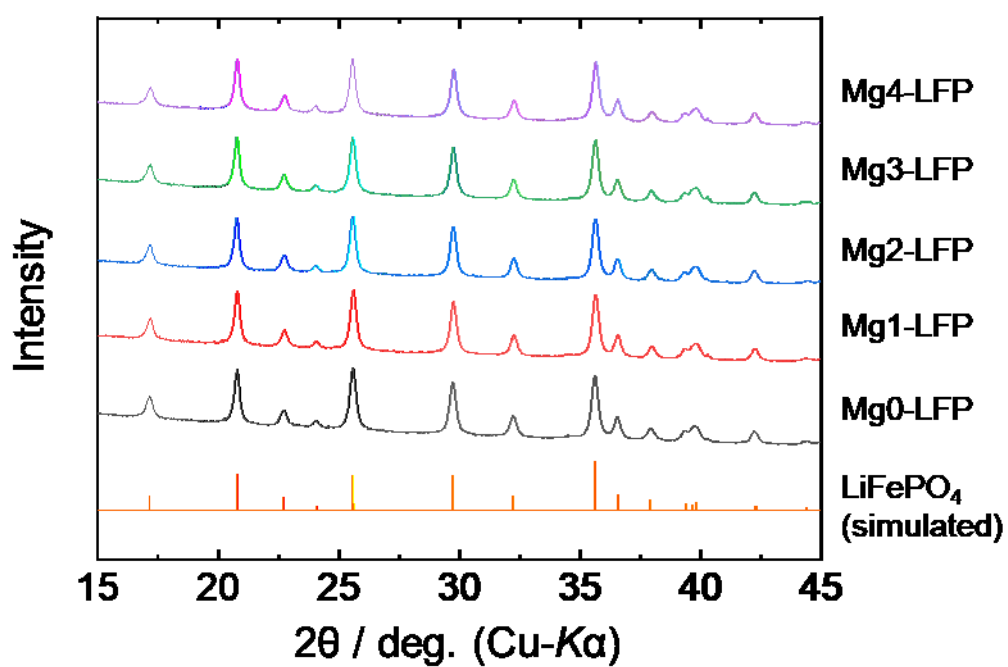


Figure 6-1. XRD patterns of the Mg_y-LFP ($y = 0, 1, 2, 3$, and 4). The simulated patterns are calculated based on crystallographic data in previous reports [15] using VESTA software.

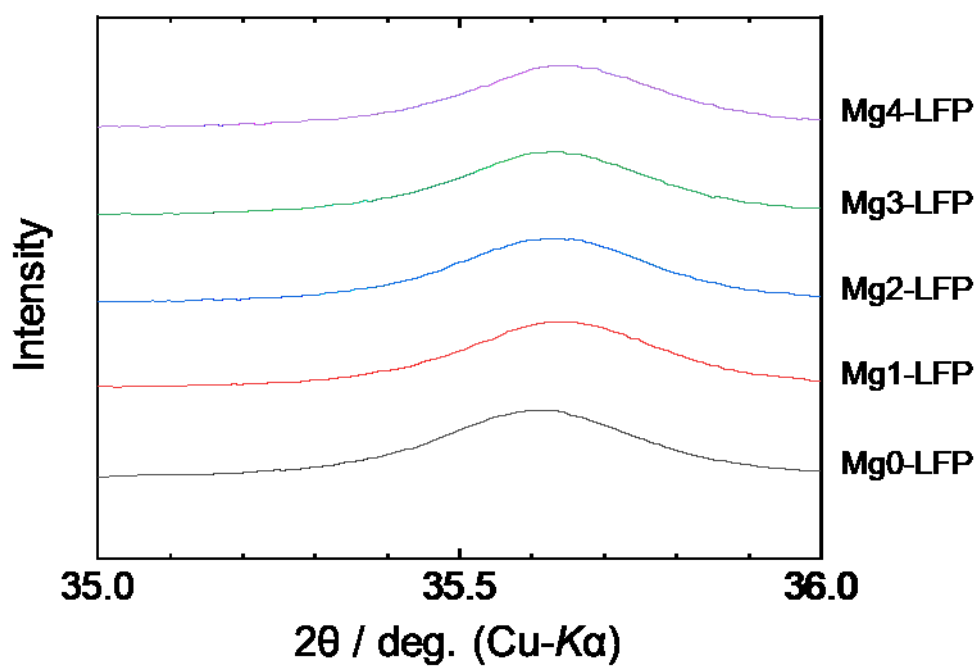


Figure 6-2. Enlarged XRD patterns of the Mg_γ-LFP ($\gamma = 0, 1, 2, 3$, and 4) around $2\theta = 35.6^\circ$.

