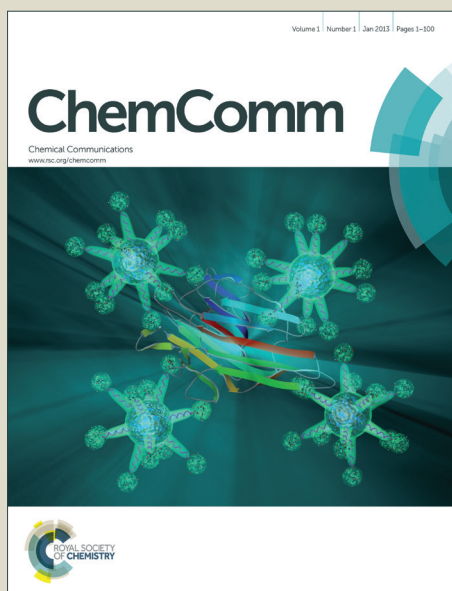


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## ARTICLE TYPE

## A new, cheap, productive FeP anode material for sodium-ion batteries

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**A novel and low-cost FeP anode synthesized by the ball-milling method for sodium ion batteries is reported with high capacity of 764.7 mAh g<sup>-1</sup>. Ex-situ X-ray diffraction and Transmission electron microscopy have been used to explore the sodium storage mechanism of FeP.**

Recently, Na-ion batteries (SIBs) have been attracting more attention as the most promising candidate for stationary batteries due to their low cost, and the abundant supply and widespread reserves of Na mineral salts.<sup>1-5</sup> Since the Na ion (radius 0.95 Å) is about 55% larger than the Li ion (0.6 Å), however, the range of potential candidate materials is seriously limited. The main goal for sodium ion battery research is to search for a candidate material with long cycle life and high capacity. Carbonaceous materials have been widely investigated as the anode for sodium ion storage due to their good cycling performance, but their capacity is low (less than 300 mAh g<sup>-1</sup>).<sup>6-10</sup> More recent reports show that some elements can alloy with sodium to deliver higher theoretical capacity as the anode in SIBs, such as Sn (847 mAh g<sup>-1</sup>),<sup>11</sup> Sb (664 mAh g<sup>-1</sup>),<sup>12</sup> and P (2596 mAh g<sup>-1</sup>).<sup>13-14</sup> The fatal defect for these anode candidates, however, is their huge volume change during the sodiation/desodiation, resulting in pulverization of the electrode material accompanied by poor cycling performance.

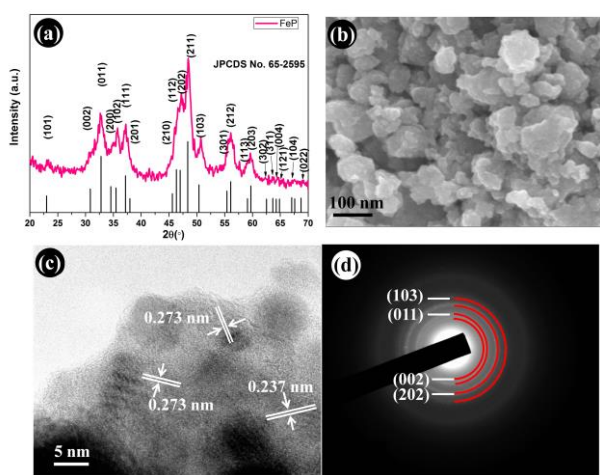
In order to prolong the cycling life of these anode candidates, preparing alloys with other elements is an effective solution. Manthiram's group reported that M<sub>x</sub>Sb (M = Cu, Fe, Ni) in a matrix of Al<sub>2</sub>O<sub>3</sub>-C had a better cycling performance than Sb in the same matrix of Al<sub>2</sub>O<sub>3</sub>-C for sodium-ion batteries.<sup>15</sup> Lin et al. reported that Sn<sub>0.9</sub>Cu<sub>0.1</sub> as anode for SIBs had a stable capacity of 420 mAh g<sup>-1</sup> for 100 cycles.<sup>16</sup> SnSb/C alloy anode for Na-ion batteries has been reported with a capacity retention of 80% after 50 cycles.<sup>17</sup> Recently, our group reported that Sn<sub>4+x</sub>P<sub>3</sub>@(Sn-P) composites as anodes for SIBs significantly extended the cycle

life, with a stable capacity of 465 mAh g<sup>-1</sup> and capacity retention of 92.6% over 100 cycles.<sup>18</sup> Kim et al. and Qian et al. also reported that Sn<sub>4</sub>P<sub>3</sub> and Sn<sub>4</sub>P<sub>3</sub>/C can deliver the capacity of 718 mAh g<sup>-1</sup> and 850 mAh g<sup>-1</sup> at the current density of 100 mA g<sup>-1</sup> and 50 mA g<sup>-1</sup>, respectively.<sup>19-20</sup> Notably, Sn<sub>4</sub>P<sub>3</sub> possesses two active elements, i.e., Sn and P, which both can alloy with Na. Therefore, Sn in the Sn<sub>4</sub>P<sub>3</sub> compound makes contributions to both the total capacity and the volume change during the sodiation/desodiation. The reported specific capacity is still far below the theoretical capacity, however.

