Battery chemistry based on earth-abundant elements has great potential for the development of cost-effective, large-scale energy storage systems. Herein, we report, for the first time, that maricite NaFePO₄ can function as an excellent cathode material for Na ion batteries, an unexpected result since it has been regarded as an electrochemically inactive electrode for rechargeable batteries. Our investigation of the Na re-(de)intercalation mechanism reveals that all Na ions can be deintercalated from the nano-sized maricite NaFePO₄ with simultaneous transformation into amorphous FePO₄. Our quantum mechanics calculations show that the underlying reason for the remarkable electrochemical activity of NaFePO₄ is the significantly enhanced Na mobility in the transformed phase, which is ~one fourth of the hopping activation barrier. Maricite NaFePO₄, fully sodiated amorphous FePO₄, delivered a capacity of 142 mA h g⁻¹ (92% of the theoretical value) at the first cycle, and showed outstanding cyclability with a negligible capacity fade after 200 cycles (95% retention of the initial cycle).

The demand for large-scale energy storage systems (EESs) has prompted considerable effort in the development of new types of batteries with cost-effective and sustainable properties. While the high cost of current Li ion batteries (LIBs) remains one of the major hurdles towards large-scale energy storage applications,¹⁻¹¹ battery chemistry based on earth-abundant elements offers a feasible solution. Recently, Na ion batteries (NIBs) have been considered as a promising alternative to LIBs since the underlying electrochemical reaction is similar to that of LIBs, but is based on the unlimited resources of Na from seawater.¹²⁻²⁰ The use of redox chemistry using earth abundant transition metals would provide the optimal combination with Na electrochemistry further highlighting the advantage of NIBs.

In recent years, considerable research has been carried out on Fe-based electrode materials for use in NIBs.¹⁶,¹⁹,²¹⁻²⁴ Komaba et al. reported a series of layered Na(Fe,Mn)O₂ cathodes exhibiting promising electrochemical properties.¹⁶ Nazar et al., Yamada et al., and Choi et al. showed that the reversible intercalation of Na ions with the Fe³⁺/Fe²⁺ redox reactions is possible in polyhionic compounds, such as Na₂FePO₄F and Na₃FeP₂O₇.²⁰,²²,²³,²⁵ More recently, our group reported Na₃Fe₂(PO₄)₂ (P₂O₇), a mixed-polyhionic compound as a new cathode for NIBs. In particular, such polyhionic compounds are capable of accommodating large Na ions in the crystal with only slight volumetric changes, thus behaving as stable reversible hosts for Na ions. Furthermore, the stable P–O covalent bond offers chemical and structural stability, even though the heavy framework generally reduces the theoretical capacity. Herein,
we introduce NaFePO$_4$ as a promising cathode material for NIBs. Although its theoretical capacity (ca. 155 mAh g$^{-1}$) can far exceed other reported Fe-based polyanion cathode materials, such as Na$_2$FePO$_4$F (ca. 120 mAh g$^{-1}$), Na$_2$FeP$_2$O$_7$ (ca. 90 mAh g$^{-1}$) and Na$_2$Fe(PO$_4$)$_2$(P$_2$O$_7$) (ca. 130 mAh g$^{-1}$),$^{17-22,26}$ maricite, the thermodynamically stable phase of NaFePO$_4$, has been regarded as electrochemically inactive in rechargeable batteries.$^{20}$ The NaFePO$_4$ composition also exhibits an olivine structure; however, the olivine structure is not stable and cannot be synthesized by conventional synthetic routes.$^{17-19}$ In this work, we show, for the first time, that maricite NaFePO$_4$ can function as an excellent cathode material for rechargeable Na batteries.

We synthesized maricite NaFePO$_4$ powder through a simple solid-state method followed by ball-milling with conductive carbon. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses (ESI Fig. S1†) show that maricite NaFePO$_4$ (particle size: ca. 50 nm) is phase-pure, i.e., without any impurities or second phases. It is identified that the amount of carbon in the carbon-mixed NaFePO$_4$ is approximately 20%, using thermo-gravimetric analysis (TGA) and carbon analysis (ESI Fig. S2 and ESI Table 1†). Details regarding the experimental conditions are provided in the ESI.† We first investigated the electrochemical activity of maricite NaFePO$_4$ in Na cells using a Na metal anode with a 1 M NaPF$_6$ (1:1 EC/PC) electrolyte. To our surprise, a maricite NaFePO$_4$ electrode could be charged and discharged with almost all Na ions participating in the electrochemical reaction (Fig. 1(a)). At a C/20 rate, we observed a capacity of ca. 142 mAh g$^{-1}$, which corresponds to 92% of its theoretical capacity. In our comparative study with lithium cells, we also found that a similar mechanism works for the maricite electrode with lithium (ESI Fig. S3†). During the first charge, Na is extracted from the maricite showing a slightly high charging voltage, followed by amorphization. After the transition, the electrochemical profile becomes similar to the well-known behavior of the amorphous FePO$_4$ in the lithium cells.$^{27,28}$ Moreover, this capacity was retained over more than 200 cycles (Fig. 1(b)) without a notable change in the electrochemical profile with the exception of the first charge curve. The inset of Fig. 1(a) shows the discharge profiles of the maricite NaFePO$_4$ electrode measured at various current rates (2 C, 1 C, C/2, C/5, C/10, and C/20 from 1.5 to 4.5 V), which indicates that ca. 70% of the initial capacity can be delivered in 1.288 hour (C/2 rate) and that ca. 60% of the initial capacity can be delivered even in 0.552 hour (1 C rate), indicating that this electrode can sustain respectable rate capabilities. Our experimental data show that Na extraction/insertion can be reversible in the maricite NaFePO$_4$ electrode, which is contrary to the conventional belief that the lack of feasible diffusion pathways of Na ions in maricite NaFePO$_4$ should make it electrochemically inactive.