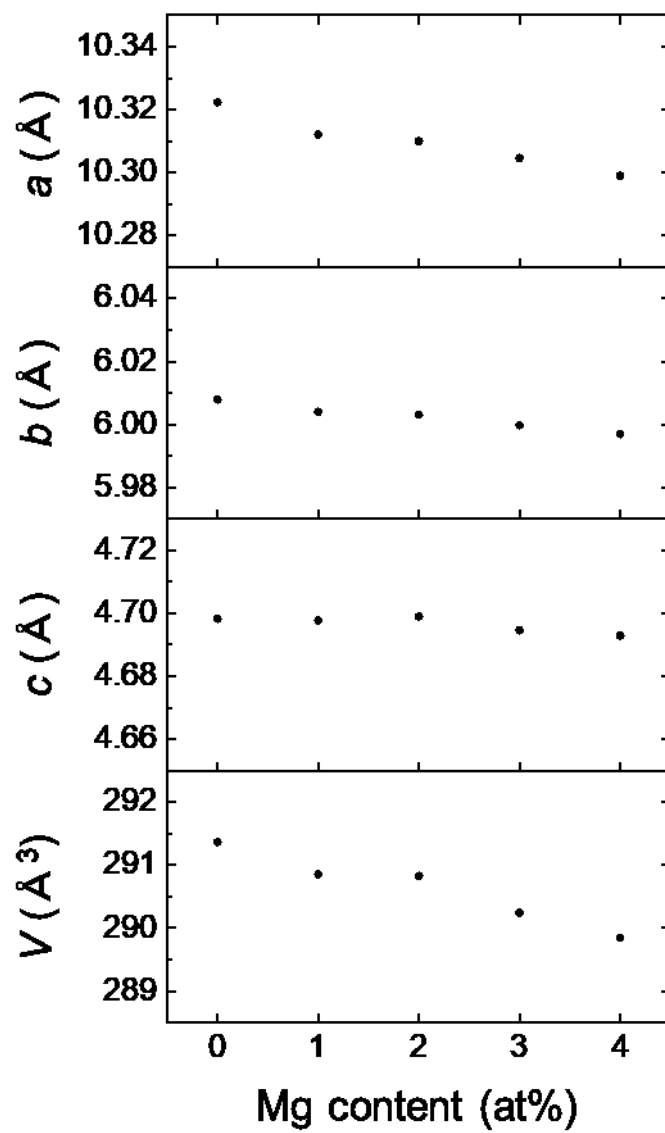


Figure 6-3. Lattice parameters and unit cell volume of the $\text{Mg}_y\text{-LFP}$ ($y = 0, 1, 2, 3$, and 4) as a function of Mg concentration.

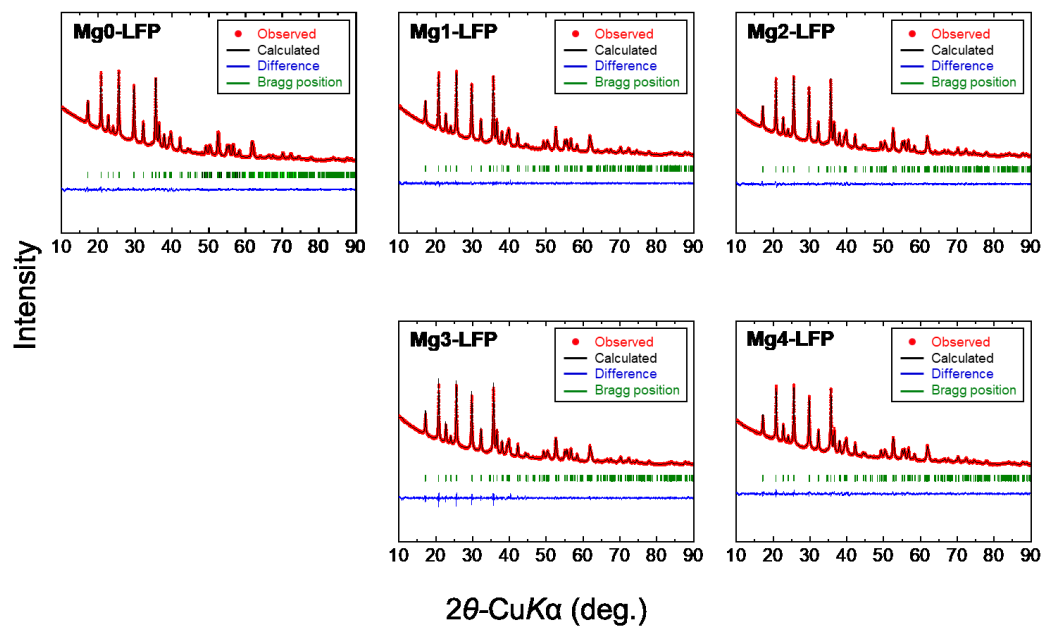


Figure 6-4. Rietveld refinement results of the $\text{Mg}_y\text{-LFP}$ ($y = 0, 1, 2, 3$, and 4).

