Nanostructured LiMnO$_2$ with Li$_3$PO$_4$ Integrated at the Atomic Scale for High-Energy Electrode Materials with Reversible Anionic Redox

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ABSTRACT: Nanostructured LiMnO$_2$ integrated with Li$_3$PO$_4$ was successfully synthesized by the mechanical milling route and examined as a new series of positive electrode materials for rechargeable lithium batteries. Although uniform mixing at the atomic scale between LiMnO$_2$ and Li$_3$PO$_4$ was not anticipated because of the noncompatibility of crystal structures for both phases, our study reveals that phosphorus ions with excess lithium ions dissolve into nanosize crystalline LiMnO$_2$ as first evidenced by elemental mapping using STEM-EELS combined with total X-ray scattering, solid-state NMR spectroscopy, and a theoretical ab initio study. The integrated phase features a low-crystallinity metastable phase with a unique nanostructure; the phosphorus ion located at the tetrahedral site shares faces with adjacent lithium ions at slightly distorted octahedral sites. This phase delivers a large reversible capacity of $\sim$320 mA h g$^{-1}$ as a high-energy positive electrode material in Li cells. The large reversible capacity originated from the contribution from the anionic redox of oxygen coupled with the cationic redox of Mn ions, as evidenced by operando soft XAS spectroscopy, and the superior reversibility of the anionic redox and the suppression of oxygen loss were also found by online electrochemical mass spectroscopy. The improved reversibility of the anionic redox originates from the presence of phosphorus ions associated with the suppression of oxygen dimerization, as supported by a theoretical study. From these results, the mechanistic foundations of nanostructured high-capacity positive electrode materials were established, and further chemical and physical optimization may lead to the development of next-generation electrochemical devices.

INTRODUCTION

Lithium insertion materials, which are electronic or ionic conductors, are indispensable to rechargeable lithium batteries extensively used in our daily life. The understanding of the chemistry of lithium insertion materials has rapidly developed in the past four decades, and the technological progress on rechargeable lithium batteries has resulted in the electric automobile applications. For electric vehicle applications, Ni/Co-containing layered oxides are the dominant positive electrode material, coupled with graphite as a negative electrode material. Critically, the market for electric vehicles is rapidly growing worldwide, and this expansion is likely to result in the shortage of Co resources. Therefore, high-energy and high-performance positive electrode materials without Co ions (and preferably without Ni ions as well) are required. In the past decade, Li$_2$MnO$_3$-based electrode materials have been extensively studied as potential high-capacity positive electrode materials. Compared with other layered materials such as LiMO$_2$, where M are transition metals, Li$_2$MnO$_3$-based 

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electrodes feature an enriched lithium content that results in higher theoretical capacities (at both the electrode and battery level) because the amount of the extractable Li content is larger. Although pure Li$_2$MnO$_3$ is electrochemically less active (or inactive), solid-solution samples such as Li$_{1.2}$Co$_{0.13}$Ni$_{0.13}$Mn$_{0.54}$O$_2$ deliver large reversible capacities as electrode materials. Charge compensation at high levels of lithium extraction has been demonstrated by the reversible oxidation of oxide ions in addition to the conventional redox of transition metal ions. However, a continuous phase transition associated with the formation of trivalent Mn ions, presumably coupled with oxygen loss on the charge, restricts its use for practical applications, especially in such rigid layered structures.

Redox reactions of such anionic species dramatically change the requirements of the host materials and hence the material design strategies for energy storage applications. New lithium-excess and high-capacity positive electrode materials have appeared in the past several years. Charge compensation at high levels of lithium extraction has been demonstrated by the reversible oxidation of oxide ions in addition to the conventional redox of transition metal ions. However, a continuous phase transition associated with the formation of trivalent Mn ions, presumably coupled with oxygen loss on the charge, restricts its use for practical applications, especially in such rigid layered structures.

RESULTS AND DISCUSSION

Synthesis of Materials and Detailed Phase Characterization. Figure 1a shows X-ray diffraction patterns of mixtures of LiMnO$_2$, Li$_3$PO$_4$, and various compositions in (1 − x)LiMnO$_2$−xLi$_3$PO$_4$ after mechanical milling. After mechanical milling, the well-defined diffraction pattern of LiMnO$_2$ (x = 0) with a zigzag-type layered structure is completely lost, and low crystallinity phases with cation-disordered rocksalt structures are observed, consistent with our previous report. In contrast, no change in the crystal structure for Li$_3$PO$_4$ (x = 1) was observed after milling under the same experimental conditions; however there was a noticeable decrease in the crystallinity. For the binary system, where x = 0.1 and 0.2, the diffraction pattern of Li$_3$PO$_4$ was completely lost, and a cation disordered rocksalt phase formed. The phase evolution process of x = 0.2 with different milling times, which was reformulated as Li$_{1/3}$P$_{1/6}$Mn$_{2/3}$O$_2$, is shown in Supporting Figure S1. After milling, TEM analysis revealed that a primary particle size reduced into less than 20 nm (Figure 1b and Supporting Figure S2), consistent with the observation of broad reflections in the diffraction patterns. Moreover, such nanoparticles are tightly agglomerated around each other, forming relatively larger secondary particles. Therefore, nanosized samples prepared by mechanical milling generally have a relatively small surface area. Note that a uniform distribution of Mn and P is evidenced from scanning transmission electron microscopy (STEM) coupled with elemental mapping by energy dispersive X-ray spectroscopy (EDX), as shown in Supporting Figure S2. Nevertheless, when the fraction of Li$_3$PO$_4$ increases to x = 0.3, a reflection characteristic of Li$_3$PO$_4$ with low-crystallinity at 2θ = 22° appears. Phase segregation was also observed by EDX mapping, as shown in Supporting Figure S3. These results clearly indicate that the “solubility” of Li$_3$PO$_4$ in LiMnO$_2$ is limited in a relatively narrow range using the milling method.

