Recent research progress on iron- and manganese-based positive electrode materials for rechargeable sodium batteries

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Abstract

Large-scale high-energy batteries with electrode materials made from the Earth-abundant elements are needed to achieve sustainable energy development. On the basis of material abundance, rechargeable sodium batteries with iron- and manganese-based positive electrode materials are the ideal candidates for large-scale batteries. In this review, iron- and manganese-based electrode materials, oxides, phosphates, fluorides, etc, as positive electrodes for rechargeable sodium batteries are reviewed. Iron and manganese compounds with sodium ions provide high structural flexibility. Two layered polymorphs, O3- and P2-type layered structures, show different electrode performance in Na cells related to the different phase transition and sodium migration processes on sodium extraction/insertion. Similar to layered oxides, iron/manganese phosphates and pyrophosphates also provide the different framework structures, which are used as sodium insertion host materials. Electrode performance and reaction mechanisms of the iron- and manganese-based electrode materials in Na cells are described and the similarities and differences with lithium counterparts are also discussed. Together with these results, the possibility of the high-energy battery system with electrode materials made from only Earth-abundant elements is reviewed.

Keywords: sodium batteries, insertion materials, abundant elements

1. Introduction

The demand for advanced energy storage technology is rapidly increasing throughout the world. A large-scale energy storage system for the grid is undoubtedly necessary for the efficient use of electrical energy and for peak shift operation [1]. Such energy storage devices may also be utilized to store electricity generated from solar cells and wind turbines as green energy resources. Over the last two centuries, a number of energy storage devices based on electrochemical reactions as the driving force have been commercialized. Among them, the lead-acid battery is the oldest (invented in 1860 [2]), but it is still widely used in our daily life, especially for starting, lighting, and ignition batteries in automobiles. Additionally, lead-acid batteries are used in part for electrical energy storage (EES) [1]. Although lead-acid batteries are durable and reliable energy storage devices, their volumetric gravimetric energy density is relatively low among currently commercialized rechargeable batteries. Moreover, some lead compounds are known to be extremely toxic to humans, and
Therefore, lead-acid batteries may present environmental hazards without a well-established battery recycling system such as those used in developed countries.

Rechargeable lithium batteries (often called Li-ion batteries, or LIBs) have become the most successful and sophisticated energy storage devices since their commercialization in 1991. LIBs were originally developed as a power source with high energy density for portable electronic devices. LIBs are now used as an alternative power source for electric motors in motor vehicles instead of combustion engines with a fuel tank. Electric vehicles equipped with large-scale lithium batteries as power sources have been introduced into the automotive market, which may reduce the energy dependence of future transportation systems on fossil fuels. Although the available energy density is inevitably lower when compared with that of cobalt/nickel-based layered materials used for small-scale batteries, spinel-type LiMn$_2$O$_4$ is often used in current large-scale batteries.

Manganese-based materials, and preferably iron-based materials, are used because of the abundance of Mn in the Earth’s crust (figure 1). Although lithium batteries with manganese/iron-based materials potentially provide a solution to the tough challenge of achieving sustainable energy development, we must reconsider the feasibility of lithium [7], which is the element inherent in lithium batteries. The relative abundance of lithium in the Earth’s crust is only 20 ppm, as shown in figure 1 and table 1 [8]. Indeed, the cost of materials is increasing following the commercialization of lithium batteries [9]. Moreover, lithium resources are unevenly distributed (mainly in South America), and therefore, the production of LIBs depends on the import of lithium from South America. In contrast, sodium resources are unlimited everywhere, as sodium is one of the most abundant elements in the Earth’s crust. Vast sodium resources are also found in the ocean. Additionally, sodium is the second-lightest and second-smallest alkali metal next to lithium. On the basis of material abundance and standard electrode potential, rechargeable sodium batteries (i.e., Na-ion batteries, or NIBs) are the ideal alternative to LIBs [9-11].

NIBs are operable at ambient temperature without metallic sodium, which is different from commercialized high-temperature sodium-based technology, e.g., Na/S [12] and Na/NiCl$_2$ [13] batteries. These batteries utilize alumina-based solid (ceramic) electrolyte and therefore require high-temperature operations (∼300 °C) to increase the conductivity of sodium ions in the solid electrolyte. Because molten sodium and sulfur are used as active materials at high temperatures, safety issues regarding these batteries are not fully resolved for consumer appliances. In contrast, NIBs consist of two different sodium insertion materials as positive and negative electrodes with aprotic solvent as electrolyte and therefore are free from metallic sodium unless unfavorable reactions (e.g., overcharge) cause battery failure. Structures, components, systems, and reaction mechanisms are essentially the same except that lithium ions are replaced with sodium ions [10].

Historically, studies of Li$^+$/Na$^+$ ions as charge carriers for electrochemical energy storage at ambient temperature were begun before 1980. Electrochemical lithium insertion into TiS$_2$ and its application for energy storage devices were first proposed in the 1970s [14, 15]. Soon after that report, electrochemical and highly reversible sodium insertion into TiS$_2$ at room temperature was demonstrated in 1980 [16]. Electrode performance of lithium cobalt oxide, LiCoO$_2$, which is a lithium-containing layered oxide and is still widely used as a high-energy positive electrode material in LIBs, was first reported in 1980 [17]. Similarly, electrochemical properties of sodium-containing layered oxides, Na$_{x}$CoO$_2$, were also...
reported [18]. The early history of sodium insertion materials was reviewed in 1982 [19]. Nevertheless, in the last three decades, significant research efforts have been undertaken only for LIBs, and studies of sodium insertion materials for energy storage became almost nonexistent at one point. This difference may originate from the fact that available energy density was much lower for the Na system compared with the Li system. Figure 2 compares typical charge/discharge curves of Li/LiCoO₂ and Na/NaCoO₂ cells. Because the ionic radius of cobalt is relatively small compared with those of both lithium and sodium ions, as shown in table 1, layered materials with both Li and Na are easily prepared. Although both samples have the same crystal lattice built up by sheets of edge-sharing CoO₆ octahedra, the operating voltage of LiCoO₂ for the region at end of discharge (start of charge) is >1.0 V higher than that of NaCoO₂. When both cells are charged to >100 mAh g⁻¹, the difference in voltage decreases to approximately 0.4 V, which is similar to the difference in standard electrochemical potential for Li (−3.04 V) and Na (−2.71 V). The reduction of voltage becomes significant with the increase in the Na content. As a result, the available energy density of Na₃CoO₂ as positive electrodes is approximately 30% lower than that of Li₃CoO₂ (figure 2). This fact also suggests that different chemistry compared with the Li system is needed to overcome the problem of low energy density for NIBs.

In this article, iron- and manganese-based materials—oxides, phosphates, fluorides, etc—are reviewed as positive electrodes for NIBs. Iron and manganese compounds containing reversibly extractable sodium ions provide high structural flexibility. Therefore, many materials with different crystal structures are easily prepared under thermodynamic equilibrium conditions, as shown in this article. Moreover, interesting electrode chemistry is found in the compounds containing trivalent iron ions in Na cells. For instance, O₃-type layered LiFeO₂ is electrochemically inactive in Li cells, whereas NaFeO₂, which possesses the same crystal structure, is surprisingly active in Na cells, as first reported by Okada and co-workers [20, 21]. The abundance of iron is an important factor for NIB electrode materials. A combination of Na and Fe is attractive as a battery system, especially for EES, and could become competitive with the LiCoO₂/graphite system, which is the system most widely used in LIBs with high energy density, when innovation in materials (e.g., high-voltage materials) for iron-based sodium insertion is achieved.

Figure 3. The classification of Na–Me–O layered materials with the sheets of edge-sharing MeO₆ octahedra and phase transition processes induced by sodium extraction. See the text for more details.
2. Layered oxides as Na insertion host materials

2.1. Classification of layered structures

Na-containing 3d-transition metal layered oxides are widely studied as positive electrode materials for NIBs. The most common layered structures are built up from a sheet of edge-sharing MeO₆ octahedra. Polyhedron polymorphs appear when these sheets are stacked in different ways along the c-axis. Sodium-based layered materials can be categorized into two main groups using the classification proposed by Delmas et al [22]: O₃ type or P₂ type, in which the sodium ions are accommodated at octahedral and prismatic sites, respectively, as shown in figure 3. Schematic illustrations of crystal structures used in this article were drawn using the VESTA program [23]. O₃-type NaMeO₂ consists of a cubic close-packed (ccp) oxygen array, in which sodium and 3d-transition metal ions are accommodated at distinct octahedral sites because the ionic radius of sodium ions (1.02 Å) is much larger than those of 3d-transition-metal ions in the trivalent state (≤0.7 Å) [24]. O₃-type layered phases are classified as cation-ordered rock-salt superstructure oxides [25]. Edge-shared NaO₆ and MeO₆ octahedra are ordered into alternate layers perpendicular to [111] for the rock-salt lattice (corresponds to [001] for the crystal lattices used for layered structures), forming the NaO₂ and MeO₂ slabs, respectively. As a layered structure, Na₂MeO₃ is composed crystallographically of three different MeO₂ layers (AB, CA, and BC layers in figure 3, and the layered stacking of MeO₂ is isosstructural with that of CdCl₂) to describe the unit cell, and sodium ions are accommodated at the octahedral (O) sites between MeO₂ layers. The structure is therefore classified as an O₃-type layered structure. The structure is also classified as 3R phase with a space group (SG) of R₃m. P₂-type Na₃MeO₆ also consists of two MeO₂ layers (AB and BA layers). However, the sodium environment is different from that of the O₃ type. Because sodium ions are much larger than lithium ions, sodium ions can also be located at trigonal prismatic (P) sites. When a sodium off-stoichiometry condition (typically 0.6 < x ≤ 0.7) is applied to materials synthesis, the P₂-type phase is empirically known to be structurally stabilized. The P₂-type layered structure is also often classified as 2H phase with an SG of P6₃/mmc. Moreover, a prime symbol (') is added to the abbreviation when the crystal lattice contains in-plane distortion, such as O′₃-type NaMnO₂ with a monoclinic lattice (SG C2/m) [26] and P′₂-type Na₃MnO₆ with an orthorhombic lattice (SG Cmcm) [27]. These layered oxides can be easily prepared by conventional solid-state reaction from a mixture of a stoichiometric amount of a sodium salt (sodium carbonate, sodium peroxyde, etc) with 3d-transition metal oxides (and hydroxides, carbonates, etc). See the literature cited in this review article about the detailed synthesis conditions for each sample.