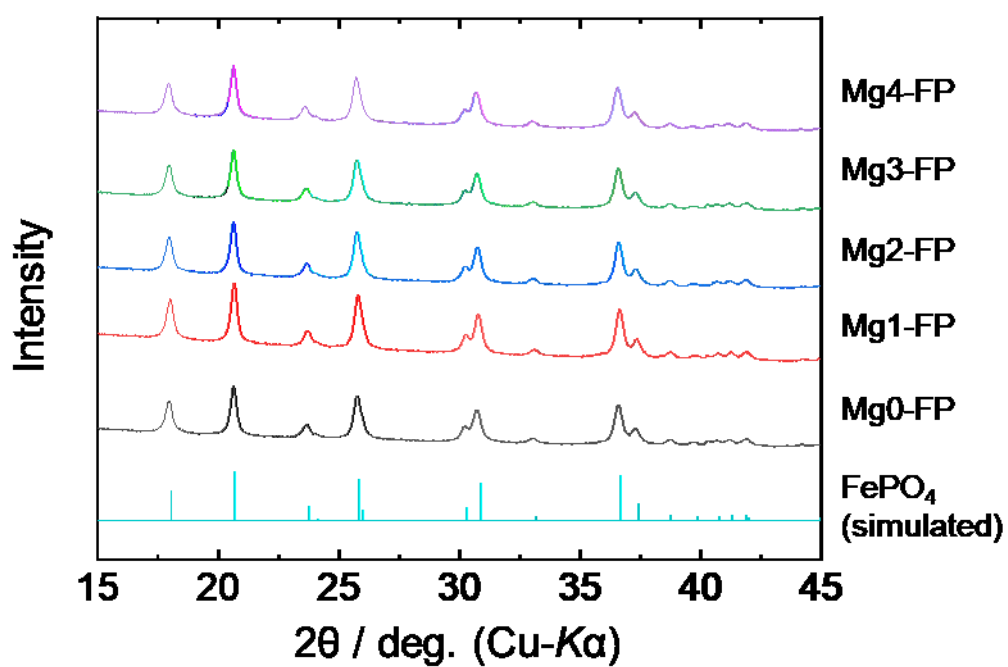


Figure 6-5. XRD patterns of the obtained Mg-doped FePO₄/C (Mg_y-FP ($y = 0, 1, 2, 3$, and 4)). The simulated patterns are calculated based on crystallographic data in previous reports [15] using VESTA software.

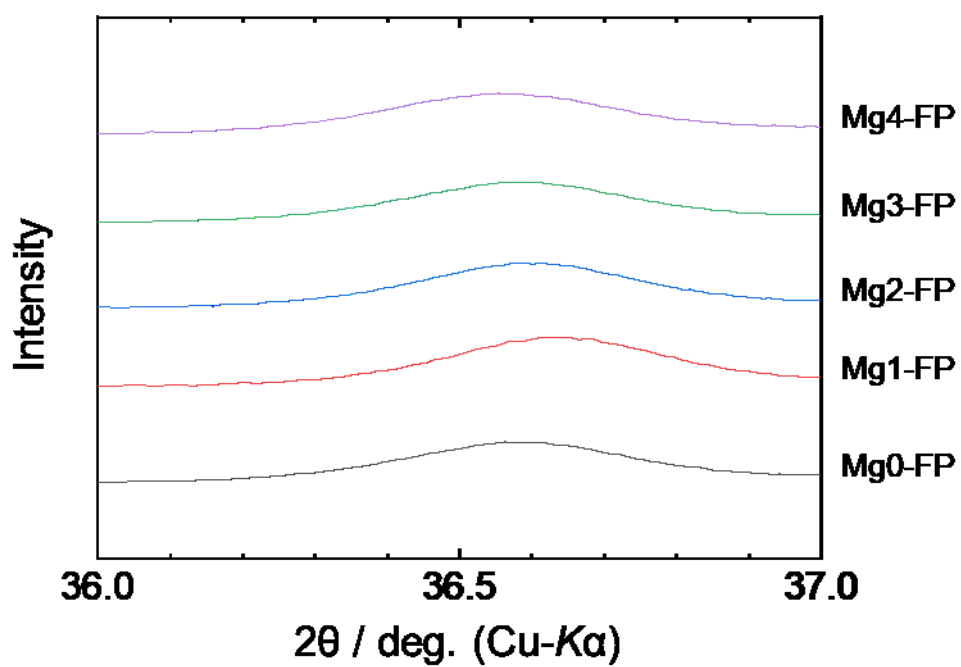


Figure 6-6. Enlarged XRD patterns of the Mg γ -FP ($\gamma = 0, 1, 2, 3$, and 4) around $2\theta = 36.6^\circ$.