To fully utilize the capacity from P, herein, we prepared iron phosphide (FeP) in large amounts by a simple ball-milling method. In this sample, the metal (Fe) is inactive and acts as a conductive matrix to buffer the volume expansion. The as-obtained FeP compound was investigated as anode in SIBs in half cells and showed high reversible capacity of more than 500 mAh g<sup>-1</sup>, which offers a new alternative to carbonaceous anode materials in Na cells. Iron phosphide (FeP) would be a promising anode for sodium ion storage due to the fact that Fe has a very abundant natural reserves, and is non-toxic and cheap.

FeP was prepared by simple ball milling for 20 h using the corresponding stoichiometric molar ratio of the metal (Fe) to P. Figure 1(a) shows the X-ray diffraction (XRD) pattern of the FeP, which can be indexed to the orthorhombic phase with space group *Pnma* (JPCDS No. 65-2595, *a* = 5.187 Å, *b* = 3.095 Å, *c* = 5.793 Å). The as-prepared FeP showed broad peaks with low intensity, suggesting that the particle size of the as-prepared sample after the ball milling is very small. The morphology of FeP was examined by field emission scanning electron microscopy (FE-SEM), as shown in Figure 1(b). The FE-SEM images of FeP show that the particle size is about 30-50 nm. Figure 1(c, d) shows a high resolution transmission electron

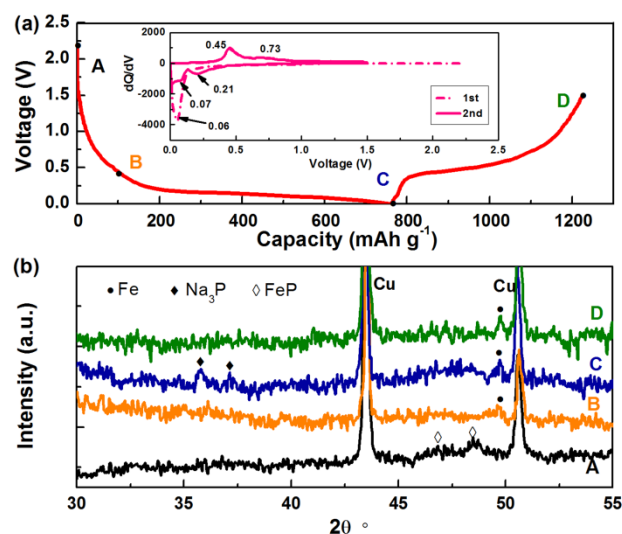
microscope (HRTEM) image and the corresponding selected area electron diffraction (SAED) pattern, respectively, of the as-prepared FeP. As shown in Figure 1(c), small crystals 10-20 nm in size are embedded in the amorphous matrix. The *d*-spacings of these FeP nanoparticles are 0.273 nm and 0.237 nm, corresponding to the (011) and (201) planes, respectively. The SAED pattern of the as-prepared FeP presents the characteristics of polycrystalline rings (Figure 1(d)). X-ray photoelectron spectra (XPS) of the as-prepared FeP were collected and are shown in Figure S1 (in the Supporting Information). The binding energies for P 2p at 129.3 eV and Fe 2p<sub>3/2</sub> at 706.9 eV are ascribed to the FeP.<sup>21</sup>



**Figure 1.** Characterization of FeP: (a) XRD pattern; (b) FE-SEM image; (c) high resolution TEM image; (d) the corresponding SAED pattern.