The maricite crystal structure has the same anionic framework as olivine; however, the M1 and M2 cation site occupations are completely reversed. For example, in olivine LiFePO$_4$, the M1 sites are fully occupied by Li$^+$, while Fe$^{3+}$ occupies the M2 sites. In contrast for maricite, Fe$^{3+}$ atoms are in M1 sites, while Na$^+$ occupies all the M2 sites. Due to the long distance between M2 sites in maricite, it has been assumed that Na hopping between sites is not plausible.$^{29}$ Indeed we carried out our Quantum Mechanics (QM) calculations (the PBE flavour of Density Functional Theory, DFT) confirming that extracting Na ions from the maricite NaFePO$_4$ structure would be almost impossible under typical battery operating conditions (Fig. 2). Thus using the nudged elastic band (NEB) method in QM calculations, we find that diffusion of Na ions in maricite Na$_{1-x}$FePO$_4$ (x = 0) can proceed via two most plausible paths: path 1 in the bc plane and path 2 along the b direction as shown in Fig. 2(a). However, we calculate an activation barrier for Na hopping along path 1 to be ~1.46 eV and that along path 2 is ~1.79 for Li or Na hopping in conventional battery materials ranging between 0.2 and 0.6 eV.$^{30-32}$ The diffusivity of Na in maricite would likely be several orders of magnitude lower, making Na diffusion quite unlikely at room temperature.$^{14}$ Without the creation of a new path having far lower activation barriers for Na diffusion, Na ions could not be extracted from the electrode materials.

This expectation from the QM is directly contradicted by our experiments. While carrying out experimental studies to explain

![Fig. 1](image-url)
this discrepancy, we observed that the shape and voltage of the first charge curve are always clearly different from the subsequent charge–discharge profiles in Fig. 1(a). This indicates that the desodiation of maricite may have induced a transformation into a different desodiated phase. To probe possible phase transformations of the maricite structure, we carried out QM calculations to compare the formation energies of various Na_{x}FePO_4 phases including olivine NaFePO_4, FePO_4, maricite NaFePO_4 and FePO_4. As shown in ESI Table S2, we found that the olivine FePO_4 is more stable than maricite FePO_4 by 30 meV per formula unit, while NaFePO_4 is more stable in the maricite structure than in the olivine structure. This indicates that desodiating Na_{x}FePO_4 provides a driving force for the maricite structure to undergo a phase transformation during desodiation. To confirm the phase transformation of the desodiated phase, we prepared fully desodiated maricite FePO_4 (detailed conditions of desodiation and the analysis are in the ESI and ESI Table S3). However, XRD measurements showed no peaks after desodiation, Fig. 3(a), indicating the formation of an amorphous structure.

Furthermore, the ex situ electrochemical desodiation in Fig. 3(b) shows that the intensity of the XRD peaks of maricite NaFePO_4 gradually decreases with charging, suggesting the loss of long-range order and the amorphization of the maricite crystal. Any growth or change of peaks was not observed in the XRD pattern when Na ions are fully re-inserted into the structure (discharging at 1.5 V). Moreover, the extended X-ray absorption fine structure (EXAFS) measurements, Fig. 3(c), reveal a pattern similar to that of amorphous FePO_4 (denoted as a-FePO_4), indicating that the long-range order is lost. We conclude that the first desodiation transforms maricite into the amorphous phase rather than into an energetically more favourable olivine structure, probably due to kinetic limitations of Fe atoms to migrate at room temperature. We expect that this incomplete motion of Fe atoms to form olivine may have caused significant disordering of the crystal resulting in the formation of the amorphous phase. Even so, the X-ray absorption near
edge structure (XANES) analysis indicates that reversible Fe$^{2+}$/Fe$^{3+}$ redox reactions still occur in the electrode during charge/discharge cycling (Fig. 3(d)).