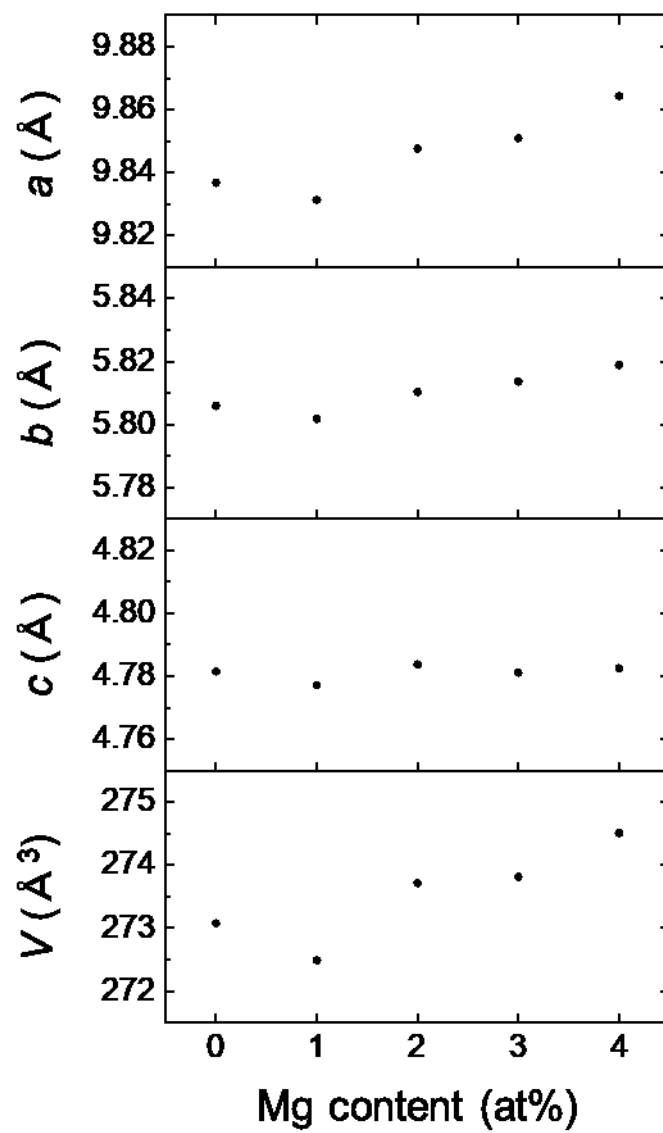


Figure 6-7. Lattice parameters and unit cell volume of the $\text{Mg}_y\text{-FP}$ ($y = 0, 1, 2, 3$, and 4) as a function of Mg concentration.

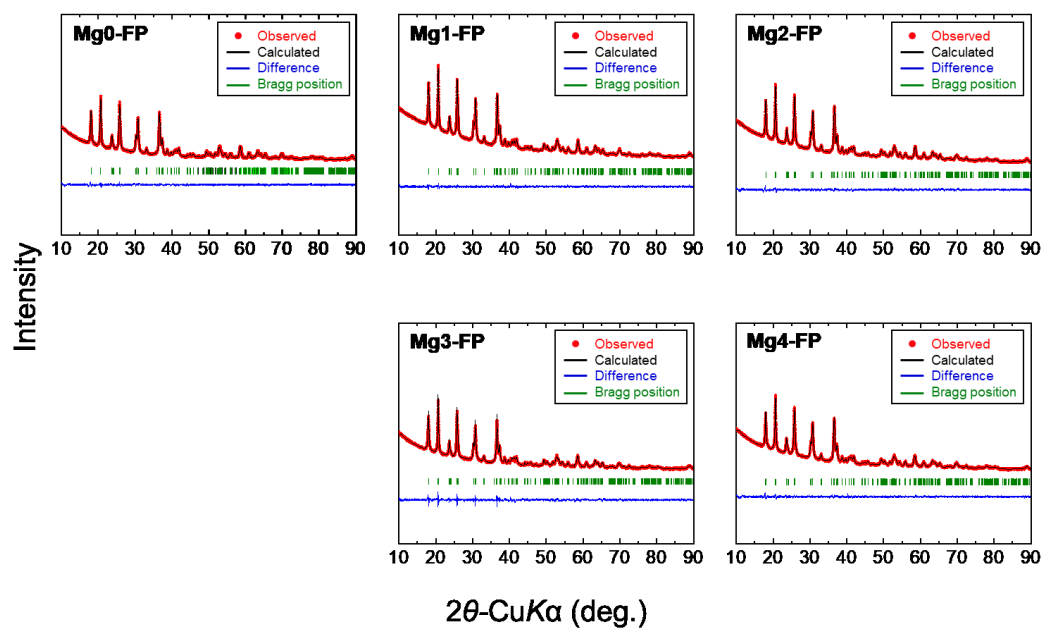


Figure 6-8. Rietveld refinement results of the Mg_y-FP ($y = 0, 1, 2, 3$, and 4).

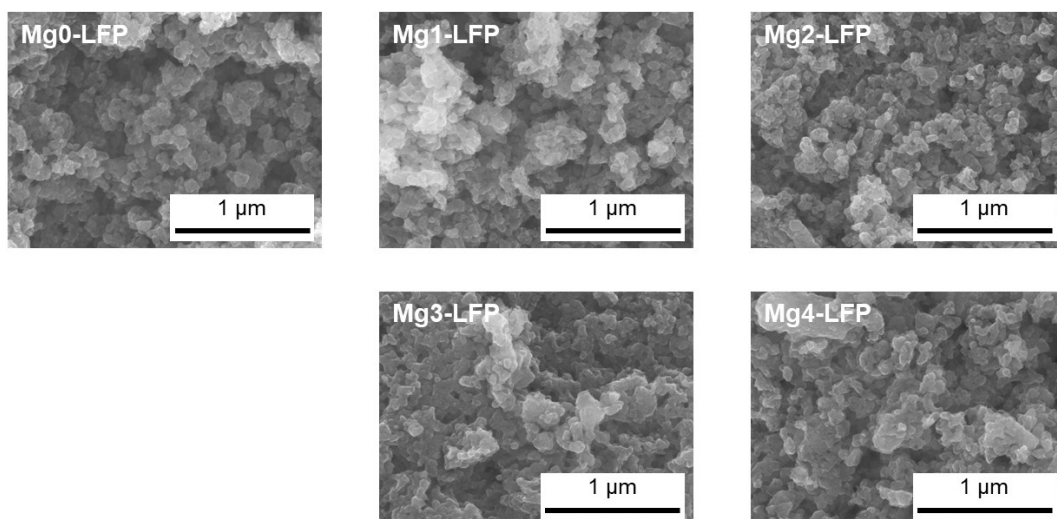


Figure 6-9. SEM images of the $\text{Mg}_\gamma\text{-LFP}$ ($\gamma = 0, 1, 2, 3$, and 4).

