Self-Standing, Collector-Free Maricite NaFePO₄/Carbon Nanofiber Cathode Endowed with Increasing Electrochemical Activity

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ABSTRACT: A new electrode design for sodium ion batteries with a self standing, collector free, binder free maricite NaFePO₄/carbon nanofiber hybrid cathode is successfully realized via electrospinning. An increasing capacity is observed in the initial cycles, and finally, the electrode reached a capacity of 108 mAh g⁻¹ at a 0.1 C rate after 200 cycles. In comparison, a slurry based NaFePO₄ electrode yields a capacity of only around 20 mAh g⁻¹. An overall improved electrochemical performance was obtained in the hybrid cathode compared to pure slurry based NaFePO₄ electrode and pure carbon nanofibers. A comprehensive study of the morphology, structure, and electrochemical performance of the hybrid electrode is conducted. Mössbauer spectra show an increasing Fe³⁺ content from 43.2% in the first charged state to 63.0% in the charged state after 100 cycles, demonstrating an activating process of maricite NaFePO₄ upon extensive charge–discharge cycling. This work has explored a direct electrospun self standing maricite NaFePO₄ electrode and its feasibility and mechanism as a cathode material in sodium ion batteries.

1. INTRODUCTION

Sodium ion batteries (SIBs) have received increasing attention from researchers as a result of the wide availability and low cost of sodium compared to lithium.¹ SIBs show great potential, especially in large scale stationary energy storage systems, where the requirement of abundance and low cost of raw materials is yet to be fulfilled.² Although sharing similar chemical properties and electrochemical reactions with Li⁺, Na⁺ possesses a higher mass and larger ionic radius.¹,³ Thus, a stable structure of a Na⁺ host material that can both withstand the volume change for long cycle life and deliver a reasonable high rate capability is in high demand.⁴ Inspired by the success of LiFePO₄ in the case of Li batteries, iron based phosphates are in focus because they show good structural stability during cycling with only a 6.8% volume reduction from LiFePO₄ to FePO₄.⁵ Moreover, in comparison to other candidates, the use of iron also avoids environmentally unfriendly metals, such as cobalt, and toxic elements, such as vanadium.⁶ Furthermore, among iron based cathode materials, NaFePO₄ offers the highest theoretical capacity up to 154 mAh g⁻¹ and a decent working voltage range.⁷,⁸

Triphylite and maricite structures are two crystal structures of NaFePO₄, of which the triphylite structure is not thermodynamically stable and the maricite structure is inhibited from applications as a result of its electrochemically inactive nature.⁹⁻¹¹ However, LiFePO₄ was also once believed to be incapable of performing as a cathode material as a result of its low electrical conductivity until approaches of particle size reduction and coating with conductive materials were used for its commercialization.¹² Consequently, also for maricite NaFePO₄, attempts, such as particle downsizing and carbon addition, have been undertaken in recent studies to successfully deliver high capacities of maricite NaFePO₄.¹³ For example, Kim et al. proved a full deintercalation of Na⁺ ions from nanosized maricite NaFePO₄.¹⁴ Rahman et al. synthesized a hybrid material of NaFePO₄/C/graphene by ball milling with the addition of graphene to achieve an improved cycle performance with a capacity of 142 mAh g⁻¹ at 0.1 C after 300 cycles.¹⁵ Fan’s group has used electrospinning for nanoparticle synthesis, realizing an embedding of NaFePO₄ nanodots (≈1.6 nm) in N doped carbon fibers to obtain a high reversible capacity of 145 mAh g⁻¹ at 0.2 C.¹⁶ Via electrospinning, Fan’s group has realized a binder free electrode without the procedure of slurry making and coating, which were necessary in other reported work. However, the aluminum foil was unavoidably included during the whole procedure. The question has been raised: is it possible to
synthesize a binder free, collector free, self standing NaFePO₄ electrode material. Moreover, a high surface area of the electrode material can be generated from the nanoparticles and carbon content, which may unavoidably result in a surface storage of charges contributing to the overall capacity. This capacitive charge storage contribution was often neglected in such nanostructured maricite NaFePO₄ electrodes.