Sodium extraction from O₃- and P₂-type phases generally induces phase transitions. Sodium ions in the O₃-type phase are originally stabilized at edge-shared octahedral sites with MeO₆ octahedra. Prismatic sites for Na ions often become energetically stable when sodium ions are partially extracted from the O₃-type phase—associated with the formation of vacancies, similar to the P₂-type phase. The formation of prismatic sites is achieved by the glideing of MeO₂ slabs without breaking Me-O bonds [18, 22]. As a result, oxygen packing changes from ‘AB CA BC’ to ‘AB BC CA’, and this phase is classified as P₃-type, as shown in figure 3. It is also possible to directly crystallize this P₃-type phase by solid-state reaction without electrochemical sodium extraction in Na cells in some cases. For instance, P₃- and P₂-type Na₂/3[Ni₁/₃Mn₂/₃]O₂ are known as low- and high-temperature phases, respectively [28]. The phase transition from P₃/O₃-type to P₂-type phase is, however, impossible in Na cells because its phase transition is achieved only by breaking/re-forming Me–O bonds, and a higher-temperature environment is therefore required.

Instead, the P₂ phase changes into an O₂-type phase in Na cells (figure 3). Because large prismatic sites in the P₂-type phase are energetically stabilized by large sodium ions, MeO₂ slabs move (glide) to form octahedral sites after the extraction of sodium ions [29, 30] (assisted also by Na"Li" ion exchange [31]). Such MeO₂ gliding leads to the formation of a new phase with a unique oxygen packing, ‘AB AC AB’ (figure 3). This phase contains crystallographically two different MeO₂ layers with AB and AC oxygen arrangements. Vacancies left between AB and AC layers are octahedral sites, that is, the O₂-type phase. Both O₃- and O₂-type phases have close-packed oxygen arrays. In the O₃-type phase with the ccp array (ABC-type oxygen arrangement), Na₂O₃ layers share only edges with MeO₂ layers on both sides. In contrast, the O₂-type phase is locally composed of ABA-type and ACA-type (figure 3) oxygen arrangements; namely, local structures are classified as a hexagonal close-packed (hcp) oxygen array. On the basis of oxygen packing, the O₂-type structure is classified as an intergrowth structure between ccp and hcp arrays. Note that two glide vectors of MeO₂ slabs, (1/3, 2/3, z) and (2/3, 1/3, z), exist to form the O₂ phase. This often induces the formation of stacking faults after sodium extraction from the P₂ phase [29]. Although only a few studies of the P₂-O₂ phase transition in Na cells have been reported so far [29, 30], a number of reports on P₂–O₂ phase transitions via Na"Li" ion exchange, including the formation of a variety of stacking faults, are available in the literature [28, 31–36].

2.2. O₃-type NaFeO₂

Alpha-NaFeO₂ is known as a typical example of O₃-type layered structures and is easily prepared by conventional solid-state reaction [37]. In contrast, there are no reports of direct synthesis of LiFeO₂ with O₃-type layered structures by solid-state reaction. Because the ionic radii of Li⁺ and Fe³⁺ are similar (table 1), the cation-disordered rock-salt phase is easily obtained by solid-state reaction at high temperatures. However, the single phase of LiFeO₂ has been successfully obtained by hydrothermal treatment at 230 °C with concentrated KOH aqueous solution so that the synthesized LiFeO₂ was electrochemically inactive in the Li cells [38]. Instead, triphylite-type LiFePO₄ has been
extensively studied with a view to developing iron-based positive electrode materials for LIBs [39]. Electrochemical reversibility of sodium extraction/insertion processes for a single phase of O3-type NaFeO2 is shown in figure 4(a). Electrochemical Na extraction from NaFeO2 using a Li/NaFeO2 hybrid-ion cell was first demonstrated by Takeda and co-workers [40]. Reversible charge and discharge processes for a Na/NaFeO2 cell were first reported by Okada and co-workers as previously mentioned [20, 21]. Reversibility in electrode materials is significantly influenced by cutoff conditions upon charge (sodium extraction) as shown in figure 4. Although charging capacity, corresponding to

Figure 4. (a) Galvanostatic charge/discharge curves of Na/NaFeO2 cells [41]. (b) Changes in XANES spectra of Na_{1−x}FeO2 at the Fe K-edge and (c) the radial distribution functions obtained from EXAFS spectra. The area of pre-edge peaks of the Fe K-edge is enlarged in the inset in (b). (d) A proposed mechanism of the iron migration process during sodium extraction.
amounts of sodium ions extracted from the crystal lattice, increases as a function of cutoff voltage, reversible capacity obviously decreases when the material is charged beyond 3.5 V. Excellent reversibility with small polarization is observed with the cutoff voltage of 3.4 V. The observed reversible capacity reaches 80 mAh g$^{-1}$, indicating that approximately 0.3 mole of Na is reversibly extracted from NaFeO$_2$ and inserted into the Na$_{0.7}$FeO$_2$ host structures. Such deterioration of the electrode properties beyond 3.5 V originates from the irreversible phase transition as suggested by ex situ x-ray diffraction (XRD) [41] and x-ray absorption spectroscopy (XAS) in figures 4(b), (c). Intensity of the pre-edge peak, which is observed at 7114 eV in x-ray absorption near the edge structure (XANES), increases with the increase in the sodium extraction amount. The intensity of the pre-edge peak for Fe$^{3+}$ is often intensified when iron ions are located at tetrahedral sites [42]. In addition, clear changes in the local environment of Fe are noted from the extended x-ray absorption fine structure (EXAFS). Decreases in length for the first coordination shell (Fe–O bond) and in intensity for the second coordination shell (Fe–Fe bond) are also found. These facts suggest that some of the Fe$^{3+}$

Figure 5. Comparison of galvanostatic charge/discharge curves of layered Na$_{x}$MeO$_2$ samples with different structures. The morphology of particles for each sample is shown in the right-hand column.
ions migrate into the tetrahedral sites. Note that because the XAS spectra were collected after discharge to 2.0 V in Na cells, this Fe$^{3+}$ migration process is irreversible. A proposed degradation mechanism is summarized in figure 4(d). When sodium ions are extracted from the crystal lattice, vacancies are created at tetrahedral sites that are face-shared with FeO$_6$ octahedra. Because trivalent iron ions are energetically stabilized at tetrahedral sites, iron ions easily migrate to the face-shared sites, similar to LiCo$_{1-x}$Fe$_x$O$_2$ [43]. Solid-state diffusion of sodium ions is easily disturbed by iron at tetrahedral sites, leading to the degradation of electrode properties. As a result, the reversible range of Na$_x$FeO$_2$ is limited to be narrow. This reversible process in the Na cell is expressed as follows:

$$\text{NaFeO}_2\xrightarrow{\text{oxidation}} \text{Na}_0.1\text{FeO}_2 + 0.3\text{Na}^+ + 0.3\text{e}^-$$ (1)

where the open square denotes the vacant sites created in the structure. The energy density available in terms of electrode material is also limited (300 mWh g$^{-1}$ vs Na). Although the reversible range is narrow, the rather small polarization between charge/discharge processes with sub-micrometer-size particles is attractive in terms of electrode material, as shown in figure 5. The rate capability of Na$_x$FeO$_2$ in Na cells is shown in figure 6(a). Such cells can deliver >50% of discharge capacity at 1 C rate. (The C rate is defined as the current that delivers a nominal capacity in 1 h, and the nominal capacity here is defined as one-electron redox of iron, i.e., 241 mA g$^{-1}$).

Another drawback of NaFeO$_2$ as an electrode material is the Na$^+/H^+$ ion exchange when NaFeO$_2$ is in contact with water [44]. NaFeO$_2$ changes into FeOOH and NaOH (Na$_2$CO$_3$ and/or NaHCO$_3$ by uptake of CO$_2$). Such Na$^+/H^+$ ion exchange is generally observed in O3-type NaMeO$_2$.

Recently some iron-based layered materials have also been reported with a wider reversible range. In these materials, Ni, Mn, and Co ions are partially substituted for Fe ions [45, 47]. The metal substitution effectively changes the phase transition behavior for NaFeO$_2$. For the pure iron system, the crystal structure of Na$_{0.5}$FeO$_2$ was reported as an O$3$-type phase with monoclinic lattice distortion [48]. O$3$–P$3$ phase transition is not evidenced for Na$_x$FeO$_2$ and, therefore, such iron migration to adjacent face-shared tetrahedral sites may be unavoidable. The O$3$–P$3$ phase transition in Na cells, however, occurs for the metal-substituted NaFe$_{1-x}$Me$_x$O$_2$ samples. Because iron migration to the large prismatic sites is expected to be unlikely, the formation of the P$3$ phase can effectively extend reversible ranges for the electrode materials in Na cells. Stabilization of the P$3$ phase has also been theoretically predicted for Na$_{0.5}$MeO$_2$ (Me = Ni, Mn, and Co) [49]. Among layered materials with 3$d$-transition metal ions, the P$3$-type phase is significantly stabilized for Na$_x$CoO$_2$ [49], and excellent electrode performance has been reported for NaFe$_{1/2}$Co$_{1/2}$O$_2$ [46] and NaNi$_{1/3}$Co$_{1/3}$Fe$_{1/3}$O$_2$ [50]. These experimental and theoretical approaches are consistent with each other, and the substitution of metal ions for iron ions is an important strategy to further improve the reversibility of iron-based O$3$-type layered materials.

2.3. O$3$-type NaMnO$_2$ and P$2$-type Na$_x$Mn$_2$O$_7$

O$3$-type LiMnO$_2$ is also known as a metastable phase [51–53], similar to O$3$-type LiFeO$_2$. The orthorhombic phase (zigzag-type layered phase) crystallizes as a thermodynamically stable phase. Although relatively large reversible capacity is obtained using O$3$-type and zigzag-type layered phases, lowering operating voltage (and changing the voltage profile) during continuous electrochemical cycling is known to be a disadvantage for electrode materials [54–57]. The voltage profile closely resembles that of spinel-type Li$_x$Mn$_2$O$_4$ after electrochemical cycle tests. These Li–Mn
oxides are composed of the common ccp oxygen lattice. Therefore, two polymorphs of LiMnO$_2$ easily transform into spinel as the energetically favorable phase during electrochemical cycles.