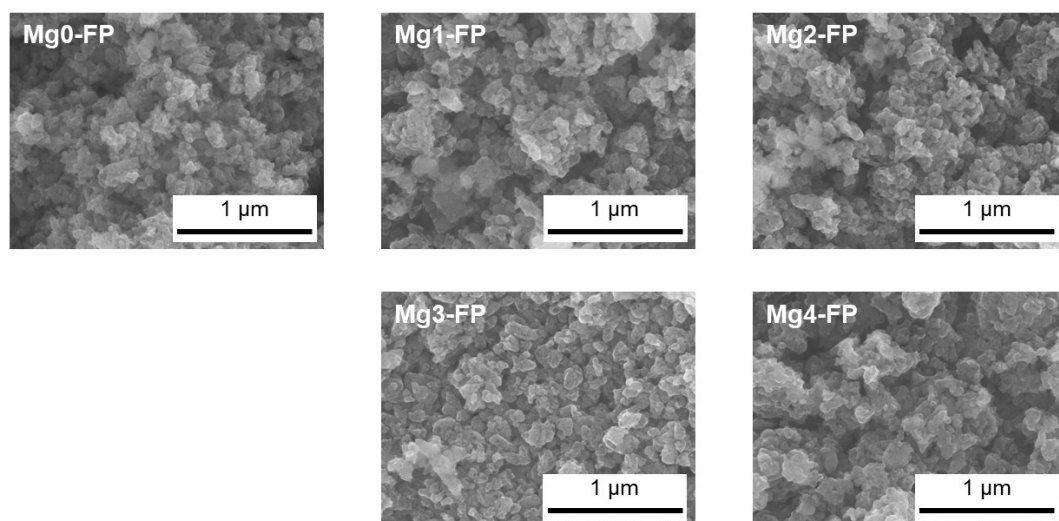


Figure 6-10. SEM images of the Mg γ -FP ($\gamma = 0, 1, 2, 3,$ and 4).

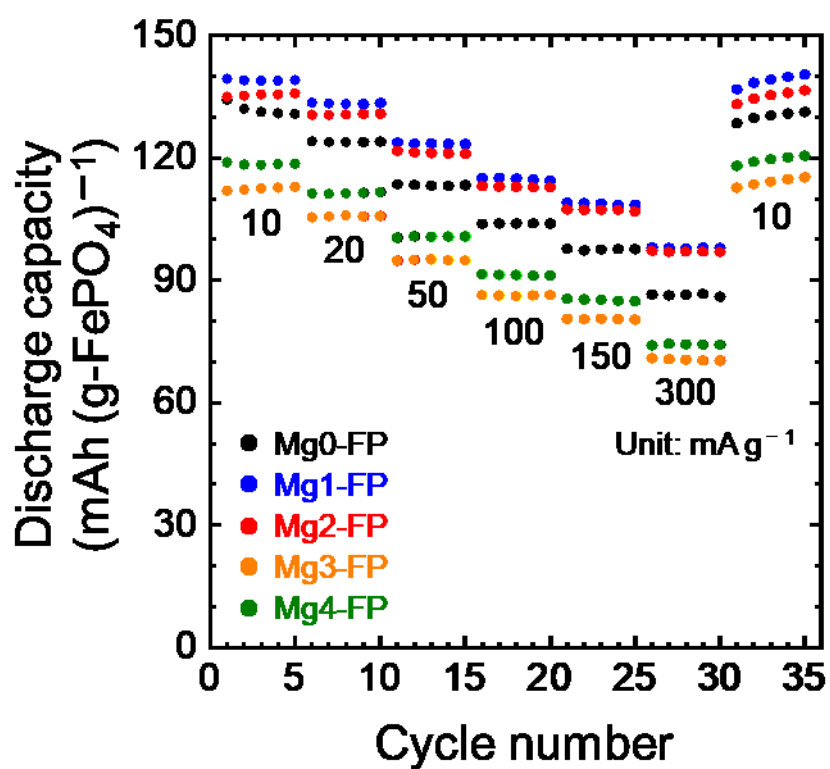


Figure 6-11. Rate capability of Na/Mg_y-FP ($y = 0, 1, 2, 3$, and 4) half cells at varied current rates (10, 20, 50, 100, 150, and 300 mA (g-FePO₄)⁻¹).