Electrospinning is usually used as one method for the synthesis of nanoparticles for a binder free electrode. In general, there are two different approaches: (i) nanoparticle synthesis: starting materials are first dissolved in polymer solutions for electrospinning (aqueous or organic solvent), and the crystalline nanoparticles are synthesized during subsequent calcination along with the decomposition of polymer fiber; (ii) post carbon nanofiber coating: nanoparticles of the electrodes are directly dispersed in the carbon source polymer solutions, and the carbon nanofiber coated composites are formed during the high temperature carbonization. Bach tin et al. improved the electrical conductivity of LiFePO₄ and its cycle stability via a direct electrospinning from the hybrid solution of LiFePO₄ and polyacrylonitrile (PAN), resulting in a carbon decorated LiFePO₄ after carbonization of PAN. However, a corresponding electrode fabrication/design from the electrospinning of maricite NaFePO₄ product has, to our knowledge, not yet been reported. In comparison to the reported electrospinning methods from starting materials of NaFePO₄, this direct carbon coating approach is less time consuming and more straightforward. In this way, not only can improved electrical conductivity be introduced, but the carbon nanofiber network can also function as the current collector, realizing a self standing and collector free electrode material, which can be used in flexible, soft, and wearable batteries.

Herein, we synthesized for the first time a collector free, self standing NaFePO₄/carbon nanofiber (NaFePO₄/CNF) electrode via electrospinning of ball milled NaFePO₄ and PAN/N,N-dimethylformamid (DMF) solution. A comprehensive investigation of the electrode morphology, structure, and electrochemical performance before and after cycling is carried out. The study of such a composite electrode material will enlighten the knowledge on (1) the Na⁺ ion transfer mechanism in carbon containing cathode material, (2) the capacitive contribution of the carbon content and nanomaterials in SIBs, and (3) potentials of such self standing, collector free, binder free electrodes in the field of energy storage systems.

2. EXPERIMENTAL SECTION

2.1. Preparation of Self-Standing NaFePO₄/CNF. Na₂CO₃ (99.99%, Acros), FeC₂O₄·2H₂O (99%, Alfa Aesar), and NH₄H₂PO₄ (99%, Sigma Aldrich) with the molar ratio of 0.5:1:1 were used as starting materials for the synthesis of NaFePO₄ nanoparticles as described before by Kim et al. All starting materials were ground and then loaded into the ball milling container with ZrO₂ milling balls. The mixed precursors were milled for more than 24 h at 500 rpm and then calcined at 350 °C under an argon atmosphere for 5 h before being re-ground and pressed into pellets. The pellets underwent a second calcination at 600 °C under argon for 10 h and then were ground for further use. Next, the ground NaFePO₄ nanoparticles were dispersed in a PAN/N,N-dimethylformamid (DMF) solution under strong stirring overnight with a mass ratio of NaFePO₄/PAN of 1:2. This composite solution was then loaded into a 1 mL syringe attached to an assembled injecting needle with a diameter of 0.8 mm. A climate controlled electrospinning apparatus (EC CL1, IME Technologies) was used with the temperature and humidity set to 25 °C and 20%, respectively. A high voltage of 13–16 kV was applied between the needle tip and the collector covered by a sheet of aluminum foil. The flowing rate of solution was 0.5 mL h⁻¹, and the tip to collector distance was 15 cm. In total, the 1 mL solution was spun 2 times into one fiber mat. The fiber mat was then vacuum dried and stabilized in air with heating steps to the highest temperature of 280 °C before being carbonized under argon at 600 °C for 1 h.

2.2. Material Characterization. The morphology of electrodes was observed with Merlin field emission scanning electron microscopy (FE SEM, Carl Zeiss SMT AG). Energy dispersive X ray spectroscopy (EDX) was performed to analyze the elemental compositions (Bruker Quantax, 400 SDD). X ray diffraction (XRD) measurements were carried out on a STOE STADI P X ray powder diffractometer with a Mythen 1K detector and Mo Kα radiation (λ = 0.7093 Å). Thermogravimetric analysis (TGA) was performed to determine the content of carbon and active material in the composite electrode. It was carried out on a STA 449 C Jupiter instrument (NETZSCH) with a heating rate of 10 K min⁻¹ up to 1200 °C in an oxygen atmosphere. The Brunauer—Emmett—Teller (BET) specific surface area was detected via the nitrogen adsorption method (Gemini VII 2390, Micromeritics). In situ high temperature XRD (HT XRD) was carried out at synchrotron at Paul Scherer Institute (PSI), Villigen, Switzerland. NaFePO₄ powders were heated in air with a heating rate of 20 °C min⁻¹ from 90 to 400 °C and then cooled to 90 °C. During heating and cooling, 53 XRD patterns were recorded. The wavelength (λ) was 0.1051 Å, and a MYTHEN II detector was used.