O’3-type NaMnO$_2$ with a monoclinic lattice (SG C$2/m$) [26] and P’2-type Na$_x$MnO$_2$ with an orthorhombic lattice (SG Cmcm) [27] are prepared as thermodynamically stable polymorphs of layered Na–Mn oxides. Non-distorted P2-Na$_x$MnO$_2$ with a hexagonal lattice (SG P6$_3$/mmc) is also obtained by controlling synthesis conditions [27]. Here only layered Na–Mn oxides are described, and the structural complexity of Na–Mn oxides will be further discussed in a later section. Electrochemical reversibility of Na extraction/insertion from/into O’3-type NaMnO$_2$ was first reported in 1985 [26]. A very narrow reversible range ($x$<0.2 in Na$_{1-x}$MnO$_2$) was, however, reported in this original publication. Electrochemical properties of O’3-type NaMnO$_2$ were revisited in 2011 [58], and it was found that O’3-type Na$_{1-x}$MnO$_2$ shows a wide reversible range ($x$<0.8). Although this reversible range is much wider than that of Na$_{1-x}$FeO$_2$, cyclability in the Na cell is insufficient for electrode materials. Large reversible capacity rapidly declines by subsequent electrochemical cycles. Selected charge/discharge curves of O’3-type NaMnO$_2$ are shown in figure 5. The Na/NaMnO$_2$ cell delivers 120–30 mAh g$^{-1}$ of reversible capacity (approximately 50% of Na ions are extracted/inserted) with small polarization. The operating voltage of Na$_{1-x}$MnO$_2$ is lower than that of Na$_{1-x}$FeO$_2$, as shown in figure 5.

Electrode performance of P2-Na$_x$MnO$_2$ was also examined in some early studies [26, 59]. Its reversible compositional range for Na extraction/insertion is wider than that of O’3 Na$_{1-x}$MnO$_2$. More than 150 mAh g$^{-1}$ of reversible capacity in the Na cell was reported in the early study [59]. The reversible limit is greatly increased ($x$≈0.8 in P2-Na$_x$MnO$_2$) when battery-grade (high-purity with <20 ppm of water) electrolyte solution is used [60]. Approximately 190 mAh g$^{-1}$ of reversible capacity with good capacity retention is obtained, as shown in figure 5. The electrode performance of P2-Na$_x$MnO$_2$ is much better than that of O’3-
Na$_{1-x}$MnO$_2$. Although in-plane conduction of electrons/holes in MnO$_2$ layers must be the same for both polymorphs, the difference is expected to originate from the manner of in-plane Na-ion conduction between MnO$_2$ layers. Schematic illustrations of in-plane Na-ion conduction in different phases are compared in figure 7. For the O3-type layered system, because direct hopping from one octahedral site to an adjacent octahedral site requires high activation energy, sodium ions migrate through interstitial tetrahedral sites (similar to O3-type Li$_x$CoO$_2$ [61]), which are face-shared sites with MeO$_6$ octahedra in MeO$_2$ layers. According to the results of first-principles calculations, the diffusion barrier of sodium ions (vacancies) in the O3-type layered framework structure is relatively small (180 meV for O3-type Na$_{1-x}$CoO$_2$ [62]). The diffusion barrier of sodium ions is expected to be slightly smaller than that of Li in O3-type Li$_x$CoO$_2$ (205 meV) [62]. In contrast with the O3-type layered system, because the P2-type layered framework has an open path for Na ions, a lower diffusion barrier than that of the O3-type phase is expected. Sodium ions migrate from one prismatic site to adjacent sites through open rectangular bottlenecks surrounded by four oxide ions (and thus smaller repulsive interaction from oxide ions is anticipated [63]) because of no interstitial tetrahedral sites dissimilar to the O3 structure. Indeed, higher ionic conductivity of P2-type layered materials than of O3-type layered materials is observed for the samples containing similar chemical compositions for sodium/vacancy [63]. Note that O3–P3 and P2–O2 phase transition may alter the mechanism of in-plane Na-ion diffusion. For instance, according to the results of first-principles calculation, the activation energy of Na-ion diffusion in P2-type Na$_x$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ ($2/3>x>1/3$) significantly increases (>100 meV) in O2-type Na$_x$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ ($1/3>x>0$) [64] even though the P2–O2 phase transition is unavoidable for Na$_x$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ in Na cells. On the other hand, O3-type Na$_x$[Fe$_{1/2}$Co$_{1/2}$]O$_2$ shows excellent rate capability in Na cells, which may originate from the fast ion conduction for the P3 phase formed by the O3–P3 phase transition in the desodiation process [46]. Note that the local environment of Na ions at prismatic sites and the diffusion pathway in the P2 and P3 phases are different, as shown in figure 7. It is expected, therefore, that the mobility of Na ions in both phases may be different. Although an NMR study on P2 and P3 Na$_x$CoO$_2$ suggested that the mobility of Na ions in both phases clearly differs on the NMR time scale [65], the difference in Na-ion mobility in terms of electrode materials is not known so far. Further systematic studies of the diffusion process of Na ions in these different phases are necessary.

2.4. O3-type Na[Fe$_{1/2}$Mn$_{1/2}$]O$_2$ and P2-type Na$_x$[Fe$_{1/2}$Mn$_{1/2}$]O$_2$

The electrode performance of P2-Na$_x$MnO$_2$ is promising based on reversible capacity as shown in the preceding section. The average operating voltage based on the Mn$^{3+}$/Mn$^{4+}$ redox couple is, however, limited to less than 3 V versus metallic Na. The average operating voltage of O3-NaFeO$_2$ with an Fe$^{3+}$/Fe$^{4+}$ redox couple is much higher (3.2–3.3 V) than that of P2 Na$_x$MnO$_2$, even though the figure 8. XAS analysis of the P2-type Na$_x$[Fe$_{1/2}$Mn$_{1/2}$]O$_2$ samples charged to 3.8 and 4.2 V: iron K-edge XANES (a) and radial distribution of the iron ion (b). (c) Comparison of the Mössbauer spectra of the as-prepared and the fully charged samples. Observed spectra are shown as black dots and deconvoluted spectra as colored lines. Here $s$ and $d$ represent sextet and doublet, respectively. The purple curve corresponds to the sextet component. This minor sextet component can be assigned to neither Fe$^{3+}$ nor Fe$^{4+}$. Instead, this component could be assigned to Fe$^{5+}$ because of a relatively low isomer shift. Fe$^{5+}$ probably originates from the charge disproportionation of Fe$^{4+}$ (Fe$^{4+}$→Fe$^{3+}$+Fe$^{5+}$) as reported in the literature [158, 159].
reversible range associated with irreversible iron migration is narrower. From these pieces of experimental evidence, P2-type Na2/3[Fe1/2Mn1/2]O2 is predictably considered to be a possible candidate for high-capacity, high-energy electrode material. All of our trials, however, failed because Fe4+ cannot be stabilized in the oxide-ion framework under ambient conditions [66]. Therefore, manganese ions were partially substituted for iron to stabilize the P2-type phase, and we finally succeeded in the synthesis of P2-type Fe-based layered oxide, Na2/3[Fe1/2Mn1/2]O2 [67]. P2-Na2/3[Fe1/2Mn1/2]O2 can be easily prepared via solid-state reaction of Na2O2 (or Na3CO3), Fe2O3, and Mn3O4 at 900 °C for 12 h [67]. The electrochemical performance of P2-type Na2/3[Fe1/2Mn1/2]O2 is also better than that of O3-NaFeO2 as compared in figure 5. P2-Na2/3[Fe1/2Mn1/2]O2 delivers large reversible capacity, similar to Na2/3[Fe1/2Mn1/2]O2 at the iron K-edge are also increased compared with P2-Na2/3MnO2; this will be discussed in a later section.

O3-type Na2/3[Fe1/2Mn1/2]O2 can be also prepared by changing the ratio of sodium/(iron and manganese) [67]. The electrode performance of O3-Na2/3[Fe1/2Mn1/2]O2 in the Na cell is shown in figure 5. Large polarization (>1 V) between oxidation (charge) and reduction (discharge) processes is observed when the Na cell is cycled in the voltage range 1.5–4.2 V. In comparison with the O3 phase, the P2 phase clearly shows larger reversible capacity. Because the P2 and O3 phases have similar particle morphology (figure 5), the kinetic limitation related to the diffusion length is not responsible for the difference in performance. Research interest in the Na–Fe–Mn system as high-capacity electrode material is rapidly increasing, and now the electrode performance for P2- and O3-Na2/3[Fe1/2Mn1/2]O2 with different chemical compositions has been determined [68–70].

Charge compensation mechanisms in the sodium extraction process were further analyzed by XAS. XANES spectra of P2-Na2/3[Fe1/2Mn1/2]O2 at the iron K-edge are shown in figure 8(a). When Na2/3[Fe1/2Mn1/2]O2 is oxidized from 3.8 V to 4.2 V, a shift in the iron K-edge absorption spectrum is found in the higher-energy region. The shift may be attributable to complicated situations, including changes in the local structures—for example, sodium extraction from the iron face-shared sites and phase transitions [67]. Therefore, EXAFS spectra during the sodium extraction were further analyzed. The change in the radial distribution around iron during oxidation to 4.2 V is shown in figure 8(b). The radial distribution around iron is not affected by oxidation to 3.8 V, and the interatomic distance of Fe–O remains unchanged (2.00 Å for the as-prepared and 1.99 Å for the 3.8 V charged state). The Fe–O local environment is markedly changed after oxidation to 4.2 V. The intensity for both first and second coordination shells, Fe–O and Fe–Fe(Mn), is reduced, indicating distortion around Fe. This distortion also influences the local structure of neighboring manganese ions [67]. The interatomic distance of Fe–O is clearly shortened after oxidation to 4.2 V (1.90 (1) Å). A large Debye–Waller factor indicates distortion by a non-cooperative Jahn–Teller effect of high-spin Fe4+ ($t_{2g}^3e_g^1$). Mössbauer spectroscopy further supports the oxidation of Fe3+ to Fe4+, as shown in figure 8(c). The oxidation of Fe4+ was also reported for O3-NaFeO2 by Mössbauer spectroscopy [20, 21]. The results indicate that Fe3+ in P2-Na2/3[Fe1/2Mn1/2]O2 is electrochemically active in the sodium system based on the Fe3+/Fe4+ redox. Note that O3-LiFeO2 is never electrochemically active on the basis of the Fe3+/Fe4+ redox [38], or the reaction seems to be dominated by the oxygen removal process at the solid/electrolyte interface. Indeed, nanometer-sized O3-type LiFeO2 is electrochemically active in association with the Fe7+/Fe3+ redox [71]. As the Fe3+ 3d-orbital is strongly hybridized with the oxygen 2p orbital in the Li system, oxygen removal is favorable rather than oxidation to Fe4+, similar to the Li2MnO3 system. In general, the sodium system shows a lower redox potential than that of the lithium system, as shown in figure 2. Sodium ions are strongly ionized when compared with lithium ions, resulting in lower covalency with oxygen. Iron and oxygen gain more (net) electrons when compared with the lithium system. As a result, the electrochemical potential of the Fe3+/Fe4+ redox is relatively low, approaching that of Na0Na+. Thus, the Fe3+/Fe4+ redox in P2-Na2/3[Fe1/2Mn1/2]O2 may be accessible without oxygen loss and may be used as electrode material with relatively high operating voltage in the Na system. Note that tetravalent iron provides the strong hybridization character with the oxygen 2p orbital. Indeed, charge transfer from oxygen to iron has been proposed for SrFeO3 [72]. The possibility of such a charge transfer process (namely, the formation of a hole in the oxygen 2p orbital instead of the formation of Fe4+) cannot be negligible for P2-Na2/3[Fe1/2Mn1/2]O2. Further systematic study is needed to understand the charge compensation process in greater detail.