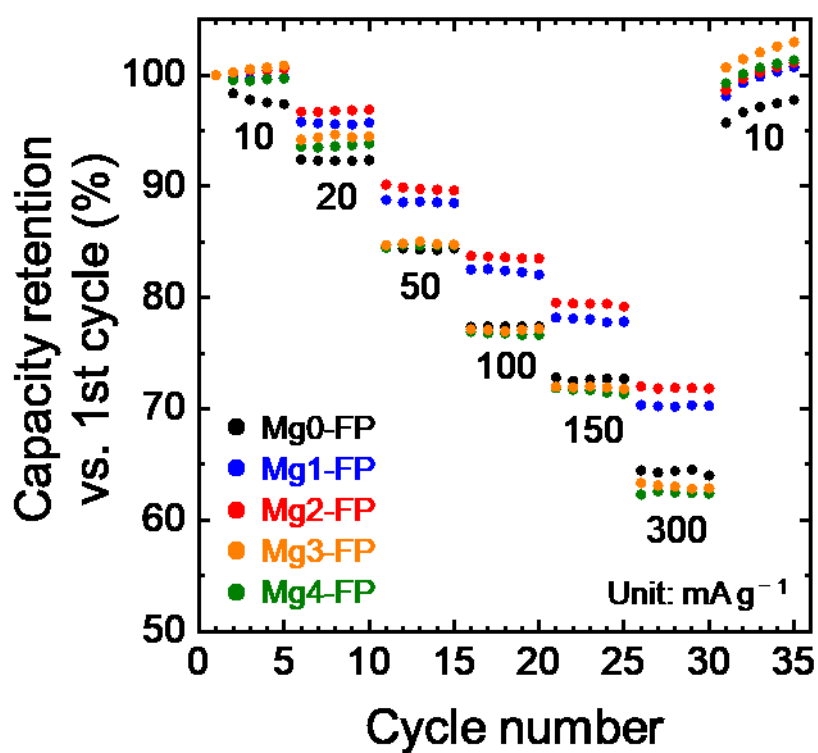


Figure 6-12. Capacity retention ratio based on the first discharge capacity of Na/Mgy-FP ($y = 0, 1, 2, 3$, and 4) half cells during rate capability tests.

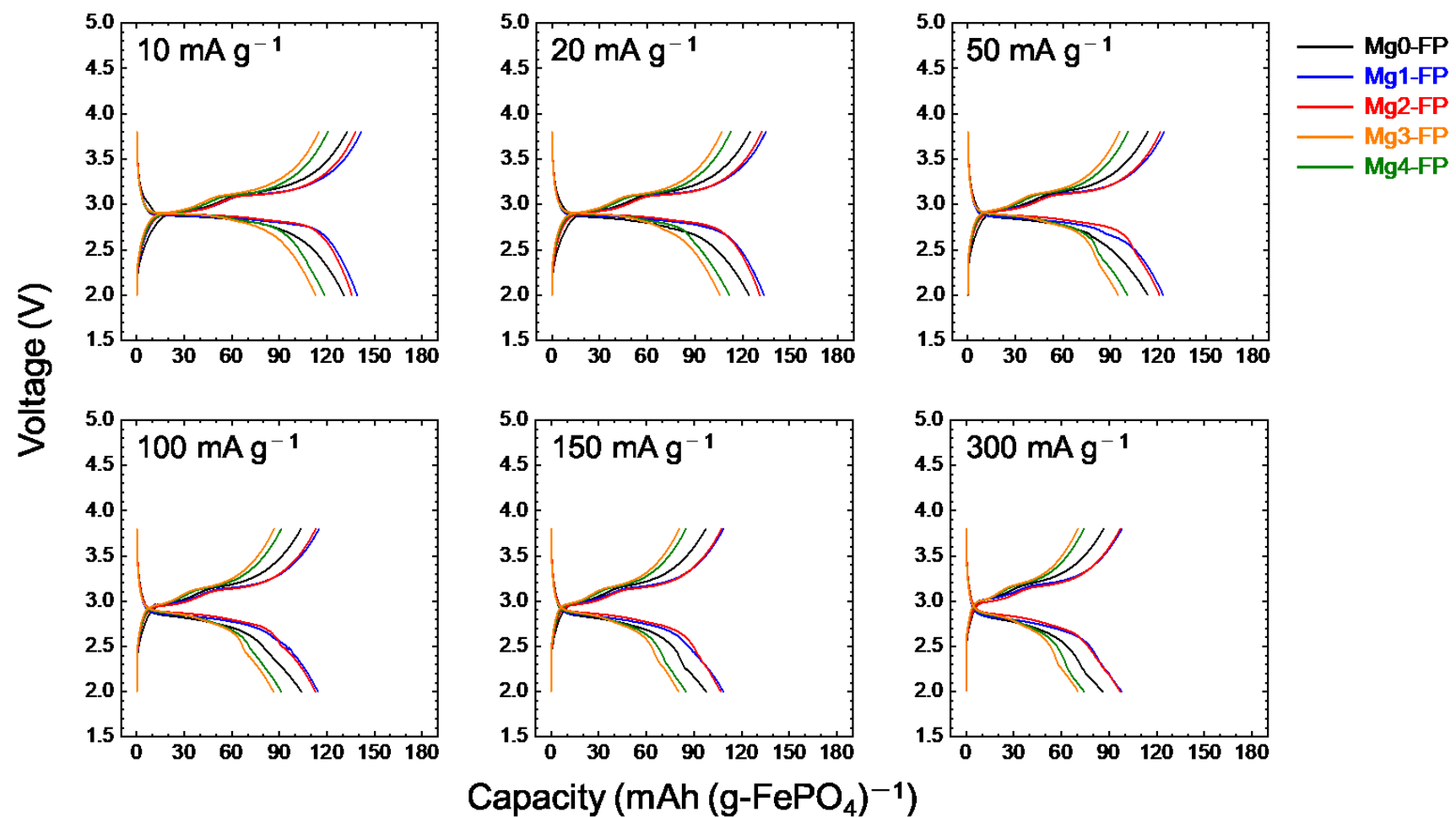


Figure 6-13. Charge-discharge curves of Na/Mgy-FP ($y = 0, 1, 2, 3, \text{ and } 4$) half cells at each current rate.