We used QM to investigate how Na ions can be reversibly deintercalated (intercalated) from (into) the Na$_x$FePO$_4$ structure after amorphization of the crystal structure. Ion diffusion in amorphous structures is generally tricky to grasp with QM calculations due to the lack of long-range order. The absence of atomic order in the amorphous material complicates the identification of representative diffusion pathways. Consequently, we adopted a new multi-scale computational method to evaluate Na diffusion in the amorphous FePO$_4$. We, first, constructed an amorphous structure of FePO$_4$ by melting and then quenching rapidly using QM molecular dynamics (MD) simulations (that is MD using QM to calculate the forces) (ESI Fig. S4†). Here we used grand canonical Monte Carlo (GCMC) simulations to identify, stable Na sites in a-FePO$_4$. We then examined diffusion pathways between these stable Na sites in a-FePO$_4$ using the bond valence summation (BVS) method. The activation energies for Na hopping through these diffusion pathways were then obtained from QM based NEB calculations.‡ Fig. 4(a) illustrates the plausible Na sites and diffusion paths in a-FePO$_4$. The coordination numbers of Na ions vary from 4 to 7 in a-FePO$_4$, whereas the coordination number is 6 in olivine FePO$_4$ or maricite FePO$_4$. We found that the diffusion pathways of a-FePO$_4$ are random and disordered, compared with olivine FePO$_4$, which has a one-dimensional diffusion tunnel along the $b$ direction (ESI Fig. S6†). Because there are no representative diffusion pathways, we statistically evaluated the activation energies of Na hopping between neighbouring Na sites in three a-FePO$_4$ structures constructed independently by the melt-and-quenching process. The activation energies for Na hopping in a-FePO$_4$ ranged from 0.16 to 1.06 eV, as shown in Fig. 4(b). Indeed these values are much lower than that in maricite Na$_{1.5}$FePO$_4$ (ca. 2.68 eV for $x \approx 1$) (ESI Fig. S7†), although some are higher than that in olivine FePO$_4$ (ca. 0.28 eV).§ We also evaluated the activation energies for Na diffusion along long pathways (>1 nm) to capture a realistic picture of Na motion in the disordered structure of a-FePO$_4$. The overall activation energy along Na$_1$–Na$_2$–Na$_3$–Na$_4$/Na$_5$ (~1 nm) was ~0.73 eV. This value is still much lower than that in maricite Na$_{1.5}$FePO$_4$ ($x \approx 1$, ca. 2.68 eV). For comparison, we estimated the activation energy for Li hopping in a-FePO$_4$ using the same computational scheme. This resulted in an activation energy of ~0.45 eV, which is comparable to that of other crystalline Li cathode materials [0.25–0.5 eV]. These results indicate that a-FePO$_4$ could be a suitable electrode for LIBs (ESI Fig. S8†).‡ We expect that the slightly higher activation energy for Na hopping compared to Li in a-FePO$_4$ is due to the larger ionic size of the Na ion. This difference is in line with that of the activation energies for Na and Li ions in olivine FePO$_4$ (0.280 vs. 0.165 eV).¶ Nevertheless, we expect that the reduction of the activation barrier for Na hopping by ~75% (from ca. 2.68 to ca. 0.73 eV) through amorphization of the maricite will increase Na diffusion by tens of orders of magnitudes, allowing Na diffusion under normal battery operating conditions. T. Shiratsuchi et al. demonstrated that the amorphous FePO$_4$ can show better electrochemical behavior than those of the trigonal crystalline FePO$_4$ structure by comparing the electrochemical performance between amorphous FePO$_4$ and trigonal FePO$_4$. This report is in excellent agreement with our observation that the electrochemical properties of the maricite NaFePO$_4$ have been remarkably enhanced by the simultaneous phase transition to the amorphous phase.

In Fig. 4(d), we propose the electrochemical mechanism of maricite Na$_x$FePO$_4$. When Na ions at the surface are extracted from the structure, maricite FePO$_4$ simultaneously transforms into a-FePO$_4$ (two-phase reaction, it was clearly confirmed by TEM analyses as shown in Fig. 5). Through new fast diffusion pathways in a-FePO$_4$, the Na ions in the inner portion of maricite FePO$_4$ are further deintercalated, transforming into a-FePO$_4$. After all Na ions are extracted and maricite FePO$_4$ has turned fully into a-FePO$_4$, subsequent electrochemical cycles proceed by reversible insertion/extraction of Na ions through a-FePO$_4$ (solid-solution reaction). We have performed the galvanostatic intermittent titration technique (GITT) measurement in particular during the first charge process, where the conversion from the maricite to the amorphous phase is expected to occur (ESI Fig. S9†). In this measurement we slowly charged the sample with a current density of 7.75 mA g$^{-1}$ and relaxed until the voltage converges within $dV/dt \sim 10^{-6}$ V s$^{-1}$. From the GITT measurement below, it is shown that the relaxed voltage follows the constant value with respect to the state of the charge indicating that the transformation from maricite NaFePO$_4$ to amorphous FePO$_4$ is based on a two-phase reaction.
a-FePO₄ as shown by XRD and EXAFS analyses. Our QM calculations show that the transformation into a-FePO₄ is the key step for reversible Na de/intercalation in the electrode. This is because a-FePO₄ allows substantially smaller barriers than maricite NaFePO₄ for Na to hop from site to site. We predict that fully desodiated maricite NaFePO₄ forms amorphous FePO₄, providing a potential candidate for low-cost Na ion battery cathodes.

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Notes and references