Although “apparently” single-phase samples for x = 0.1 and 0.2 were successfully obtained by mechanical milling, the detailed structure of the binary phase is still not clear. To further examine the crystal structures in the LiMnO$_2$−Li$_3$PO$_4$ binary system, cation distributions in the crystalline phase were determined using Rietveld analysis. Earlier work by Hayashi and co-workers on electrodes for solid-state batteries examined mechanical milling in the LiCoO$_2$ and Li$_2$SO$_4$ binary system. They proposed that nanosize LiCoO$_2$ was embedded in an amorphous matrix of Li$_2$SO$_4$, forming a nanocomposite. Further work associated with solid-state batteries examined a sputtered thin amorphous layer of Li$_3$PO$_4$ on LiNiO$_2$. A question arises; amorphous Li$_3$PO$_4$ cannot be obtained by mechanical milling, as shown in Figure 1a, and crystalline Li$_3$PO$_4$ only shows a reduction in the crystallinity with milling. Notably, synchrotron XRD data show a higher crystallinity for the rocksalt phase for x = 0.2 when compared with that of x = 0 without Li$_3$PO$_4$ (Supporting Figure S4). Therefore, the possibility of PO$_4^{3−}$ incorporation into crystalline domains with Mn ions cannot be eliminated.

To validate this hypothesis, a detailed structure of nanosize and rocksalt LiMnO$_2$ without phosphorus ions was first analyzed. An ideal rocksalt model in which both cations, Li and Mn ions, are located at the same octahedral 4a site is not suitable (Supporting Figure SS) as the intensity of the 111 reflection at 2θ = 12° is unmatched. The March distribution function was used along the 111 direction, resulting in a
significantly better fit. Note that this model contains a preferred orientation term. For Li$_{7/6}$P$_{1/6}$Mn$_{2/3}$O$_2$, phosphorus ions were modeled at tetrahedral 8c sites with the preferred orientation term, and a good fitting result was obtained (Supporting Figure S5). The lattice parameter of the sample increased from $a = 4.156$ Å to $4.181$ Å by phosphorus incorporation. This model assumes the formation of an atomic solid-solution-like phase, Li$_{1+x}$P$_x$Mn$_{1-2x}$O$_2$. It should be noted that this is likely a metastable phase with enriched structural defects, and is therefore segregated into LiMnO$_2$ and Li$_3$PO$_4$ upon heating (Supporting Figure S6a); however, the metastable phase is stable after one-year storage in the glovebox at room temperature (Supporting Figure S6b).
the solid-solution model, a large repulsive electrostatic interaction is unavoidable for face-shared sites between octahedral and tetrahedral sites (discussed later).

To clarify the structural analysis, detailed nanostructures were analyzed by STEM combined with electron energy loss spectroscopy (EELS), with atomic distributions observed with a 1.5 nm spatial resolution. Typical EELS spectra of the P L-edge are also shown in Figure 1b, and Mn L-edge and Li K-edge spectra are shown in Supporting Figures 7a; atomic distributions of P and Mn ions obtained from the intensity in the EELS spectra are also shown in Figure 1b. EELS analysis reveals that P ions are well integrated with Mn ions at the nanoscale, and uniform distributions of cationic species are also noted. The major phase appears to be a nanosize crystalline phase with a size of less than 5 nm (Figure 1b and Supporting Figure S7b), and the XRD and TEM observations and data are inconsistent with the scenario of the formation of amorphous Li3PO4 and a composite structure with crystalline LiMnO2. The redistribution of both cationic species clearly proceeds by mechanical milling in this binary system. Surface conversion reactions were also proposed for the nano-composite of LiF and MnO31, but a more uniform distribution of the cationic species is noted in the binary system of LiMnO2−Li3PO4. In addition, the incorporation of P ions into the crystalline LiMnO2 phase is further supported from the file of P L-edge EELS spectra. P L-edge EELS spectra collected from different spots are clearly different from those of Li3PO4 (Figure 1b), with a small but notable energy shift in the spectra relative to Li3PO4. A similar trend is also noted in the Li K-edge and Mn L-edge EELS spectra (Supporting Figure S7a).