As described previously, the available reversible capacity of P2-Na2/3[Fe1/2Mn1/2]O2 reaches 190 mAh g–1 with an average voltage of 2.75 V versus sodium metal. The energy density is estimated to be 520 mWh g–1 vs Na, which is comparable to that of LiFePO4 (about 530 mWh g–1 versus Li) and slightly higher than that of LiMn2O4 (about 450 mWh g–1). The density of P2-Na2/3[Fe1/2Mn1/2]O2 is estimated from x-ray diffraction to be 4.1 g cm–3, which is higher than that of LiFePO4 (3.6 g cm–3), and the submicrometer-sized primary particles are electrochemically active without carbon coating. In addition, the many voltage plateaus observed for P2-/O3-Na2MnO3 are not observed for P2-Na2/3[Fe1/2Mn1/2]O2 (figure 5). The appearance of voltage plateaus is closely correlated with in-plane sodium/vacancy ordering (presumably coupled with charge ordering in MnO2 layers). Stabilization of the Na/vacancy ordering also results in bi-phasic reactions (two phases with, generally, different unit cell volume coexist in a single particle) in the region of voltage plateaus. Rate capability in terms of electrode material is expected to be restricted because of the phase boundary movement for two-phase regions [46]. The partial Fe substitution for Mn reduces the tendency of in-plane sodium/vacancy ordering. These characteristics are beneficial for...
increasing the energy and power density of the electrode materials in sodium batteries.

Although the P2-type Na–Fe–Mn system is a promising candidate as a high-capacity positive electrode material for NIBs, three major drawbacks are known: (1) large volume change (11.3% shrinkage after charge to 4.2 V) during electrochemical cycles, (2) the system’s hygroscopic character, which restricts sample handling in moist air (as-prepared P2-Na2[Fe12Mn12]O2 is somewhat oxidized by water, forming P2-Na2[Fe12Mn12]O2 and NaOH), and (3) sodium deficiency in the as-prepared sample. In the first discharge process, the sodium ions are in part inserted beyond the starting composition of x = 2/3 in Na2[Fe12Mn12]O2. The excess amount of sodium is estimated to be 0.2 (~50 mAh g−1), forming P2-Na0.36[Fe12Mn12]O2 in the fully discharged state [67]. It is difficult to directly prepare this sodium-rich phase because this phase is metastable. The O3 and/or O’3 phases are thermodynamically stable. Compensation for the deficient sodium ions is, therefore, needed to design the NIBs and to use the full capacity of P2-Na2[Fe12Mn12]O2. One idea to compensate for the sodium ions is the addition of sacrificial salts. For instance, NaN4 electrochemically decomposes into sodium ion and N2 gas, and this reaction is irreversible. Mixing P2-Na2[Fe12Mn12]O2 with NaN4, therefore, increases the initial charge capacity and thus effectively compensates for the sodium deficiency for the P2 phase in the initial state [73]. Further optimization is clearly needed to overcome these disadvantages in terms of electrode material and to develop high-energy NIBs on a large scale in the future.

3. Other oxides as Na insertion host

Two layered polymorphs, O3- and P2-type layered oxides, are summarized in the preceding section. In addition to these layered materials, many different non-layered oxides have been studied as electrode materials. Table 2 summarizes the Fe/Mn-based oxides that have been studied as electrode materials. Table 2 summarizes the structural data and electrode performance of Li counterparts are reviewed. Two layered polymorphs, O3- and P2-type layered oxides, are summarized in the preceding section. In addition to these layered materials, many different non-layered oxides have been studied as electrode materials. Table 2 summarizes the Fe/Mn-based oxides that have been studied as electrode materials.
Table 2. Overview of Fe/Mn-based oxides studied as positive electrode materials for rechargeable Li/Na batteries.

| system | material     | space group | electrode performance | remark                          | material     | space group | electrode performance | remark                          |
|--------|--------------|-------------|-----------------------|---------------------------------|--------------|-------------|-----------------------|---------------------------------|
| Li     | α-LiFeO$_2$  | Fm-3m       | inactive              |                                 | α-NaFeO$_2$  | R-3m        | ~100 mAh g$^{-1}$ 3.3 V |                                 |
|        | β-LiFeO$_2$  | C$_2$/c     | inactive              |                                 | β-NaFeO$_2$  | Pna2$_1$    | inactive              |                                 |
|        | γ-LiFeO$_2$  | I$_4$/amd   | inactive              |                                 |              |             |                       |                                 |
|        | α-LiFeO$_2$  | Fm-3m       | 130–200 mAh g$^{-1}$  | phase transition into spinel    | α-NaMnO$_2$  | C2/m        | ~150 mAh g$^{-1}$ 2.9 V | distorted O3-type               |
|        |              |             | ca. 3 V               | on electrochemical cycle        | β-NaMnO$_2$  | Pmmm        | active 2.9 V          | iso-structural with LiMnO$_2$   |
| Mn(III)| Li$_2$MnO$_2$| Pmmm        | 110–120 mAh g$^{-1}$  | 4.1 V                           |              |             |                       |                                 |
|        |              |             |                       |                                 | Na$_{2/3}$MnO$_2$ | P6$_3$/mmc | ~200 mAh g$^{-1}$ 2.8 V | Na-deficient phases            |
|        |              |             |                       |                                 | Na$_{0.4}$MnO$_2$ | Pham        | ~120 mAh g$^{-1}$ 2.8 V |                                 |
|        |              |             |                       |                                 | Na$_{0.4}$MnO$_2$ | C2/m        | active 2.5 V          |                                 |
of \(\beta\text{-NaMnO}_2\) in a Na cell was also reported [26]. The potential difference between charge/discharge processes in a Na cell appears to be relatively small, similar to \(\alpha\text{-NaMnO}_2\) (figure 10(b)).

When the fraction of sodium to manganese ions is reduced, two different phases, \(\text{Na}_{0.44}\text{MnO}_2\) and \(\text{Na}_{0.4}\text{MnO}_2\), are obtained. The Na insertion properties of \(\text{Na}_{0.44}\text{MnO}_2\) (\(\text{Na}_4\text{Mn}_9\text{O}_{18}\)) were first examined in the 1990s at 85 °C with solid-state polymer electrolyte [81, 82] and revisited in 2007 to be examined at room temperature with aprotic solvent [83]. A crystal structure of \(\text{Na}_{0.44}\text{MnO}_2\) is also shown in figure 9. A framework structure of \(\text{Na}_{0.44}\text{MnO}_2\) (SG \(\text{Pbam}\)) consists of four MnO\(_6\) octahedra and one MnO\(_5\) square pyramid. Trivalent manganese ions are energetically stabilized at the square-pyramidal sites. These octahedral and square-pyramidal sites are connected to each other by either edge or corner sharing (vertex sharing), forming the complicated framework structure with two different tunnels along the \(c\)-axis direction. Sodium ions are accommodated at three different sites in the framework structure, and the sodium ions in both large and small tunnels are highly mobile [84]. However, trivalent manganese ions at the square-pyramidal sites cannot be oxidized to the tetravalent state [84], and thus 20% of the sodium ions cannot be extracted from the framework structure. During the discharge (reduction) process, \(\text{Na}_x\text{MnO}_2\) is reversibly uptaking sodium ions to form \(\text{Na}_{0.67}\text{MnO}_2\), and approximately 120 mAh g\(^{-1}\) of reversible capacity is obtained as electrode material. Complicated phase transitions occur in the insertion/extraction of sodium ions, as expected from the galvanostatic charge/discharge curves in figure 10(c) [83].

Figure 9. Crystal structures of miscellaneous iron/manganese-based oxides: (a) \(\beta\text{-NaFeO}_2\), (b) \(\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3\), (c) \(\beta\text{-NaMnO}_2\), (d) \(\text{Na}_{0.44}\text{MnO}_2\), (e) \(\alpha\text{-MnO}_2\), and (f) \(\text{Na}_{0.4}\text{MnO}_2\).
Figure 10. Electrode performance of miscellaneous iron/manganese-based oxides: (a) $\beta$-NaFeO$_2$, (b) $\beta$-NaMnO$_2$ [26], and (c) Na$_{0.44}$MnO$_2$ [83]. (d), (e) Nanowires of Na$_{0.44}$MnO$_2$ are highly active as electrode material in the Na cell [85]. (f) Charge/discharge curves of Na$_{0.4}$MnO$_2$ in the Na cell [24]. (b), (f) Reproduced with permission from [26]. Copyright 1983 Elsevier. (c) Reprinted with permission from [83]. Copyright 2007 American Chemical Society. (d), (e) Reproduced with permission from [85]. Copyright 2011 John Wiley and Sons.
Detailed configurations of sodium ion ordering in Na$_x$MnO$_2$ in electrochemical cycles have been studied by first-principles calculations [84]. Recently well-crystallized, uniform nanowires (diameter $\sim$ 50 nm and growth orientation along [001]) of Na$_{0.44}$MnO$_2$ were prepared (figure 10(d)) by a polymer-pyrolysis method [85]. The Na$_{0.44}$MnO$_2$ nanowires demonstrate relatively good rate capability and excellent capacity retention, as shown in figure 10(e). Approximately 100 mAh g$^{-1}$ of reversible capacity is obtained in the Na cells, even after 100 cycles.