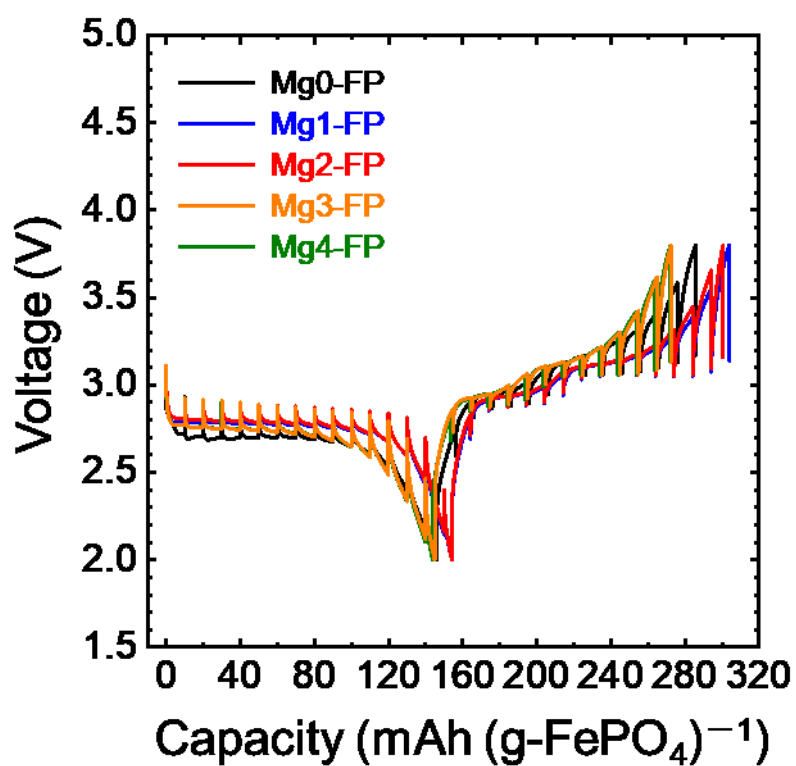


Figure 6-14. GITT curves for Na/Mgy-FP ($y = 0, 1, 2, 3,$ and 4) half cells at $10 \text{ mA (g-FePO}_4\text{)}^{-1}$ with a relaxation time of 5 h .

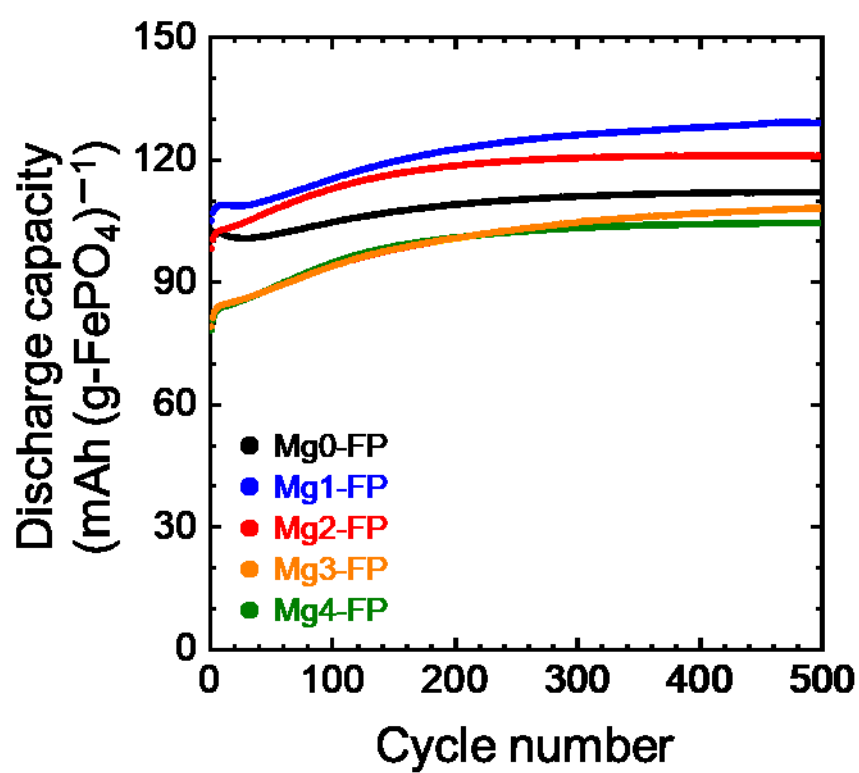


Figure 6-15. Cycle performances of $\text{Mg}_y\text{-FP}$ ($y = 0, 1, 2, 3, \text{ and } 4$) at $100 \text{ mA (g-FePO}_4\text{)}^{-1}$.

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Chapter 7

General Conclusions

There is a pressing need to develop environmentally friendly and cost-effective energy storage systems to meet the increasing societal demand for sustainability and to promote renewable energy usage. Amid rising prices of elements like Co and Ni, which are commonly used in layered oxide type positive electrode materials for lithium-ion batteries (LIBs), LiFePO_4 has regained attention as a promising alternative due to its resource advantages. However, to further promote a sustainable society and achieve higher-energy-density batteries, the development of next-generation batteries such as sodium-ion batteries (SIBs), lithium metal batteries (LMBs), and sodium metal batteries (SMBs) is essential. Chemical oxidation using oxidizing agents presents a compelling approach, offering the potential to uncover insights beyond the reach of electrochemical oxidation methods and to open up new avenues for material development and innovation. This doctoral dissertation explores the chemical oxidation methods of LiFePO_4 and the potential applications of chemically oxidized LiFePO_4 in next-generation batteries.