The incorporation of P ions into the crystalline LiMnO2 phase is further evidenced by total X-ray scattering measurements, with patterns in reciprocal space for different samples shown in Supporting Figure S8. The reduced pair distribution functions (PDFs) for rocksalt LiMnO2 and Li7/6P1/6Mn2/3O2 are shown in Figure 2. Analysis of local structures for the as-prepared sample x = 0.2, Li7/6P1/6Mn2/3O2. (a) Experimental X-ray pair distribution function (PDF), (b) Raman spectra, and (c) solid-state NMR spectra. The data for the reference materials are also shown. From the all data, the clustering of phosphorus ions is not seen for Li7/6P1/6Mn2/3O2, indicating that phosphorus is diluted to crystalline rocksalt LiMnO2.
Figure 3. Electrochemical properties of the \((1 - x)\)LiMnO\(_2\)-Li\(_3\)PO\(_4\) binary system. (a) Galvanostatic charge–discharge curves of the samples with different compositions prepared by mechanical milling, (b) rate-capability of the sample \(x = 0.2\), Li\(_{7/6}\)P\(_{1/6}\)Mn\(_{2/3}\)O\(_2\), and (c) dependency of cutoff voltages on reversible capacities and capacity retention. The electrode loading was ca. 6.0–6.5 mg cm\(^{-2}\) for these electrochemical tests.

are shown in Figure 2a. Although both samples show similar PPDFs in the \(r\)-range over 3 Å, a clear difference is visible in first and second peaks at 1.6 and 2.0 Å, respectively. The intensity of the 2.0 Å peak originating from Mn–O bonds decreases, while that of the 1.6 Å peak increases; this originates from P–O bonds, as clearly found in reference PDF data for Li\(_3\)PO\(_4\). Note that no change in the PDF data before and after milling was observed for Li\(_3\)PO\(_4\) (Supporting Figure S9), indicating that amorphous Li\(_3\)PO\(_4\) was not formed by mechanical milling. Li\(_{7/6}\)P\(_{1/6}\)Mn\(_{2/3}\)O\(_2\) is a metastable phase (Supporting Figure S6a) that transforms to zigzag LiMnO\(_2\) and Li\(_3\)PO\(_4\) during heating to 550 °C, as is clearly observed in the PDF by taking the sum of the data for LiMnO\(_2\) and Li\(_3\)PO\(_4\) (Figure 2a). The clustering of PO\(_4^{3-}\) ions in the 550 °C heated structure clearly influences the profile of the PDF data in the wide \(r\)-range (Figure 2a) and is in contrast with mixed Li\(_{7/6}\)P\(_{1/6}\)Mn\(_{2/3}\)O\(_2\) and rocksalt LiMnO\(_2\), where the wide \(r\)-range data essentially overlap. This is strong evidence that phosphorus ions are nonclustered and diluted to rocksalt LiMnO\(_2\) in the milled Li\(_{7/6}\)P\(_{1/6}\)Mn\(_{2/3}\)O\(_2\). A solid solution was formed rather than clusters.

These observations are also supported by Raman and solid-state NMR spectroscopy. Figure 2b compares the Raman spectra of LiMnO\(_2\), Li\(_3\)PO\(_4\), and Li\(_{7/6}\)P\(_{1/6}\)Mn\(_{2/3}\)O\(_2\). Two clearly resolved peaks were observed for the sample after milling. The peak at 623 cm\(^{-1}\) is assigned as the vibration of the Mn–O bonds in the MnO\(_2\) octahedra, and a similar peak is also visible for rocksalt LiMnO\(_2\) at 614 cm\(^{-1}\). In the binary system, a minute energy shift (wavenumber) compared with that of rocksalt LiMnO\(_2\) was noted. In addition, another peak at 930 cm\(^{-1}\) for rocksalt LiMnO\(_2\) is present, originating from the symmetric stretching mode of PO\(_4\) tetrahedra. However, a clear shift in the wavenumber was also compared with the spectrum of pure Li\(_3\)PO\(_4\) (955 cm\(^{-1}\)). Note that the peak shift to 930 cm\(^{-1}\) was observed for the high-temperature phase of Li\(_3\)PO\(_4\) originating from differences in the P–O interatomic distances (1.55 Å for the low-temperature phase and 1.86 Å for the high-temperature phase). The P–O distance for Li\(_{7/6}\)P\(_{1/6}\)Mn\(_{2/3}\)O\(_2\) was calculated to be 1.81 Å, assuming that phosphorus ions were located at tetrahedral sites in the ccp lattice (also see Supporting Figure S12a). The P–O interatomic distance is almost the same with that of the high-temperature phase of Li\(_3\)PO\(_4\); therefore, the Raman peak shift for Li\(_{7/6}\)P\(_{1/6}\)Mn\(_{2/3}\)O\(_2\) is also consistent with the solid solution model. In addition, the increase of the P–O distance after mixing with LiMnO\(_2\) was also found for the PDF data (Figure 2a). Such differences in the local environments are further supported by solid-state NMR spectroscopy. \(^{7}\)Li and \(^{31}\)P NMR spectra collected, including reference materials, are shown in Supporting Figure S10. There is a positive chemical shift (36 ppm) in the \(^{7}\)Li NMR spectra for zigzag-type LiMnO\(_2\) originating from the interaction of electrons in Mn\(^{3+}\) ions via oxygen (Li–O–Mn bonding). After milling, a small chemical shift for the \(^{7}\)Li NMR spectra was noted (Figure 2c). In the disordered rocksalt structure, a number of different local environments for Li ions are created; therefore, the total spin density transferred to Li ions from Mn ions may be canceled out. Note that a broad peak centered at 36 ppm is also present, which may originate from the presence of defects in the structure that resemble LiMnO\(_2\). No difference in the chemical shift was noted for Li\(_3\)PO\(_4\) for \(^{7}\)Li and \(^{31}\)P NMR spectra before and after milling, as shown in Figure 2c and Supporting Figure S11, respectively. This is also consistent with the data obtained by Raman scattering (Supporting Figure S12b). Peak broadening was observed for Li\(_3\)PO\(_4\) after milling, probably associated with the lowered crystallinity by milling. For Li\(_{7/6}\)P\(_{1/6}\)Mn\(_{2/3}\)O\(_2\), the chemical shift of the \(^{7}\)Li NMR spectra is the same as that of rocksalt LiMnO\(_2\); however, there is a modification of chemical shift in \(^{31}\)P NMR spectra, indicating that there is interaction of the PO\(_4\) tetrahedra with Mn ions with d electrons. These
results are also consistent with the observation from PDF analysis, EELS spectra, and Raman spectra, and it was concluded that PO$_4^{3-}$ ions are nonclustered for Li$_{7/6}$P$_{1/6}$Mn$_{2/3}$O$_2$ and successfully dissolved into LiMnO$_2$.