Other manganese (di)oxides studied for lithium insertion materials, such as $\alpha$-MnO$_2$ and $\beta$-MnO$_2$, have also been tested as sodium insertion host materials [86]. Framework structures of both $\alpha$-MnO$_2$ and $\beta$-MnO$_2$ consist of MnO$_6$ octahedra that are connected by both edge and corner sharing. The structure of $\beta$-MnO$_2$ is classified as rutile-type with relatively small 1 $\times$ 1 tunnels along the c-axis direction, which is built up with chains of edge-shared MnO$_6$ octahedra. Alkali ions, even small lithium ions, cannot be inserted into the small tunnels of bulk $\beta$-MnO$_2$ [87]. However, nanosized $\beta$-MnO$_2$ with ordered mesopores is electrochemically active in Li cells [87]. Large reversible capacity of >250 mAh g$^{-1}$ is obtained by using nanosized $\beta$-MnO$_2$. Although the crystalline phase is lost (changes into an amorphous phase) following electrochemical cycles, the electrode performance of $\beta$-MnO$_2$ is activated by using such nano-engineered samples. Therefore, it is also expected that this methodology can be used for Na insertion materials, similar to iron oxides, as described in an earlier section. Indeed, recently it was reported that $\beta$-MnO$_2$ nanorods prepared by a hydrothermal method with a diameter of 100 nm, which preferably grow along [001], deliver large reversible capacity (>200 mAh g$^{-1}$) in a Na cell. Because the radius of sodium ions is much larger than that of lithium ions, phase transitions from the rutile structure are expected to take place in Na cells. Although large reversible capacity is obtained with the $\beta$-MnO$_2$ nanorods, note that the difference in voltage between the charge/discharge in Na cells is much larger compared with Na insertion reactions in highly crystallized particles based on the topotactic reaction as shown in figure 5.

Alpha-type MnO$_2$, of the group of minerals called hollandite, has been studied in a Na cell. The structure of $\alpha$-MnO$_2$ shown in figure 9(e) is built up with edge- and corner-shared MnO$_6$ octahedra. Alkali ions, even small lithium ions, cannot be inserted into the small tunnels of bulk $\alpha$-MnO$_2$ [87]. However, nanosized $\beta$-MnO$_2$ with ordered mesopores is electrochemically active in Li cells [87]. Large reversible capacity of >250 mAh g$^{-1}$ is obtained by using nanosized $\beta$-MnO$_2$. Although the crystalline phase is lost (changes into an amorphous phase) following electrochemical cycles, the electrode performance of $\beta$-MnO$_2$ is activated by using such nano-engineered samples. Therefore, it is also expected that this methodology can be used for Na insertion materials, similar to iron oxides, as described in an earlier section. Indeed, recently it was reported that $\beta$-MnO$_2$ nanorods prepared by a hydrothermal method with a diameter of 100 nm, which preferably grow along [001], deliver large reversible capacity (>200 mAh g$^{-1}$) in a Na cell. Because the radius of sodium ions is much larger than that of lithium ions, phase transitions from the rutile structure are expected to take place in Na cells. Although large reversible capacity is obtained with the $\beta$-MnO$_2$ nanorods, note that the difference in voltage between the charge/discharge in Na cells is much larger compared with Na insertion reactions in highly crystallized particles based on the topotactic reaction as shown in figure 5.

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chains, are found in a mineral called psilomelane, as shown in figure 9(f) [89]. Large Ba$^{2+}$ ions and water molecules are incorporated as a template to stabilize such large tunnels in psilomelane. A Na$^{+}$ sample substituted for Ba$^{2+}$ and H$_2$O in psilomelane, Na$_{0.4}$MnO$_2$, is also prepared by a simple solid-state method [26, 80]. The sample shows rather small polarization in a Na cell, even though the mechanism of sodium insertion into Na$_{0.4}$MnO$_2$ with 2×3 tunnels is not fully understood. At least 0.3 mole of sodium ions are reversibly inserted/extracted into/from the framework structure of psilomelane with the large tunnels [26].

### 3.3. Spinel-type manganese oxides

Spinel-type LiMn$_2$O$_4$ is the one of the most widely studied materials in terms of positive electrodes for LIBs [3–6]. Layered O$^{3-}$-type LiMnO$_2$ which is also prepared by a Na/Li ion-exchange method from O$^{3-}$-NaMnO$_2$, is isostructural with O$^{3-}$-NaMnO$_2$ [51, 52]. Although the electrode performance of O$^{3-}$-LiMnO$_2$ in Li cells has also been reported, its major problem as an electrode material is the gradual phase transition to spinel with the common ccp oxygen lattice. Trivalent manganese ions should be highly mobile in the ccp lattice, and therefore, LiMnO$_2$ easily transforms into spinel as the energetically favorable phase during electrochemical cycles in Li cells.

In contrast, a Na counterpart, O$^{3-}$-NaMnO$_2$, can be used as electrode material without such a phase transition into spinel. The difference probably originates from a large gap in size between Na and Mn ions. A three-dimensional framework structure such as that of spinel is stable for the Li system and not for the Na system. The question arises here whether spinel-type manganese oxides are used as electrode materials in Na cells without phase transition [90, 91]. Figure 12 compares charge/discharge curves of stoichiometric LiMn$_2$O$_4$ cycled in 1.0 mol dm$^{-3}$ lithium or sodium perchlorate dissolved in propylene carbonate. LiMn$_2$O$_4$ shows two voltage plateaus at approximately 3.92 and 4.16 V in a Li cell in a first charge process. Although the almost identical voltage profile is observed in a Na cell, the voltage of the Na cell is 0.34 V lower than that of the Li cell. This observation directly relates to the difference in the standard electrode potential, as similarly shown in figure 2. As shown in figure 12(a), a voltage profile upon the first charge in the Na cell is superimposed on that in the Li cell when voltage is shifted higher by 0.34 V. These results clearly suggest that the same reaction proceeds in both Na and Li systems, i.e., lithium extraction from LiMn$_2$O$_4$, forming Li$_x$Mn$_2$O$_4$ ($x$=ca.0.1). A clear difference
between the two cells is found via a discharge (reduction) process. In the Li cell, Li ions are reversibly inserted into the spinel framework structure with similar voltage profiles on charge. In the Na cell, voltage rapidly decreases to 3.2 V versus Na/Na⁺, at which time a long plateau is observed (approximately 100 mAh g⁻¹ of discharge capacity), and then the voltage gradually decreases to 2.0 V. First-discharge capacity reaches approximately 200 mAh g⁻¹ in this experimental condition. Although lithium ions are extracted in Na cells, the extracted lithium ions are not reversibly inserted into Na cells, and instead Na ions seem to be inserted into Li₂MnO₄ (x=ca.0.1). Figure 12(b) shows tenth charge/discharge curves of LiMn₂O₄ electrodes cycled in Li and Na cells. Voltage profiles change during the electrochemical cycling in the Na cell. For the tenth cycle, the voltage profiles are completely different for both cells, suggesting a phase transition from the spinel phase to another phase in the Na cell. The changes in crystal structures of stoichiometric LiMn₂O₄ cycled in Na cells were examined by XRD. Figure 13 shows the XRD patterns of LiMn₂O₄ electrodes before and after the electrochemical cycling in Na cells. When the electrodes are cycled in Na cells, the XRD patterns of electrodes drastically change. Peak profiles of all the Bragg lines from LiMn₂O₄ are significantly broadened, which is indicative of the phase transition induced by sodium insertion into the spinel phase. After 5 cycles in the voltage range 2.0–4.0 V versus Na/Na⁺, new peaks appear at 17 degrees (in two theta) with the appearance of some additional peaks. After 10 cycles in the range 2.0–4.0 V, these new peaks become more visible. These new peaks observed after 10 cycles resemble those of O³-type NaMnO₂. From the XRD patterns, newly formed O³-type NaMnO₂ seems to coexist with the peak broadened spinel-type phase. Because some lithium-ions still exist in the spinel phase by electrochemical oxidation to 4.0 V in Na cells, the phase transition to the layered phase may be partially suppressed. Such spinel-to-layered phase transition in common oxygen lattices (schematic illustrations are shown in figure 13) is different compared with the Li system, and the results suggest that the layered sodium manganese phase seems to be energetically stable, as recently supported by the results of first-principles calculation [49]. Stabilization of layered manganese systems is another advantage of the Na system for battery applications.

### 4. Polyanionic compounds as Na insertion host

Similar to layered and non-layered oxides, the high structural flexibility of sodium-containing polyanionic compounds is an attractive feature when it comes to electrode materials for a battery system. Therefore, many different polyanionic compounds have been revisited or newly found in the last few years, as summarized in table 3. In this section, Fe/Mn-based polyanionic compounds as the Na insertion host are reviewed.

#### 4.1. Phosphates with Fe(II) and Mn(II)

Because layered lithium iron(III) oxide LiFeO₂ shows unimpressive battery performance based on the Fe²⁺/Fe³⁺ redox couple after oxygen loss in the Li cells as previously discussed, polyanionic compounds of iron have been extensively studied based on the use of the Fe²⁺/Fe³⁺ redox couple [92]. Lithium iron(II) phosphate, LiFePO₄, is the most widely studied polyanionic compound in terms of positive electrode materials for LIBs because of the interest with regard to practical applications [93]. A crystal structure of LiFePO₄ is classified as the triphylite-type structure (SG Pnma) with a distorted hcp oxygen lattice. The structure is closely related to the olivine-type structure, and two cations (lithium and iron ions in the case of LiFePO₄) are located in two distinct octahedral sites in the common framework structure composed of XO₄ (X=Si, P, Mo, etc) tetrahedra. Phosphate ions, (PO₄)³⁻ tetrahedra, share one edge and four corners with FeO₆ octahedra, forming the framework structure of triphylite-type FePO₄, as shown in figure 14(a). Formation of edge-shared sites between FeO₆ octahedral and PO₄ tetrahedral units relatively stabilizes the energy of the Fe²⁺/Fe³⁺ redox couple through the inductive effect, resulting in high voltage (3.45 V versus Li metal) for iron-based compounds based on the Fe²⁺/Fe³⁺ redox [39, 93]. Although the FeO₆ octahedra share corners in the triphylite-type structure (figure 15(a)), electrical conductivity is still too low for electrode materials. The electrode performance of LiFePO₄ is significantly improved by carbon coating [94] and shortening of a Li diffusion path with nanosized particles. Such engineered nanosized particles deliver large reversible capacity in Li cells, which now almost reaches its theoretical limit (170 mAh g⁻¹). Conduction mechanisms of Li ions in triphylite-type LiFePO₄ have been extensively studied [95, 96]. LiFePO₄ crystallizes into a maricite-type structure as the thermodynamically stable phase. Its crystal structure is also closely related to the olivine-type structure with a distorted hcp oxygen lattice. A large gap in the size of ionic radii between Na and Fe results in significant distortion in the hcp oxygen lattice (figure 15(b)) in comparison to triphylite-type LiFePO₄. Iron ions are located at octahedral sites, and FeO₆ octahedra share edges with one another, forming 1D chains as shown in figure 15(c). Li ions migrate with a low diffusion barrier (~150 meV [62]) along the 1D chains throughout particles if the formation of antisite defects between Li and Fe sites is negligible [96].