Chapter 3 proposed the LiFePO_4 oxidation technique using Cl_2 gas to produce FePO_4 which is used as an electrode material for SIBs. This study revealed that Cl_2 gas did not damage the host framework of the heterosite-structured FePO_4 . The delithiated FePO_4 demonstrated a highly stable sodium insertion/extraction reaction between

heterosite FePO_4 and triphylite NaFePO_4 over 1000 cycles with a high capacity retention of 88.6%. As revealed in Chapter 4, LiFePO_4 can also be oxidized using O_2 gas. However, Cl_2 gas, which is used with acetonitrile as a solvent, allows for processing in non-aqueous systems, making it suitable for handling materials sensitive to water. These findings underscore the potential of chemical oxidation of electrode materials using Cl_2 gas as an effective technique for the mass production of oxidized materials.

Chapter 4 focused on a sustainable FePO_4 production route from LiFePO_4 using O_2 gas. The obtained FePO_4 showed comparable electrochemical performance to those prepared by other oxidation methods. This work also demonstrated that the extracted lithium during the delithiation process was recovered as lithium acetate that can be used to resynthesize LiFePO_4 , enabling closed-loop lithium recycling and a more sustainable FePO_4 production. The obtained FePO_4 was utilized as a positive electrode for SMBs, and an SMB in this study exhibited highly stable cycle performance and a relatively high gravimetric energy density ($300 \text{ Wh (kg-Na} + \text{FePO}_4)^{-1}$) comparable to the conventional SMBs. These results highlight a state-of-the-art technology that simultaneously achieves sustainability through lithium recovery and high-energy-density battery through SMB application.

Chapter 5 further expanded the LiFePO_4 oxidation technique using O_2 gas to LMBs. This study demonstrated the concept of charged-state lithium metal batteries (CSLMBs), where the initial cell configuration consists of a charged-state positive electrode (FePO_4) combined with a lean lithium metal negative electrode, showcasing

superior cycle stability and higher energy density. This study offers a potential approach involving the reuse of spent LiFePO_4 electrodes to recover Li source while utilizing the remaining FePO_4 for CSLMB applications.

Chapter 6 investigated the effect of Mg doping into heterosite FePO_4 on the electrochemical performances as an electrode for SIBs to address the challenge of the limited electrochemical performance of triphylite NaFePO_4 and heterosite FePO_4 at room temperature. The 1% and 2% Mg-doped FePO_4 produced from Mg-doped LiFePO_4 showed improved discharge capacity and rate capability, benefiting from the enhanced electronic and ionic conductivity due to Mg doping. This work demonstrates the potential of doping to enhance the performance of FePO_4 as an electrode for SIBs, contributing to the development of high-performance batteries while promoting sustainability.

Overall, the findings gained from these studies contribute to the development of sustainable and high-energy-density next-generation secondary batteries utilizing heterosite FePO_4 electrodes. The chemical oxidation technology of LiFePO_4 enables lithium recovery, and the resulting FePO_4 can be applied to next-generation batteries including SIBs, LMBs, and SMBs, promoting the development of more sustainable secondary batteries. These insights are expected to drive the innovation and practical application of higher-performance, more sustainable, and cost-effective secondary batteries.

List of Publications

Chapter 3

Fumiyasu Nozaki, Sho Shomura, Jinkwang Hwang, Kazuhiko Matsumoto, Rika Hagiwara

ACS Sustainable Chemistry & Engineering, 11 (2023) 1037-1043.

“Delithiation of LiFePO_4 with Cl_2 Gas: Preparation of FePO_4 for Sodium-Ion Batteries with High Li Recovery”

Chapter 4

Fumiyasu Nozaki, Shaoning Zhang, Martin Hoffmann Petersen, Jinkwang Hwang, Jin Hyun Chang, Juan María García-Lastra, Kazuhiko Matsumoto

Energy & Environmental Science, in press, <https://doi.org/10.1039/D4EE03951C>.

“Oxygen-Powered Sustainable FePO_4 Preparation for Sodium Metal Batteries with Li Acetate Recovery”

Chapter 5

Fumiyasu Nozaki, Jinkwang Hwang, Kazuhiko Matsumoto

Advanced Energy and Sustainability Research, under review.

“Sustainable Reuse of FePO_4 for Charged-State Lithium Metal Battery with High Energy Density and Stable Cycle Performance”

Chapter 6

Fumiyasu Nozaki, Jinkwang Hwang, Kazuhiko Matsumoto

To be submitted.

“Mg-doped Heterosite FePO₄ for Sodium-Ion Batteries”

Related work

Huazhen Liu*, Fumiyasu Nozaki*, Jinkwang Hwang, Kazuhiko Matsumoto

Journal of Power Sources, 630 (2025) 236172.

“Journey of Olivine Materials from Classic to State-of-the-Art Technologies for Next-Generation Batteries”

*Equally contributed.

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Fumiyasu Nozaki