**Electrochemistry.** Electrochemical properties of the binary system of LiMnO$_2$−Li$_3$PO$_4$ as metastable phases were examined as positive electrode materials in Li cells. Galvanostatic charge−discharge curves of the binary system are shown in Figure 3. Rocksalt LiMnO$_2$ shows ca. 90% of the theoretical capacity (286 mA h g$^{-1}$) calculated from the Li content and Mn$^{3+}$/Mn$^{4+}$ redox.$^{28}$ Reversible capacities of the binary system increase relative to the parent with the addition of Li$_3$PO$_4$. The highest reversible capacity was obtained for the $x = 0.1$ sample of over 300 mA h g$^{-1}$. The reversible capacity was slightly reduced for $x = 0.2$ (Li$_{7/6}$P$_{1/6}$Mn$_{2/3}$O$_2$). However, the reversible capacity reached nearly 300 mA h g$^{-1}$, which clearly exceeds the theoretical capacity based on Mn$^{3+}$/Mn$^{4+}$ redox (218 mA h g$^{-1}$). This fact suggests that anionic redox is activated in this system, which also supports the successful integration of LiMnO$_2$ and Li$_3$PO$_4$. Li ions, which are originally found in the structure of Li$_3$PO$_4$, are effectively extracted by the electrochemical oxidation of oxide ions for the integrated phase (anionic redox in this system is discussed further in a later section). The initial discharge capacity is slightly larger than that of the initial charge capacity. A similar trend was also observed for nanosized samples prepared by mechanical milling, originating from the partial oxidation of the sample during milling (also see the Supporting Information).
Interestingly, the further enrichment of Li$_3$PO$_4$ in the binary system results in the reduction of the reversible capacities. This observation is also consistent with the results obtained by XRD, where phase segregation of Li$_3$PO$_4$ was observed for $x = 0.3$. Li ions cannot be extracted from the segregated phase because Li$_3$PO$_4$ is an electronic insulator. Nevertheless, the well-integrated phase, $x = 0.2$, shows a relatively good rate capability and delivers 190 mA h g$^{-1}$ at a rate of 640 mA g$^{-1}$, (Figure 3b), which is significantly better than those of rocksalt LiMnO$_2$ prepared by mechanical milling without Li$_3$PO$_4$. Electrochemical properties of the sample of $x = 0.2$ were further tested with different cutoff voltages in Li cells. Initial discharge capacities are shown in Figure 3c, and charge–discharge curves and capacity retention are also compared in Supporting Figure S13. The discharge capacity increased to ca. 320 mA h g$^{-1}$ with a 5.2 V cutoff. However, cyclability as electrode materials is not acceptable, and nearly 50% of the reversible capacity was lost after 30 cycles. In contrast, good capacity retention is observed with a 4.5 V cutoff, and the sample retained 80% of the reversible capacity. Although the reversible capacity was reduced to 180 mA h g$^{-1}$, excellent capacity retention was achieved with a 4.1 V cutoff. Note that the reversible capacities and capacity retention are also significantly influenced by the operating temperature (Supporting Figure S14). A large reversible capacity of 320 mA h g$^{-1}$ was observed at 50 °C, but a deterioration of the capacity retention was observed. In contrast, good capacity retention was realized at 0 °C even though the reversible capacity was reduced to 235 mA h g$^{-1}$. This observation suggests that irreversible oxygen loss occurs on electrochemical cycles and is accelerated at elevated temperatures, as observed in Li$_2$MnO$_3$-based electrode materials.