A sodium counterpart, NaFePO₄, is also studied as an electrode material for NIBs [97]. NaFePO₄ crystallizes into a maricite-type structure as the thermodynamically stable phase. Its crystal structure is also closely related to the olivine-type structure with a distorted hcp oxygen lattice. A large gap in the size of ionic radii between Na and Fe results in significant distortion in the hcp oxygen lattice (figure 15(b)) in comparison to triphylite-type LiFePO₄. Iron ions are located at octahedral sites, and FeO₆ octahedra share edges with one another, forming 1D chains as shown in figure 15(d). The structure of the 1D chains of FeO₆ in the maricite phase is essentially the same as that of the 1D LiO₆ chains in the triphylite phase. Sodium ions are located at large tetrahedral sites (note that such a site is also regarded as an irregular site coordinated by 10 oxygen within 3 Å [98]), which share corners with PO₄ tetrahedra (figure 15(b)). Because sodium sites are isolated in the structure, as shown in figure 15(b), a large barrier to sodium migration is expected in the maricite-type NaFePO₄. Indeed, the reversibility of Na
Table 3. Overview of phosphate-related and fluoride compounds containing Fe(II), Fe(III), and Mn(II), studied as positive electrode materials for rechargeable Li/Na batteries.

| System        | Material                  | Space Group | Electrode Performance | Remark   | Material                  | Space Group | Electrode Performance | Remark   |
|---------------|---------------------------|-------------|-----------------------|----------|---------------------------|-------------|-----------------------|----------|
| LiFePO₄       | LiFePO₄                   | Pnma        | 160 mAh g⁻¹ 3.4 V     | Triphylite type | NaFePO₄                   | Pnma        | inactive              | maricite-type |
| Li₂FePO₄      | P₂₁/c                     | ~130 mAh g⁻¹ 3.3 V | | | Na₂Fe₃O₇                 | P-1         | ~80 mAh g⁻¹ 2.8 V | | |
| Li₃Fe₂(PO₄)₃  | P₂₁                      | ~100 mAh g⁻¹ 2.9 V | | | Na₂Fe₃(PO₄)₂(P₂O₇)       | Pnma₂₁      | ~100 mAh g⁻¹ 2.8 V | | |
| LiFePO₄F      | Pbcn                      | ~110 mAh g⁻¹ 3.0 V | | | Na₂Fe₃(PO₄)₃             | C₂₁/c       | ~45 mAh g⁻¹ 2.5 V | R-3c, > 95 °C |
| Li₂FeP₂O₇     | P₂₁                      | ~60 mAh g⁻¹ 2.9 V | | | Na₂Fe₃(PO₄)₄             | Pnma        | ~80 mAh g⁻¹ 2.5 V | | |
| LiMnPO₄       | NaMn₂Fe₃(PO₄)₃            | C₂₁/c       | ~50 mAh g⁻¹ 2.5 V | inactive    | NaMnPO₄                   | Pnma        | inactive              | maricite-type |
| Li₂MnP₂O₇     | P₂₁/c                     | ~140 mAh g⁻¹ 4.0 V | Triphylite type | | Na₂MnP₂O₇                 | P-1         | ~80 mAh g⁻¹ 3.3 V | | |
| Li₂MnP₂O₇F    | inactive                  | NaMnP₂O₇F    | P₂₁/c                 | ~50 mAh g⁻¹ 3.3 V | | NaFeF₃                   | Pnma        | ~150 mAh g⁻¹ 2.8 V | | |
Figure 14. Crystal structures of phosphate-based compounds containing Fe(II) ions: (a) Na(Li)FePO₄ (triphylite-type), (b) NaFePO₄ (maricite-type), (c) Na₂Fe(P₂O₇), and (d) Na₄Fe₃(PO₄)₂(P₂O₇).

Figure 15. Crystal structures of Na(Li)FePO₄ (triphylite-type) and NaFePO₄ (maricite-type): the arrangement of (a) FeO₆-PO₄ in triphylite and (b) NaO₄-PO₄ in maricite, and 1D chains of (c) LiO₆ octahedra in triphylite and (d) FeO₆ octahedra in maricite.
extraction/insertion for maricite-type NaFePO₄ seems to be unacceptable in terms of electrode material [97, 99].

In contrast, triphyllite-type NaFePO₄, which is a metastable polymorph of NaFePO₄, is electrochemically active [97, 100]. Triphyllite-type NaFePO₄ can be prepared by an ion-exchange method from LiFePO₄. Li ions are chemically (and electrochemically) extracted from triphyllite-LiFePO₄ without the destruction of its core structure, forming heterosite-type FePO₄. Chemical (and electrochemical) Na insertion into heterosite-type FePO₄, which possesses the same framework structure as triphyllite-LiFePO₄, results in the formation of triphyllite-type NaFePO₄. Triphyllite-type NaFePO₄ is stable below 480 °C in inert atmosphere and transforms into maricite-NaFePO₄ by further heating above 480 °C [100, 101]. Charge/discharge (oxidation/reduction) curves of triphyllite-NaFePO₄ in a Na cell [100] are shown in figure 16(a). Nearly one mole of Na ions are reversibly inserted/extracted into/from triphyllite-NaFePO₄. Because the ionic radius of the sodium ion is much larger than that of the lithium ion, the unit cell volume of triphyllite-NaFePO₄ is approximately 10% larger than that of triphyllite-LiFePO₄. Two voltage plateaus are observed on discharge (figure 16(a)). Open-circuit voltage on the plateaus is observed to be 2.87 V and 2.97 V [100], which is slightly lower than that of ~3.1 V versus Na as expected from LiFePO₄ (3.45 V vs Li). The voltage difference between Li and Na cells is, however, less significant than that observed for the layered oxides (figure 2). The appearance of two voltage plateaus originates from the formation of an intermediate phase (a sodium-ion ordered phase) as Na₀.₄FePO₄ (point B in figure 16(a)). Such an intermediate phase is not generally found in LiₓFePO₄ under equilibrium conditions. Larger repulsive interaction for Na ions, as compared with Li ions, may result in the formation of the intermediate phase [100, 102], similar to layered oxides. According to the DFT calculation, the barrier of sodium migration in narrow 1D chains is much larger (270 meV) compared with Li ions (150 meV) [62]. Diffusion barriers correlate highly with diffusion paths in host structures. Indeed, experimentally measured sodium insertion kinetics in triphyllite-NaₓFePO₄ appear to be much slower compared with Li ions [103].

The thermodynamically stable phase of NaMnPO₄ is also maricite type [104]. Similar to triphyllite-NaFePO₄, it is also expected that lithiophilite-type NaMnPO₄, which is isomorphous with triphyllite-type Li(Na)FePO₄, is obtained by ion-exchange reaction and/or related soft chemical methods. It has been demonstrated that lithiophilite-type NaMnPO₄ is prepared by topochemical reaction below 100 °C from NH₄MnPO₄·H₂O as the precursor [104]. Electrode performance of triphyllite-NaMnₓFe₁₋ₓPO₄ prepared by topochemical reaction has also been reported [104]. Electrode reversibility of lithiophilite-NaMnPO₄ may be limited without the preparation of nano-engineered particles, similar to LiMnPO₄, because of the formation of antisite defects [105, 106] and/or the slow nucleation rate for the delithiated (desodiated) phase [107].
4.2. Pyrophosphates with Fe(II) and Mn(II)

Following reports touting lithium iron(II) pyrophosphate, \( \text{Li}_2\text{FeP}_2\text{O}_7 \), as a positive electrode material for LIBs [108, 109], a great deal of literature has been published regarding the pyrophosphate system. The use of pyrophosphate, instead of phosphate, as the framework structure has been extended to the Na system, i.e., \( \text{Na}_2\text{FeP}_2\text{O}_7 \) [110–112]. \( \text{Na}_2\text{FeP}_2\text{O}_7 \) is isosstructural with one of the polymorphs of \( \text{Na}_2\text{CoP}_2\text{O}_7 \), with an SG of \( \text{P1} \) [113]. The crystal structure of \( \text{Na}_2\text{FeP}_2\text{O}_7 \) contains corner-shared \( \text{FeO}_6 \) octahedra (fe(2)O11 units), which are connected by \( \text{P}_2\text{O}_7 \) units, forming the 3D framework structure with open sodium diffusion paths (figure 14(c)). Na ions are located at large distorted square-pyramidal sites. One Na ion is reversibly extracted from \( \text{Na}_2\text{FeP}_2\text{O}_7 \) based on the \( \text{Fe}^{2+}/\text{Fe}^{3+} \) redox couple, and reversible capacity reaches 90 mAh g\(^{-1}\) (theoretical capacity: 97 mAh g\(^{-1}\)) as shown in figure 16(b). Although the available energy density is lower than that of triphylite-\(\text{NaFePO}_4\), direct synthesis of \( \text{Na}_2\text{FeP}_2\text{O}_7 \) is possible by conventional solid-state methods. Additionally, rate capability seems to be much better for \( \text{Na}_2\text{FeP}_2\text{O}_7 \), even though \( \text{FeO}_6 \) octahedra and \( \text{FeO}_5 \) square pyramids are isolated by the pyrophosphate ions in the framework structure. This result is probably because of the presence of open diffusion paths formed by pyrophosphate ions. Na diffusion barriers in \( \text{Na}_2\text{FeP}_2\text{O}_7 \) have been also calculated by first-principles calculation [112]. Sodium ions can diffuse through 1D paths along [011] with a relatively low migration barrier (\( \sim 480 \text{ meV} \)), and all Na sites are interconnected by 1D/2D paths with a diffusion barrier below 540 meV.

Recently it has been reported that one of the \( \text{Na}_2\text{MnP}_2\text{O}_7 \) polymorphs, \( \beta\)-\( \text{Na}_2\text{MnP}_2\text{O}_7 \), which is isosstructural with \( \text{Na}_2\text{FeP}_2\text{O}_7 \), also shows good electrode performance in Na cells [114]. Although the polarization seems to be large, \( \text{Na}_2\text{MnP}_2\text{O}_7 \) is potentially usable as a 3.6 V cells [114]. Although the polarization seems to be large, \( \text{Na}_2\text{FeP}_2\text{O}_7 \) also shows good electrode performance in Na cells [117].