2.3. Ex Situ Characterization. Mössbauer spectroscopy was performed at room temperature with a constant acceleration spectrometer in transmission mode and a ⁵⁷Fe(Rh) source. All isomer shifts are given relative to that of α Fe metal. The cells were charged to 4.5 V and discharged to 1.5 V in the initial cycle and the 100th cycle, separately. The cells were disassembled afterward, and cathode materials were washed with dimethyl carbonate (DMC), dried at 60 °C for 12 h, and then sealed in polyethylene/aluminum bags in an argon filled glovebox (O₂ and H₂O < 0.1 ppm). Raman spectroscopy was performed on a LabRam Evolution HR instrument (HORIBA Jobin Yvon) applying a 532 nm wavelength laser. Each spectrum was taken as the average of three 4 s accumulations. For the transmission electron microscopy (TEM) measurements, the samples were prepared inside a glovebox and transferred to the microscope without exposure to air using a vacuum transfer holder. The dry powder was directly dispersed on the TEM holey carbon membrane without the use of solvents. The measurements were performed using a Themis300 electron microscope working at 300 kV and equipped with a DCOR probe corrector and a Super X EDX detector. High angle annular dark field (HAADF) and scanning transmission electron microscopy—energy dispersive X ray spectroscopy copy (STEM—EDX) elemental mapping were performed to elucidate the morphology of the carbon fibers.

2.4. Electrochemical Performance. The electrochemical performance was studied in coin cells (CR2032) with sodium metal as the counter/reference electrode, glass fiber (Whatman, GF/D) as the separator, and 0.8 M NaClO₄ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, w/w) as the electrolyte. The electrospun self standing electrodes were punched into the right size (% Ø = 12 mm) and directly assembled in the coin cells without any additional current collector. Galvanostatic cycling, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were carried out on a multichannel potentiostat (VMP3, Bio Logic). The voltage ranges of galvanostatic cycling and CV tests are 4.5−1.5 V versus Na⁺/Na. The galvanostatic mode was a constant current−constant voltage (CC−CV) charging mode at 0.1 C, with the voltage of 4.5 V holding for 5 h with a current limit of 0.05 C. The calculation of the specific capacity of NaFePO₄/CNF is based on the mass of NaFePO₄. EIS tests were carried out at the charged state (4.5 V) and discharged state (1.5 V) with an alternating current signal of a 5 mV amplitude and frequencies ranging from 1 MHz to 0.01 Hz.
3. RESULTS AND DISCUSSION

3.1. Material Characterization. Maricite NaFePO₄ nano particles were first prepared via mechanical ball milling and then dispersed in the polymer solution under strong stirring for further electrospinning. Under high voltages, the nanofibers were collected on an aluminum foil and then treated with a two step heating procedure, resulting in a flexible, black colored, self standing mat, which can be cut into electrodes and directly assembled in coin cells without further handling. It is generally known that maricite NaFePO₄ is electrochemically inactive as a result of the lack of pathways for Na⁺ ion transport. By integration of maricite NaFePO₄ particles onto carbon nanofiber (CNF) mats, the high porosity of the fiber network can enhance the contact between the electrolyte and active material, as proposed in Figure 1a. Moreover, the carbon content can improve the electrical conductivity, facilitating a better electrochemical performance of such a hybrid electrode. A 30 wt % weight percentage of NaFePO₄ within the hybrid electrode was determined by TGA measurement (see Figure S1 of the Supporting Information). The morphology of the obtained self standing electrode is shown in Figure 1b, with the NaFePO₄ particles dispersed homogeneously in the carbon nanofibers. Clusters of the active material as a result of agglomeration can also be observed. The EDX results in panels c−i of Figure 1 show that the active material particles consist of Na, Fe, P, and O and are embedded in the nanofibers that consist of C and N. Noteworthy, the traces of nitrogen are the residue from the low temperature carbonization process of PAN.25