**Charge Compensation Mechanisms.** Reaction mechanisms of the binary system of LiMnO$_2$–Li$_3$PO$_4$ as electrode materials were examined by synchrotron X-ray diffraction (SXRD) combined with hard-soft X-ray absorption spectroscopy (XAS) and online gas analysis focusing on temperatures, as observed in Li$_2$MnO$_3$-based electrode materials. This observation is also consistent with the non-negligible deterioration of cyclability after charging to 5.2 V and at elevated temperatures (Supporting Figures S13 and S14). Significantly better capacity retention was achieved with a 4.5 V cutoff as shown in Figure 3c. The changes in electronic structures of phosphorus ions were also studied, and P K-edge XAS spectra were collected, as shown in Supporting Figure S16d. A gradual shift of the spectra to a higher energy region was noted on the charge process. A similar phenomenon was also observed for Li$_{1-x}$FePO$_4$ and the peak shift was expected to originate from changes in local structures (shrinkage of the crystal lattice) and bonding characters associated with the oxidation of Mn ions. These changes in P K-edge spectra also support the successful integration of phosphorus ions into LiMnO$_2$.

To understand the charge compensation process, soft X-ray absorption spectroscopy was applied to study changes in electronic structures based on previous work indicating oxygen redox activity for Li-excess electrode materials using this technique. However, ex-situ soft XAS spectroscopy requires high-vacuum conditions that, when coupled with possible extrinsic changes induced in the samples during washing, drying, and long exposure to vacuum, can provide misleading information. Therefore, *operando* soft X-ray absorption spectroscopy was developed and utilized in this study (Figure 4b). Instead of a conventional carbonate electrolyte, lithium bis(trifluoromethanesulfonyl)amide (TFSA) dissolved in acetonitrile was utilized as the electrolyte to reduce X-ray absorption. Although TFSA anions contain oxygen in the structure, the major absorption was observed above 533.5 eV, as shown in Supporting Figure S15a; therefore, changes in O K-edge XAS spectra near pre-edge regions from the electrode materials could be clearly detected. Aluminum-sputtered Si$_3$N$_4$ was used as windows to allow the transmittance of the synchrotron X-rays. Acetonitrile is reactive with metallic Li; therefore, a delithiated phase of lithium iron phosphate, Li$_{1-x}$FePO$_4$, was used as a counter electrode. A charge curve taken during the operando measurement is shown in Supporting Figure S15b. The irreversible capacity was relatively large, probably originating from electrolyte decomposition. Therefore, the chemical composition and amount of extracted Li ions (equaling the charge capacity) were estimated and calibrated by comparing the cutoff voltages. A clear shift of the O K-edge spectra was noted on charge, as shown in Figure 4c, and a similar trend was observed with the *ex situ* study shown in Supporting Figure S16. After charging to 110 mA h g$^{-1}$ (corresponding to 4 V vs Li$^+$/Li), Mn was in the tetravalent state, and no further change was observed beyond the 4 V region for the oxidation state of Mn ions. Pronounced changes in the O K-edge XAS spectra were subsequently noted, and peak intensity around 532 eV increased as the charge capacity and voltage increased. A similar trend is noted with other Li-excess materials with Mn ions. This peak is proposed to originate from the hole creation and stabilization by a π-type interaction with Mn t$_2g$ orbital. The appearance of a clear peak at 532 eV is noted for Li$_{1.2}$Ti$_{0.4}$Mn$_{0.4}$O$_2$, suggesting that the stability of the holes created by electrochemical oxidation is energetically less stable for the nanosize samples prepared by mechanical milling. This finding is also consistent with the non-negligible deterioration of cyclability after charging to 5.2 V and at elevated temperatures (Supporting Figures S13 and S14). Significantly better capacity retention was achieved with a 4.5 V cutoff as shown in Figure 3c. The changes in electronic structures of phosphorus ions were also studied, and P K-edge XAS spectra were collected, as shown in Supporting Figure S16d. A gradual shift of the spectra to a higher energy region was noted on the charge process. A similar phenomenon was also observed for Li$_{1-x}$FePO$_4$ and the peak shift was expected to originate from changes in local structures (shrinkage of the crystal lattice) and bonding characters associated with the oxidation of Mn ions. These changes in P K-edge spectra also support the successful integration of phosphorus ions into LiMnO$_2$.

Note that on the discharge process the partial Mn reduction to a divalent state, associated with minor oxygen loss on charge, is evidenced by the *ex situ* XAS study (Supporting Figure S16). Such phenomena are generally observed in Li$_2$MnO$_3$-based high-capacity electrode materials. Nevertheless, the profiles of O K-edge XAS spectra for second charge–discharge are superimposed with those for first charge–discharge as shown in Supporting Figure S17, indicating the high reversibility in the anionic redox for Li$_{1-x}$P$_{1/6}$Mn$_{2/3}$O$_2$ on the charge–discharge processes.