### 4.3. Fluorophosphates, carbophosphates, and fluorosulfate with Fe(II) and Mn (II)

The mixed-anions system containing fluoride and phosphate ions is also used as electrode material for NIBs. The layered fluorinated iron phosphate \( \text{Na}_2\text{FePO}_4\text{F} \) has been widely examined as a positive electrode material for rechargeable batteries [119, 120]. The crystal structure of \( \text{Na}_2\text{FePO}_4\text{F} \) is isostructural with \( \text{Na}_2\text{CoPO}_4\text{F} \)-type structures [121] (or \( \text{Na}_2\text{FePO}_4\text{O}(\text{OH}) \)-type structures) as two-dimensional layered fluorophosphates (figure 17(a)). Na ions are accommodated between \( \text{FePO}_4\text{F} \) layers, in which \( \text{FeO}_2\text{F} \) octahedra share edge and corners. According to the results of first-principles calculation, sodium ions migrate between \( \text{FePO}_4\text{F} \) layers through a two-dimensional path [122]. The crystal structure of \( \text{Na}_2\text{MnPO}_4\text{F} \) is different from that of \( \text{Na}_2\text{FePO}_4\text{F} \) [123]. All \( \text{MnO}_2\text{F} \) octahedra share each corner and form 1D \( \text{Mn}_2\text{O}_5\text{O}_3 \) chains. The chains are connected by \( \text{PO}_4 \) tetrahedra via corner sharing, thus forming a less dense 3D framework structure (figure 17(b)). \( \text{Na}_2\text{[Fe}_x\text{Mn}_(1-x)\text{]PO}_4\text{F} \) (0 < \( x < 1.0 \)) samples have also been synthesized, and it was found that the \( \text{Na}_2\text{MnPO}_4\text{F} \)-type 3D structure is thermodynamically stable at \( x < 0.75 \) in \( \text{Na}_2\text{[Fe}_x\text{Mn}_(1-x)\text{]PO}_4\text{F} \) [120].

The electrochemical behavior of carbon-coated \( \text{Na}_2\text{FePO}_4\text{F} \) and \( \text{Na}[\text{Fe}(1/2\text{Mn}(1/2))\text{PO}_4\text{F} \) in Na cells is compared in figure 18 [124, 125]. \( \text{Na}_2\text{FePO}_4\text{F} \) demonstrates a relatively high operating voltage (ca. 3.0 V versus Na) and fair reversibility as an electrode material. The carbon-coated \( \text{Na}_2\text{FePO}_4\text{F} \) sample delivers approximately 110 mAh g\(^{-1}\) of reversible capacity, which corresponds to approximately 90% of theoretical capacity based on the one-electron redox of iron (\( \text{Fe}^{2+}/\text{Fe}^{3+} \)). Two well-defined voltage plateaus, which are centered at 3.06 and 2.91 V with small polarization, are observed in figure 18(a). The Na/Na\(_2\)[Fe\(_{1/2}\)Mn\(_{1/2}\)]PO\(_4\)F cell also shows a reversible capacity of 110 mAh g\(^{-1}\) (figure 18(b)). In addition, from the operating voltage, the reaction in the Na cell consists of three different regions. Differential capacity dQ/dV plots of both samples are also shown in figures 18(a), (b) (insets). In the discharge process for the Na/Na\(_2\)[Fe\(_{1/2}\)Mn\(_{1/2}\)]PO\(_4\)F cell, three peaks are clearly observed at 3.36, 3.04, and 2.86 V. A redox couple centered at 3.53 V is found in the dQ/dV plot of Na\_2[Fe\(_{1/2}\)Mn\(_{1/2}\)]PO\(_4\)F, which may be attributable to a Mn\(^{2+}/\text{Mn}^{3+} \) redox reaction. The polarization of the Mn redox is larger than that of \( \text{Fe}^{2+}/\text{Fe}^{3+} \), similar to the iron/manganese phosphates. Although the layered framework structure seems to be preferable for the sodium migration process in the fluorophosphates system, carbon-coated, nanosized \( \text{Na}_2\)[Fe\(_{1/2}\)Mn\(_{1/2}\)]PO\(_4\)F samples...
show good reversibility as electrode material in Na cells [125].

Recently synthesis and electrode performance have been reported for sodium-based carbonophosphates, \( \text{Na}_3\text{MePO}_4\text{CO}_3 \), which are the new series of mixed-anion compounds used as electrode materials, similar to \( \text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7) \) [126, 127]. \( \text{Na}_3\text{MePO}_4\text{CO}_3 \) contains two different anions of carbonate \( (\text{CO}_3)^{2-} \) and phosphate \( (\text{PO}_4)^{3-} \) ions, and its Mn compound, \( \text{Na}_3\text{MnPO}_4\text{CO}_3 \), is found in the natural mineral sidorenkite [126]. The crystal structure of \( \text{Na}_3\text{MnPO}_4\text{CO}_3 \) is shown in Figure 17(c). FeO\(_6\) octahedra and PO\(_4\) tetrahedra share each corner and CO\(_3\) triangles share one edge with the FeO\(_6\) octahedra, resulting in a large distortion of the FeO\(_6\) octahedra. \( \text{Na}_3\text{MnPO}_4\text{CO}_3 \) can be prepared by hydrothermal reaction at 120 °C [116]. Two Na ions are extracted from \( \text{Na}_3\text{MnPO}_4\text{CO}_3 \) based on the Mn\(^{2+}/\text{Mn}^{4+}\) two-electron redox reaction, resulting in large initial charge capacity (Figure 18(c)). Although the initial charge capacity is large (\( \sim 200 \text{ mAh g}^{-1} \)), it has been reported that the sample shows relatively large irreversible capacity (\( \sim 75 \text{ mAh g}^{-1} \)) in the initial cycle, with acceptable capacity retention in subsequent continuous cycles [126].

Metal fluorosulfates are also used as the framework structure for the Na insertion host. Recently sodium iron fluorosulfate, \( \text{NaFeSO}_4\text{F} \), was successfully prepared and its electrode performance was examined in Na cells. The crystal structure of \( \text{NaFeSO}_4\text{F} \) is isostructural with the mineral tavorite, LiFe(PO\(_4\))OH [128]. Although the results of first-principles calculation suggest diffusion of sodium ions in the 1D path along [101] [129], reversibility of \( \text{NaFeSO}_4\text{F} \) in terms of electrode material is limited to a narrow range [128].

4.4. Phosphates with Fe(III) and Mn(II)

Because trivalent iron Fe(III) is, in general, stable under ambient conditions, many Fe(III)-containing phosphates are found in natural minerals. Some Fe(III)-containing phosphates are known to be electrochemically active as sodium insertion hosts, based on the Fe\(^{2+}/\text{Fe}^{3+}\) redox. The simplest compounds are FePO\(_4\) with polymorphs, including an amorphous phase. A thermodynamically stable phase is isostructural with the mineral berlinite, AlPO\(_4\) [130], in which FeO\(_4\) and PO\(_4\) tetrahedra share corners with each other, forming relatively open 3D channels for the insertion of alkali ions (Figure 19(a)). The electrode performance of amorphous and crystalline FePO\(_4\) (berlinite-type) is reported by Okada and co-workers [131]. Figure 20(a) shows the electrode performance of amorphous FePO\(_4\) in Li and Na cells. Approximately 80 mAh g\(^{-1}\) of reversible capacity is obtained using amorphous FePO\(_4\) in the Na cell. Crystalline FePO\(_4\) obtained by heating the amorphous phase is also used as an electrode material [131]. FePO\(_4\) polymorphs can be prepared by topochemical reaction from hydrates, and one of them consists of corner-shared FeO\(_6\) octahedra and PO\(_4\) tetrahedra [132]. These polymorphs are electrochemically active in Li cells.
According to a study on a Na$_3$PO$_4$–FePO$_4$ binary phase diagram [133], at least three different phases exist: Na$_3$Fe(PO$_4$)$_2$, Na$_3$Fe$_2$(PO$_4$)$_3$, and Na$_3$Fe$_3$(PO$_4$)$_3$. A structural type of the most Na-rich phase, Na$_3$Fe(PO$_4$)$_2$, was reported to be related to the mineral glaserite, K$_3$Na(SO$_4$)$_2$ [134]. FeO$_6$ octahedra and PO$_4$ tetrahedra share corners, forming 2D Fe$_2$(PO$_4$)$_2$ layers. Sodium ions are accommodated between the Fe$_2$(PO$_4$)$_2$ layers. Similar to Na$_3$Fe(PO$_4$)$_2$, Na$_3$Fe$_2$(PO$_4$)$_3$ also consists of corner-shared FeO$_6$ octahedra and PO$_4$ tetrahedra, but Na$_3$Fe$_2$(PO$_4$)$_3$ has a 3D framework structure. Such a structure of Na$_3$Fe$_2$(PO$_4$)$_3$ is known to be related to the Na$^+$-ion super ionic conductors (NASICON) type of structure (figure 19(b)), and the polymorphic characteristics of Na$_3$Fe$_2$(PO$_4$)$_3$ have been extensively studied [135]. Ion-exchanged Li$_3$Fe$_2$(PO$_4$)$_3$ from Na$_3$Fe$_2$(PO$_4$)$_3$ is known to be electrochemically active in Li cells [39]. Approximately 0.4 mole of Na is reversibly inserted/extracted into/from Na$_3$Fe$_2$(PO$_4$)$_3$ in Na cells [136], even though ionic conductivity of Na$_3$Fe$_2$(PO$_4$)$_3$ is reported to be very low (1.2 × 10$^{-7}$ S cm$^{-1}$ at 50 °C) [137].

Na$_3$Fe$_3$(PO$_4$)$_4$ is also classified as a layered-type phosphate [133]. FeO$_6$ octahedra and PO$_4$ in Na$_3$Fe$_3$(PO$_4$)$_4$ tetrahedra share both edge and corners, forming 2D Fe$_3$(PO$_4$)$_4$ layers (figure 19(c)). This type of layered structure is found in K$_3$Fe$_3$(PO$_4$)$_4$•H$_2$O [138]. The electrode performance of Na$_3$Fe$_3$(PO$_4$)$_4$ in Li and Na cells has been reported [139, 140]. Approximately 2 moles of Li and Na ions are reversibly inserted into/from Na$_3$Fe$_3$(PO$_4$)$_4$ in Na cells [136], even though the operating voltage is much smaller than in the Li cell, as shown in figure 20(b). Although highly crystallized and microsized particles show good electrode performance, the operating voltage is relatively low—2.5 V versus Na, based on the Fe$^{2+}$/Fe$^{3+}$ redox.