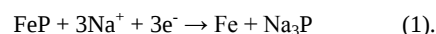
The electrochemical performance of the FeP electrode was tested at the current density of 50 mA g<sup>-1</sup> within the voltage range of 0-1.5 V in the electrolyte of 1 M NaClO<sub>4</sub> in ethylene carbonate (EC) and diethyl carbonate (DEC) (v:v=1:1) solution. The loading mass of each electrode tested in this work is about 5 mg cm<sup>-2</sup>. Figure 2(a) presents the initial charge/discharge curve of FeP and the differential curves for the first two cycles (inset). As shown in Figure 2(a), the FeP electrode delivered the discharge and charge capacity of 764.7 and 460 mAh g<sup>-1</sup>, respectively, in the initial cycle. There was one sloping plateau between 1.0 V and 0.4 V in the initial discharge curve, corresponding to the solid electrolyte interphase (SEI) formation due to the electrolyte decomposition.<sup>13,22</sup> This is the reason for the large irreversible capacity lost in the first cycle. To reveal the details of the electrochemical reactions of FeP, the differential capacity curves of the FeP in the first two cycles are plotted in the inset of Figure 2(a). It can be seen that two peaks around 0-0.3 V are observed in

the second discharge process. Since no Na-Fe-P ternary phase exists, the possible sodium storage mechanism of FeP is not the intercalation reaction. Moreover, the peaks that appeared at 0-0.3 V in the dQ/dV curves are similar to those of P, which are assigned to Na<sub>x</sub>P formation.



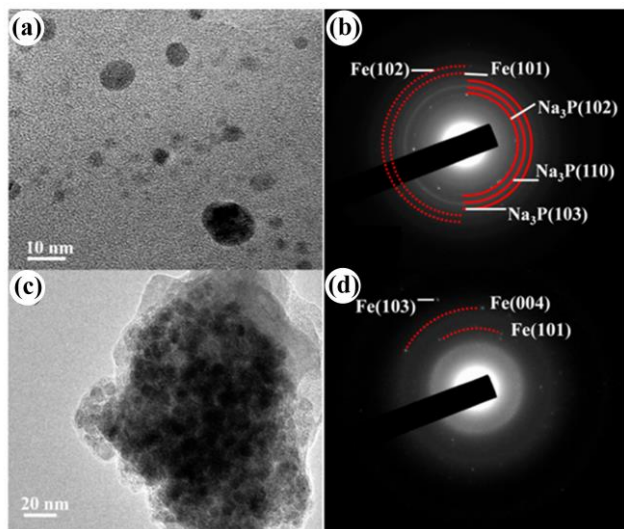
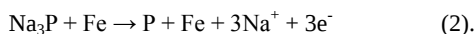
**Figure 2.** (a) Charge-discharge curve of FeP electrode and the differential curves for the first two cycles (inset). Point A is corresponding to the pristine state, Point B is corresponding to the discharged state at 0.4V, Point C and D are corresponding to the discharged state at 0V and charged state at 1.5V, respectively; (b) *ex-situ* XRD patterns of FeP tested at the current density of 50 mA g<sup>-1</sup> in the first cycle at the points indicated on the curve in (a).

To reveal the sodium storage mechanism of FeP, *ex-situ* XRD, and transmission electron microscopy (TEM) have been used. Figure 2(b) shows the XRD patterns of the FeP electrodes charged at different states in the first cycle. When the FeP electrode is discharged at 0.4 V, the characteristic peak of Fe was observed in the XRD pattern, and the characteristic peaks of FeP disappeared (Figure 2(b)). This demonstrates that FeP decomposes to form the Fe during the electrochemical reduction process. Besides Fe, Na<sub>3</sub>P was also detected in the XRD pattern when the FeP electrode was fully discharged at 0 V. Therefore, the sodium storage mechanism of FeP is described by the following equation



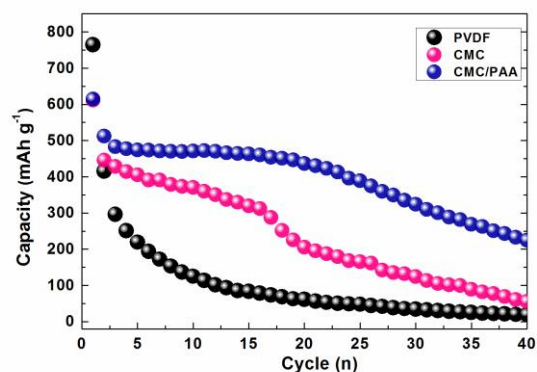
Based on this mechanism, the theoretical capacity of FeP is about 924 mAh g<sup>-1</sup>, which approaches the capacity of FeP delivered in the first cycle (764.7 mAh g<sup>-1</sup>). However, the initial capacity is lower than the theoretical one, it is possible due to the polarization resulted from both the low electronic conductivity of FeP and the SEI formation on the surface of electrode. During

the charge process, the sodium is extracted from the  $\text{Na}_3\text{P}$  to form P at the end. Only the characteristic peak of Fe was observed, however, in the XRD pattern of the electrode charged at 1.5 V (the end of the charge process). This is possibly because the P that is finally formed is amorphous or the crystal size is very small, so that it cannot be detected by XRD. Therefore, the charge process of FeP for the sodium ion battery can be summarized as follows:



**Figure 3.** TEM images (a, c) and SAED patterns (b, d) of FeP electrode discharged at 0 V (a, b) and charged at 1.5 V (c, d).