The suppression of oxygen loss for the phosphorus-integrated composition is also supported by online electrochemical mass spectrometry (OEMS) in Figure 4d and e. For comparison, nanosized Li$_2$MnO$_3$ has been prepared by
For nanosized Li$_2$MnO$_3$, the CO$_2$ partial pressure drastically increases on lithium extraction (Figure 4d), which is consistent with published data.$^{39}$ CO$_2$ is considered to originate from the mechanical milling (Supporting Figure S18). For nanosized Li$_x$MnO$_y$, the CO$_2$ partial pressure drastically increases on

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Figure 5. Theoretical calculation of Li$_{7/6}$P$_{1/6}$Mn$_{2/3}$O$_2$. (a) An optimized crystal structure of rocksalt LiMnO$_2$ after P-integration, and a local structure of the P ion in the rocksalt phase. Changes in the number of valence electrons for (b) Mn, P, and (c) O ions upon the delithiation process from Li$_9$Mn$_6$PO$_{16}$ (∼Li$_{7/6}$P$_{1/6}$Mn$_{2/3}$O$_2$). Li ions are extracted from the model one by one, which is the lowest energy in the structure. Electron density changes during delithiation are also visualized in panel d. Yellow and cyan isosurfaces (drawn at 0.01 e$^{-}$Bohr$^{-1}$) indicate electron accumulation and depletion, respectively; □ denotes vacant sites. The data for $-3$, $-7$, and $-9$ Li are also shown in Supporting Figure S20.
side reaction between the electrolyte solvent and the highly active singlet oxygen that is released from the electrode materials by irreversible anionic redox.\textsuperscript{40} Irreversible oxygen loss from the active material is a dominative process for nanosized Li$_{x}$MnO$_{2}$. In addition, hydrogen gas was detected as the charge capacity and voltage increased, which was previously detected for Li$_{1.2}$Mn$_{0.8}$Ti$_{0.2}$O$_{2}$ on charge and likely originated from the oxidative decomposition of the electrolyte solution at $>$4.7 V.\textsuperscript{35} In contrast, gas evolution for both CO$_{2}$ and H$_{2}$ was notably suppressed for Li$_{7/6}$P$_{1/6}$Mn$_{2/3}$O$_{2}$ on charge to 4.5 V (Figure 4e), although a small amount of CO$_{2}$ was detected in the higher voltage region; this amount was significantly smaller than nanosized Li$_{x}$MnO$_{2}$. This finding is consistent with the better electro-chemical reversibility for Li$_{7/6}$P$_{1/6}$Mn$_{2/3}$O$_{2}$ with a 4.5 V cutoff (Figure 3c). To further increase the cyclability as electrode materials with anionic redox, a surface coating,\textsuperscript{42} functional binder,\textsuperscript{43} and high-voltage-tolerated electrolyte\textsuperscript{44} would be effective to suppress unfavorable side reactions with electrolyte.

Theoretical Understanding of Crystal Structure and Reaction Mechanisms. To provide a unified picture of the phosphorus integration into LiMnO$_{2}$, theoretical calculations were conducted. Models used were derived from the experimental data that P ions are diluted in LiMnO$_{2}$ and no P-based clusters occur. First, a large unit cell of Li$_{16}$Mn$_{16}$O$_{32}$ was constructed, and then two Mn ions were replaced by Li and P ions, leading to the formation of Li$_{15}$Mn$_{14}$PO$_{32}$. After structural relaxation, the formation of the unique nanostructure was noted. The P ion at the tetrahedral site shares faces with three lithium ions originally located at octahedral sites. An electrostatic repulsive interaction between P and Li ions results in the displacement of Li ions from the original octahedral position, as shown in Figure 5a. The total energy of Li$_{15}$Mn$_{14}$PO$_{32}$ is 3.11 eV higher than that of a simple mixture of Li$_{16}$Mn$_{16}$O$_{32}$ (16 units of LiMnO$_{2}$) and Li$_{16}$PO$_{4}$, which is consistent with the fact that the P-integrated phase is the metastable phase (Supporting Figure S6). Nevertheless, the total energy is relatively stabilized through the structural relaxation associated with the displacement of the face-shared Li ions. Note that when the trivalent Mn ion is forced to share the face with the P ion instead of the Li ion, the energy is further destabilized by 1.4 eV. These results indicate that the formation of the Li-rich phase and the short-range ordering of one P and three Li ions are necessary to energetically stabilize such unique metastable phases.

Li extraction processes from the P-integrated LiMnO$_{2}$ were further studied by theoretical calculations, and the model with a smaller unit cell of Li$_{9}$Mn$_{9}$PO$_{16}$ was used (also see the Supporting Information). Note that the unit cell volume of Li$_{9}$Mn$_{9}$PO$_{16}$ is larger (approximately 2.3%) than that of Li$_{9}$Mn$_{9}$O$_{16}$ without phosphorus ions, and a similar trend in the unit cell volume change was observed from experimental observations (Supporting Figure S4). The calculated voltage upon Li extraction (Supporting Figure S19) shows two different regions at 3 and 4 V, which likely correspond to cationic Mn and anionic O redox, respectively. Changes in the oxidation states of the P-integrated phase were evaluated by the Bader method; the number of valence electrons on each atomic site upon Li extraction summarized is Figure 5b and c, and variations in the charge density are visualized in Figure 5d and Supporting Figure S20. From the valence electrons, oxide ions are classified as oxygen bonded or oxygen nonbonded to phosphorus. The covalency of the P–O bonds is much higher than those of the Li–O and Mn–O bonds, resulting in the difference in the number of valence electrons. On the charge process, Mn ions are oxidized and coupled with Li extraction; therefore, the number of valence electrons is reduced for Mn ions, forming $\square$Li$_{9}$Mn$_{9}$PO$_{16}$ ($\square$ denotes vacant sites). Upon further oxidation and Li extraction, a clear reduction of the number of valence electrons was observed for oxygen (Figure 5c). This finding is consistent with experimentally observed operando XAS data (Figure 4c). Note that oxygen bonded to phosphorus is not responsible for charge compensation and oxygen bonded to Mn ions is selectively oxidized, as shown in the number of valence electron and differential charge density distributions. Moreover, no dimerization of oxygen for the fully charged sample, $\square$Li$_{9}$Mn$_{9}$PO$_{16}$, was observed even after structural relaxation. It is proposed that the presence of phosphorus ions in the structure suppresses the "excess" oxidation of oxide ions; therefore, the possibility of oxygen dimerization around phosphorus ions would be reduced in this system, leading to the better reversibility of anionic redox. This is consistent with better performance for the P-integrated phase relative to that of the nanosized Li$_{x}$MnO$_{2}$ demonstrated above.