The structures of NaFePO₄ and NaFePO₄/CNF electrodes were also investigated by XRD. As shown in Figure 2a, a phase pure maricite structure of NaFePO₄ indexed on the basis of a Pmnb orthorhombic model was obtained. With a Rietveld refinement, the lattice parameters of NaFePO₄ were determined as $a = 6.8659(2)$ Å, $b = 8.9761(2)$ Å, and $c = 5.0412(2)$ Å, matching well with values reported in the literature.26−28 As shown in Figure 2b, the presence of carbon nanofibers in the composites with CNF introduced an obvious amorphous phase, underlying the reflections from crystalline
NaFePO₄. Some new reflections appeared for the NaFePO₄/CNF electrodes at low angles (5−7° and 11−14°), respectively, which may refer to some impurity phases. According to the HT XRD of NaFePO₄ in air, some new reflections start to show up at around 230 °C (Figure S2 of the Supporting Information). To gain a deeper knowledge of these new reflections, Rietveld refinement was conducted on the HT XRD patterns. Accordingly, a new NASICON phase Na₃Fe₂(PO₄)₃ (space group R3c) was detected (Figure S3a of the Supporting Information). Lattice parameters of a and c were determined as 8.7317(2) and 21.6663(2) Å, respectively. Partial oxidization of NaFePO₄ was proposed to occur during the heating under air. The lattice parameters were determined as a function of the temperature (Figure S3b of the Supporting Information), where a, b, and c first increased with an increasing temperature and again decreased to a = 6.8783(2) Å, b = 8.9831(2) Å, and c = 5.0478(2) Å when the sample was cooled, showing a reversible structural stability of the main phase. Two phases were used during the refinement of the diffraction of NaFePO₄/CNF electrodes: phase 1, NaFePO₄ (Pmn̅2); phase 2, Na₃Fe₂(PO₄)₃ (R3c). Fortunately, the NaFePO₄ lattice parameters in the NaFePO₄/CNF composites show minor changes without size broadening with a = 6.8671(2) Å, b = 8.9819(2) Å, and c = 5.0439(2) Å, which indicate that the structure of maricite NaFePO₄ was not affected during the high temperature procedures of carbon nanoﬁber formation.

3.2. Electrochemical Performance. To obtain fundamental knowledge of the electrochemical mechanism of the composite NaFePO₄/CNF cathode, it is important to study the contribution of each component to the total capacity. With a high carbon content, the electrochemical behavior of electrospun NaFePO₄/CNF may follow a diffusional process along with redox reactions. CV curves at different sweep rates can provide information on the surface controlled (capacitive) and diffusion controlled (bulk) processes. Voltammetry at scan rates from 0.05 to 1 mV s⁻¹ at a voltage window of 1.5−4.5 V were performed. From the CV curves shown in Figure 3a, a pair of broad redox peaks appear at 3.1 and 2.7 V, indicating the redox reaction of Fe²⁺ ⇌ Fe³⁺ + e⁻. The capacitive effect in the system can be analyzed on the basis of the following equation:

$$i = aν^b$$

where i is the current, ν is the scan rate, and a and b are adjustable parameters. In the well deﬁned conditions, when b = 0.5, the current is diffusion controlled, indicating a faradaic intercalation process, while for b = 1, the current is surface controlled, indicating a capacitive process. The b values as a function of potentials for NaFePO₄/CNF and pure CNF are shown in Figure 3b. We can see that, at 3.0 V, the b value for NaFePO₄/CNF is 0.75, while for CNF, the b value is 0.89. This indicates that, in NaFePO₄/CNF, the current originates partially from the Na⁺ ion intercalation reaction other than the surface charging effect. Thus, the storage mechanism of electrospun NaFePO₄ is a mixed type with both diffusion and capacitive controlled contributions. The CV curves for the b value calculations of pure carbon nanoﬁbers and cycled electrode are shown in Figure S4 of the Supporting Information.

In addition, a detailed examination of the voltammetry enables the quantitative calculation of the contribution of capacitive energy storage according to eq 2, with $k_1$ and $k_2$⁰⁻⁵⁰ corresponding to the current contributions from the capacitive surface effect and diffusion controlled intercalation process, respectively. By determination of $k_1$ and $k_2$, one can quantify the fraction of the current from each contribution. As shown in panels c–e of Figure 3, the capacitive effects contribute to about 32.5, 49.9, and 60.0% at scan rates of 0.25, 0.5, and 1 mV s⁻¹, respectively. Hence, as expected, the capacitive effect becomes more dominant with an increasing scan rate.

$$\begin{align*}
l_i &= k_1ν + k_2ν^{0.5} \\
l_i/ν^{0.5} &= k_1ν^{0.5} + k_2
\end{align*}$$