To further confirm the storage mechanism of FeP, the structure and phase change of the FeP electrode were detected by transmission electron microscopy (TEM). Figure 3 shows the structures and the SAED patterns of the FeP electrodes charged at different states. When the FeP is fully reduced (Figure 3(a)), the morphology is completely changed compared to the as-prepared FeP in Figure 1(d). Small crystallized particles 5-10 nm in size can be seen in the amorphous matrix. Moreover, the SAED pattern reveals that two phases appear at the end of the discharging. One is Fe, and the other is  $\text{Na}_3\text{P}$ , as shown in Figure 3(b), which is consistent with the *ex-situ* XRD results. After fully charging, the FeP electrode has an amorphous character, as shown in Figure 3(c). The SAED pattern of the FeP electrode charged at 1.5 V shows the main amorphous diffusion rings with some diffraction spots. The diffraction spots are indexed to Fe (Figure 3(d)). Therefore, combining the TEM results with the *ex-situ* XRD results, it is concluded that the sodium storage mechanism of FeP is through P reacting reaction with Na. In the FeP compound, the metal (Fe) is inactive and acts as a conductive matrix to buffer the huge volume expansion of P.



**Figure 4.** Cycling performance optimization of FeP electrodes prepared with different binders in the electrolyte of 1M  $\text{NaClO}_4$ /(EC: DEC).

In order to improve the electrochemical performance of FeP, optimization was conducted with three different binders (carboxymethyl cellulose (CMC), Poly(vinylidene fluoride) (PVDF), CMC/Poly(acrylic acid) (PAA)) and fluoroethylene carbonate (FEC) electrolyte additive. The cycling performances of the FeP electrodes with different binders were tested at the current density of  $50 \text{ mA g}^{-1}$  in the voltage range of 0 - 1.5 V, as presented in Figure 4. It can be seen that the FeP electrode with PVDF binder presents serious capacity decay. After 5 cycles, the capacity decreased from about  $765 \text{ mAh g}^{-1}$  in the first cycle to  $210 \text{ mAh g}^{-1}$ . When CMC was used as the binder, the capacity degradation was improved. By using CMC and PAA in a combined binder, the cycle life of the FeP electrode was greatly extended. This is because CMC/PAA binder can form a cross-linked structure which has high tolerance for the internal mechanical stresses generated by the volume expansion.<sup>23</sup> The capacity of the FeP electrode with CMC/PAA binder still dropped after 20 cycles, however. In order to enhance the cycling performance of the FeP electrode, 5% FEC was added to the electrolyte. FEC is an effective additive to help a contact SEI film formation on the surface of the electrode, as reported by Komaba et al.<sup>24-25</sup> Clearly, after 5% FEC addition, the cycle life of the FeP electrode with CMC/PAA binder was prolonged significantly (Figure S2). Capacity of  $321 \text{ mAh g}^{-1}$  was retained after 60 cycles, which is 69 % retention of the capacity in the second cycle. SEM images of the electrodes after cycling for 5 cycles show some microcracks on the electrode without FEC additive, while the electrode remains intact with 5% FEC additive, confirming that FEC additive promotes stable SEI film formation on the surface of the electrode to improve the cycling performance (Figure S3 and Figure S4, Supporting Information).

At the same time, such thick and stable solid-electrolyte interphase (SEI) layer which has higher resistivity increases the polarization of the electrode.<sup>18</sup> Therefore, the capacity of the FeP electrode close to 0 V cannot be used in the electrolyte with FEC, resulting much lower capacity. In summary, the cycling performance of the FeP electrode was improved after choosing CMC/PAA as the binder and FEC as the electrolyte additive. The rate capability of FeP was tested at various current density and shown in Figure S5 (Supporting Information). When the current density increased from 50 mA g<sup>-1</sup> to 500 mA g<sup>-1</sup>, the capacity decreased from 420 mAh g<sup>-1</sup> to 60 mAh g<sup>-1</sup>, respectively.

In summary, we prepared FeP in large quantities by direct low-speed ball milling of the P and Fe powders and studied its electrochemical performance as anode material for sodium ion batteries. The FeP electrode delivered a high capacity of 764.7 mAh g<sup>-1</sup> in sodium ion batteries. In addition, improvement of its cycling stability was also achieved by selecting appropriate binders and an appropriate additive to the electrolyte. Moreover, a variety of techniques, including *ex-situ* XRD and TEM, was used to reveal that the sodium storage mechanism of FeP. All the results indicate that FeP would be a promising anode material candidate for sodium ion batteries with low cost and long cycling stability.

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## Notes and references

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