CONCLUSIONS

In this study, a new series of electrode materials has been proposed, i.e., rocksalt-type metastable crystalline phases with atomically incorporated P ions. The successful integration of phosphorus ions with excess Li ions into nanosize and crystalline LiMnO$_{2}$ was demonstrated by the combination of different characterization techniques. The P ion is located at the tetrahedral site in the CCP lattice, which shares faces with adjacent Li ions, and a slight distortion from the ideal octahedral site for Li$_{x}$O-$\square$ sites energetically stabilizes this unique nanostructure. This phase delivers a large reversible capacity of $\sim$320 mA h g$^{-1}$ that originates from the contribution from cationic redox reaction of Mn ions coupled with oxygen anionic redox, and the superior reversibility of the anionic redox is realized by the presence of the P ion in this phase. The use of such materials with unique nanostructures is a conceptually new approach to electrode design, which may lead to the next generation of materials. This metastable system opens the possibility for a new path to design high-capacity electrode materials. Moreover, this new concept for material design could also extended to different systems, such as sodium or potassium battery applications, leading to the development of a sustainable energy society in the future.

EXPERIMENTAL SECTION

Synthesis of Materials. A nanoscale integrated LiMnO$_{2}$–Li$_{2}$PO$_{4}$ binary system was prepared by mechanical milling using a planetary ball mill (PULVERISSETTE 7; FRITSCH). For the sample of $x = 0.2$ in the $(1 - x)$Li$_{16}$Mn$_{16}$O$_{32}$-$x$Li$_{2}$PO$_{4}$ binary system, 1.146 g of LiMnO$_{2}$ and 0.354 g of Li$_{2}$PO$_{4}$ (97%, Wako) were initially mixed using a zirconia pot (45 mL) and milled for 12 h. This process was repeated three times, and the mixture was removed from the container and mixed with a mortar and pestle to ensure sample uniformity during the milling. The mixture was again milled using the zirconia pot and balls at 600 rpm for 12 h. This process was repeated three times, and the mixture was milled for 36 h in total. LiMnO$_{2}$ was prepared from Li$_{2}$CO$_{3}$ (98.5%, Kanto Kagaku) and MnO$_{3}$.
at 900 °C for 12 h in an Ar atmosphere. MnO2 was obtained by heating MnCO3 (Kishida Chemical Co., Ltd.) at 850 °C for 12 h in air. After the preparation, the samples were stored in an Ar-filled glovebox. The sample handling before and after the mechanical milling was also carried out in an Ar-filled glovebox without exposure to moist air.

**Electrochemical Measurement.** After synthetic milling, the samples were further mixed with acetylene black (HS-100; Denka Co., Ltd., LiMnO2–Li3PO4/AB 90:10 wt %) using the planetary ball mill at 300 rpm for 12 h with the zirconia container and balls. Better electrode performance was achieved through this process even though a relatively higher content of carbon sacrifices the volumetric energy density. Composite positive electrodes comprised of 76.5 wt % LiMnO2–Li3PO4, 13.5 wt % acetylene black, and 10 wt % polyvinylidene fluoride (KF 1100; Kureha Co. Ltd.) dispersed in N-methylpyrrolidone were pasted on aluminum foil as a current collector. The electrodes were dried at 80 °C for 2 h in vacuum and then heated at 120 °C for 2 h. Metallic lithium (Honojo Metal Co., Ltd.) was used as a negative electrode. The electrolyte solution used was 1.0 mol dm−3 LiPF6 dissolved in ethylene carbonate/dimethyl carbonate (3:7 by volume, battery grade; Kishida Chemical Corp., Ltd.). Two-electrode cells (TJ-AC; Tomcell Japan) were assembled in an Ar-filled glovebox. The cells were cycled at a rate of 10 mA g−1 at room temperature.