Binary phosphates containing Fe(III) and Mn(II) are also found in natural minerals. One example is the mineral alluaudite [141]. The crystal structure of alluaudite contains 1D chains made from edge-shared Fe(Mn)O$_6$ octahedra with distortion. These 1D chains are connected with PO$_4$ tetrahedra by corner sharing, forming the 1D tunnel sites for Na ions (figure 19(d)). Na ions are located at distorted octahedral sites and large eight oxygen coordinated sites. Electrode performance of alluaudite-type NaMnFe$_2$(PO$_4$)$_3$ has been tested in Na cells [140]. Na ions (ca. 0.5 mole) can be partially extracted from NaMnFe$_2$(PO$_4$)$_3$ prepared using a sol-gel method, and the reversible capacity reaches 60 mAh g$^{-1}$ in a Na cell (figure 20(c)). Much better reversibility was found in Na$_3$Fe$_3$(PO$_4$)$_4$ without Mn(II) ions.

The electrode performance of the fluorophosphate containing Fe(III), Na$_3$Fe$_2$(PO$_4$)$_2$F$_3$, was recently reported [142]. The crystal structure of Na$_3$Fe$_2$(PO$_4$)$_2$F$_3$ is isomorphous with Na$_3$Fe$_2$(PO$_4$)$_2$(OH)$_2$F [143]. The framework structure of Na$_3$Fe$_2$(PO$_4$)$_2$F$_3$ consists of Fe$_6$O$_3$F$_2$ octahedra and PO$_4$ tetrahedra, all of which share corners, forming Fe$_2$(PO$_4$)$_2$F$_3$ layers. A two-dimensional migration path for sodium ions along the a–b plane is formed by corner sharing for the FeO$_6$F$_2$ octahedra in the Fe$_2$(PO$_4$)$_2$F$_3$ layers. Na$_3$Fe$_2$(PO$_4$)$_2$F$_3$ delivers 40 mAh g$^{-1}$ of reversible capacity in a Na cell [142].
5. Miscellaneous Na insertion materials

Iron trifluoride, FeF₃, has been studied as a potential candidate to achieve high energy density as an iron-based electrode material in Li cells. The electrode performance of FeF₃ in Li cells was first examined by Arai and co-workers [144]. Fe–F bonds in FeF₃ are strongly polarized because of the high electronegativity of fluorine in comparison with oxygen. Electrons are therefore localized in FeF₃, resulting in insufficient electrical conductivity as an electrode material. FeF₆ octahedra share all corners, forming a framework structure with open channels (figure 21(a)). The structure of FeF₃ is isostructural with distorted ReO₃. (It is also classified as an A-site deficient perovskite structure). Although FeF₃ has an open structure with three-dimensional pathways for lithium migration, the electrode performance of micrometer-sized FeF₃ is limited by its insulating character. The electrode performance of FeF₃ in Li cells is significantly improved by using nano-composite materials consisting of FeF₃, resulting in insufficient electrical conductivity as an electrode material. FeF₆ octahedra share all corners, forming a framework structure with open channels (figure 21(a)). The structure of FeF₃ is isostructural with distorted ReO₃. (It is also classified as an A-site deficient perovskite structure). Although FeF₃ has an open structure with three-dimensional pathways for lithium migration, the electrode performance of micrometer-sized FeF₃ is limited by its insulating character. The electrode performance of FeF₃ in Li cells is significantly improved by using nanocomposite materials consisting of FeF₃ and conductive carbon [145]. This concept has been extended to the Na system, and it was demonstrated that FeF₃/C nanocomposite delivers large reversible capacity (∼150 mAh g⁻¹) in Na cells (figure 22(a)) [146]. LiFeF₃ is formed as a metastable phase by electrochemical (or chemical) reduction of FeF₃ in Li cells. It is impossible to prepare LiFeF₃ directly by a simple solid-state method because the vacant 6a site in FeF₃ (A-site in ABO₃-type perovskite) is too large for Li ions (the interatomic distance reaches 2.67 Å on average for the distorted 12-coordination site). Such a lithiated phase is preferable as a positive electrode material for assembling complete cells (LIBs) in combination with carbonaceous materials as negative electrodes. In contrast with LiFeF₃, NaFeF₃ is easily prepared as a thermodynamically stable phase because the large Na ions are energetically stabilized at A-sites of the perovskite structure, as shown in figure 21(a). Nanosized NaFeF₃ is electrochemically active in Na cells and is used as positive electrodes, even though relatively large polarization for charge and discharge cycles has been observed [147, 148].

Na ions are apparently coordinated by four fluoride ions at bottleneck sites when the Na ions migrate across the perovskite-type framework structure. Relatively large activation energy for Na migration is expected in the charge/discharge process for Na₄FeF₆. Therefore, the use of cyanide ions rather than fluoride ions has been proposed to reduce the activation energy with respect to the Na migration process [149]. Moreover, the cyanide ions as strong-field ligands drastically influence crystal field splitting for the 3d orbital of iron ions. Recently Prussian blue analogues, which have a framework structure similar to that of perovskite, as shown in figure 21(b), have been studied as the Na insertion host. The iron and manganese system with potassium ions, KFe₂(CN)₆ and KMnFe(CN)₆ [150], and the iron (III) system without alkaline metal ions, Fe₂(CN)₆ [151], shows 80–120 mAh g⁻¹ of reversible capacity as positive electrode materials in Na cells. Polarization of Prussian blue analogues in Na cells is much smaller than that of the perovskite system with fluoride ions. Goodenough’s research group has reported the Na-enriched iron manganese system, Na₁.72MnFe(CN)₆ (an ideal crystal structure without sodium vacancies is illustrated in figure 21(b)), as a potential positive electrode material for

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Figure 19. Crystal structures for phosphate-based compounds containing Fe(III) and Mn(II): (a) FePO₄ (berlinite-type), (b) Na₃Fe₂(PO₄)₃ (NASICON-type), (c) Na₃Fe₃(PO₄)₅ (Na₃Cr₃(PO₄)₂-type), and (d) NaMnFe₂(PO₄)₃ (alluaudite-type).
NIBs [149]. Magnetic measurements of Na$_{1.72}$MnFe(CN)$_6$ suggest the presence of low-spin Fe(II) coordinated by carbon, and the low-spin Fe(II)/Fe(III) is redox active in Na cells [149]. The reversible capacity reaches 130 mAh g$^{-1}$, with an average operating voltage of 3.2 V. The sample also shows excellent rate capability in the Na cell, as shown in figure 22(b). The electrode performance of a similar sodium manganese ferrocyanide has also been recently reported [152]. The activation energy of the charge transfer reaction for Na insertion into Prussian blue analogues greatly depends on the electrolyte solution used, and extremely small activation energy (5 kJ mol$^{-1}$) in water-based electrolyte solution has been reported [153]. Additionally, sodium ferrocyanide, Na$_4$Fe(CN)$_6$, is reported to be electrochemically active in Na cells. The studied sample delivers $\sim$90 mAh g$^{-1}$ of reversible capacity, with a flat voltage plateau at 3.4 V [154]. This reversible capacity nearly corresponds to the capacity defined by the one-electron redox reaction of iron for Na$_4$Fe(CN)$_6$.

Pyrite, FeS$_2$, which is the most common of the sulfide minerals, is also used as an electrode material for Na cells, even though its reaction mechanism is not classified as an insertion reaction [155]. FeS$_2$ consists of Fe$^{2+}$ and S$^{2-}$ (persulfide ions), and clear evidence of the presence of the S–S bond is found in the structure, as shown in figure 21(c). In the reduction process in Na cells, Fe$^{2+}$ is reduced to metallic Fe, and S$^{2-}$ is potentially reduced to form Na$_2$S. If this reaction (so-called conversion reaction [75]) is a reversible process, the theoretical capacity exceeds 950 mAh g$^{-1}$. Although large initial discharge capacity was obtained (figure 22(c)), the reversibility is insufficient for an electrode material. The use of the conversion reaction may be a strategy to design a battery system with high energy density.

6. Conclusions and outlook

Research interest in the use of sodium ions as ion carriers for energy storage at ambient conditions almost died away completely at one point after innovations in materials for the Li system (the finding of LiCoO$_2$ and graphite as lithium insertion hosts) and the commercialization of LIBs were achieved in the 1990s. However, there has been a complete turnaround in research interest regarding sodium ions as a result of increasing worldwide demand for EES. In considering the design of better batteries for EES, of primary importance is the elemental abundance (cost) together with acceptable battery performance (energy density, cycle life, safety, etc). In this regard, the most important discovery as a turning point in the research of NIBs is that NaFeO$_2$ is found to be electrochemically active in Na cells based on the Fe$^{3+}$/Fe$^{4+}$ redox couple [20]. This discovery may be on a par with the finding of LiCoO$_2$, which is still used as the primary electrode material for high-energy LIBs, in the Li system in 1980 [17]. The Fe$^{3+}$/Fe$^{4+}$ redox chemistry is unique to the Na system and has never been reported as active in the Li system. Additionally, the chemistry of the Mn$^{3+}$/Mn$^{4+}$ redox is quite different between the Li and Na systems, as
Figure 21. Crystal structures for (a) NaFeF₃, (b) NaₓMnFe(CN)₆, and (c) FeS₂ (pyrite).

Figure 22. Electrode performance of (a) FeF₃, (b) NaₓMnFe(CN)₆, and (c) FeS₂ (pyrite) in Na cells. (a) Reproduced with permission from [147]. Copyright 2009 Elsevier. (b) Reprinted with permission from [149]. Copyright 2013 John Wiley and Sons. (c) Reproduced with permission from [155]. Copyright 2007 Elsevier.
summarized in this review article. The spinel and layered phase transition problems are completely different from each other. Aside from elemental abundance, materials synthesis and processing methods also influence the cost of materials. Recently water-based electrolyte was also proposed as a cost-effective system, and the aqueous battery system with carbon/manganese oxide was commercialized for EES application by Aquion Energy [156]. However, its energy density could be significantly reduced compared with that of the non-aqueous (aprotic) system because of the lower operating voltage of aqueous cells. Cycle life is also another important factor in reducing total cost. Because the limitation of space for storing batteries may be a less significant issue for EES than for electronic devices and transportation systems, Wh versus cost of batteries is of primary importance. Therefore, the strategy of battery design (including materials) for EES is needed to balance the increase in energy density and the decrease in the total cost of batteries. Iron and manganese are believed to be key elements toward achieving high-energy and cost-effective NIBs for EES. In this article, some important points were not provided in terms of developing NIBs. Safety (especially for commonly used batteries) is another issue that needs to be discussed. Electrode performance is often dominated by the interfacial structure between electrodes and electrolytes. Electrolytes, electrolyte additives, binders, conductive materials, separators, current collectors, and all other cell components influence battery performance (and cost). Moreover, negative electrode materials for NIBs were not discussed in this article. The progress of recent research into negative electrodes for NIBs is discussed in another review article [157]. Intense research efforts all over the world will further accelerate the development of NIBs for EES in the future, even though many difficult challenges may lie ahead.

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