**Characterization of Materials.** X-ray diffraction (XRD) patterns of the samples were collected using an X-ray diffractometer (D2 PHASER; Bruker Corp., Ltd.) equipped with a one-dimensional X-ray detector using Cu Ka radiation generated at 300 W (30 kV and 10 mA) with a Ni filter. The planetary ball mill at 300 rpm for 12 h with the zirconia container and balls. Better electrode performance was achieved through this process even though a relatively higher content of carbon sacrifices the volumetric energy density. Composite positive electrodes comprised of 76.5 wt % LiMnO2–Li3PO4, 13.5 wt % acetylene black, and 10 wt % polyvinylidene fluoride (KF 1100; Kureha Co. Ltd.) dispersed in N-methylpyrrolidone were pasted on aluminum foil as a current collector. The electrodes were dried at 80 °C for 2 h in vacuum and then heated at 120 °C for 2 h. Metallic lithium (Honojo Metal Co., Ltd.) was used as a negative electrode. The electrolyte solution used was 1.0 mol dm−3 LiPF6 dissolved in ethylene carbonate/dimethyl carbonate (3:7 by volume, battery grade; Kishida Chemical Corp., Ltd.). Two-electrode cells (TJ-AC; Tomcell Japan) were assembled in an Ar-filled glovebox. The cells were cycled at a rate of 10 mA g−1 at room temperature.

**STEM–EELS was conducted using an electron microscope (Titan Cubed; Thermo Fisher Scientific) equipped with a spectroscope (GIF Quantum ERS; Gatan). The electron beam energy and EELS resolution were 300 keV and 1.3 eV, respectively. The P/Mn and Li/Mn atomic ratios were calculated with P-L2,3, Mn-M2,3, and Li-M1,2 edges at each pixel using software (DigitalMicrograph; Gatan). Calculated Li/Mn ratios were corrected using the similarly calculated ratios of the reference materials, Li3MnO4 and LiMn2O4.**

X-ray total scattering measurements was performed with an incident X-ray energy of E = 61.4 keV at the BL04B2 beamline of the Photon Factory Synchrotron Source in Japan. Hard XAS spectra were collected with a silicon monochromator in the transmission mode. The intensities of the incident and transmitted X-rays were measured using an ionization chamber at room temperature. Composite electrode samples were prepared using Li metal as the negative electrode at a rate of 10 mA g−1. The composite electrodes were rinsed with dimethyl carbonate and sealed in a water-resistant polymer film in the Ar-filled glovebox. Normalization of the XAS spectra was carried out using the program code IFEFFIT.45 The postedge background was determined using a cubic spline procedure.

**Ex situ and operando XAS measurements for O K-edge and Mn L-edge were collected at BL27SU in SPring-8, Japan. For ex situ measurements, the same sample preparation method was used as that for the hard XAS measurement. The absorption spectra were collected with the partial fluorescence mode. The detailed experimental setup of the operando XAS measurement is found in literature.34**

**An online mass electrochemical mass spectrometry (OEMS)** system was established as described in previous work.38 The custom-designed OEMS cell (Tomcell Japan) was comprised of a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC, 3:7 by volume) as the electrolyte solution. The assembled OEMS cell was rested in an Ar-filled glovebox for 2 h and linked to the OEMS apparatus in a constant-temperature container maintained at 25 °C. The OEMS cell was purged with an Ar gas (99.9999%) for a total 10 min to test the system. The cell pressure (16–18 psi) and the mass spectrum were also monitored at an open-circuit voltage at room temperature. The CO2 gas evolution from DMC vaporization stopped after 3 h, which was then set as background. The galvanostatic charging process was carried out at a current density of 10 mA g−1. The gas analysis was conducted after collecting gas products every 1 h.

**Spin-polarized DFT + U calculations were performed using the GPU-port46,49 of the Vienna Ab Initio Simulation Package (VASP). Exchange–correlation effects and ion–electron interactions were described by the Perdew–Burke–Ernzerhof (PBE) functional52 and the projector-augmented wave (PAW) method35,54, respectively. Dispersion interactions were described by DFT-D3.55 The cutoff energy for plane-wave expansion was 520 eV, and an onsite Coulomb interaction correction of U − J = 3.9 eV56 was applied to Mn 3d using the method by Dudarev et al.57 In structural relaxation calculations, atomic coordinates as well as cell parameters were optimized. The Bader method was used to determine the number of valence electrons on each atomic site.58**

**Safety Statement.** No unexpected or unusually high-safety hazards were encountered.
**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acscentsci.0c01200](https://pubs.acs.org/doi/10.1021/acscentsci.0c01200).

DFT calculation details; structural evolutions of the LiMnO$_2$–Li$_x$PO$_4$ system; STEM images; EDX maps; SEM images; comparison of SXRD patterns; Reitveld analysis of rocksalt LiMnO$_2$ and Li$_{5/6}$P$_{1/6}$Mn$_{2/3}$O$_2$; phase segregation of Li$_{5/6}$P$_{1/6}$Mn$_{2/3}$O$_2$ after heating; analysis of the Mn distribution; X-ray diffraction patterns; X-ray pair distribution functions; Raman, XAS, and solid-state NMR spectra; charge–discharge and charge curves; charge density differences, and synthesis and electrochemical properties of nanosize rocksalt Li$_x$MnO$_3$ (PDF)

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**Notes**

The authors declare no competing financial interest.

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