Figure 3. (a) CV curves at various scan rates from 0.05 to 1 mV s⁻¹, (b) b values at different potentials of pure CNF, pristine NaFePO₄/CNF electrodes, and cycled NaFePO₄/CNF electrodes, and the contribution of capacitive controlled (blue) and diffusion controlled (gray) capacities to the total capacity for NaFePO₄/CNF electrodes at different scan rates: (c) 0.25 mV s⁻¹, (d) 0.5 mV s⁻¹, and (e) 1.0 mV s⁻¹.
The charge—discharge profiles of the electrospun electrodes are shown in Figure 4a at a C rate of 0.1 C between 1.5 and 4.5 V. Different from olivine LiFePO₄ and triphylite NaFePO₄, which have a voltage plateau from the first order phase transition, the sloping curve of maricite NaFePO₄ is indicative of a different sodium ion insertion/extraction mechanism, which probably results from solid solution behavior or a second order phase transition. The specific discharge capacities are calculated on the basis of the mass of active material NaFePO₄, which is 30% of the full electrode weight. As seen, the discharge capacity is increasing from 42 mAh g⁻¹ in the initial cycle up to 108 mAh g⁻¹ in the 200th cycle, and then it is almost constant. Such an increasing capacity phenomenon was observed in many carbon containing cathode materials in SIBs. Unfortunately, the observed increase of capacities during initial cycles lack possible suggestions and explanations. The following reasons for this increasing capacity phenomenon can be considered: (1) Carbon nanofibers break upon cycling, which generates more defects and storage sites for electrons. (2) With active material particles embedded in the carbon nanofibers, the mechanical breakdown of fibers increases contact between NaFePO₄ particles and the electrolyte, hence further facilitating the accessibility of these particles by ions.

To define the capacity contribution of carbon nanofibers, the electrochemical performance of the pure electrospun CNF carbonized at the same condition was also examined. Charge—discharge profiles of CNF (shown in Figure S5 of the Supporting Information) show a capacity of 22 mAh g⁻¹ at 200 cycles with an initial discharge capacity of only 3 mAh g⁻¹. In comparison to the overall capacity of the hybrid cathode, the contribution from the non faradic reaction amounts to 20% after stabilization after 200 cycles. Other than electrospun NaFePO₄/CNF and pure CNF, a slurry made of NaFePO₄, Super P, and poly(vinylidene fluoride) (PVdF) with the same 30 wt % NaFePO₄ was also prepared and coated onto the surface of Al foil, labeled as slurry NaFePO₄. The long term performances of NaFePO₄/CNF and slurry NaFePO₄ are shown in Figure 4b with columbic efficiencies. After the initial increase in capacity, the NaFePO₄/CNF electrode reaches a capacity of 108 mAh g⁻¹ after 200 cycles at 0.1 C (≈15 mA g⁻¹). In the following cycles, the electrode shows a good long term cycling stability with 94.4% retention after 450 cycles compared to the maximum value of 100% after 200 cycles. In comparison, a capacity of only 24 mAh g⁻¹ was achieved for slurry NaFePO₄ and an irreversible capacity decay and cell failure occurred within 200 cycles, demonstrating that only the cell design of the composite of carbon nanofibers and maricite NaFePO₄ as a self standing electrode is able to deliver a stable long term electrochemical performance. The rate capability of the electrospun electrodes was also investigated (Figure 4c). Considering the increasing capacity in the first cycles, the electrode was cycled for over 150 cycles until the capacity reached a stable discharge specific capacity of 113.6 mAh g⁻¹. Afterward, different C rates were applied, delivering reversible capacities of 106.3 mAh g⁻¹ at 0.2 C, 92.0 mAh g⁻¹ at 0.5 C, 78.6 mAh g⁻¹ at 1 C, 64.4 mAh g⁻¹ at 2 C, 43.0 mAh g⁻¹ at 5 C, and 33.3 mAh g⁻¹ at 10 C. Importantly, when the cells were cycled back at 0.1 C afterward, a higher capacity with an average of 124.7 mAh g⁻¹ was recovered, which indicates a good high rate capability and a reasonable tolerance of the rapid Na⁺ ion insertion/extraction process. The specific capacity increased when the cell was brought back to 0.1 C from higher currents (124.7 mAh g⁻¹) compared to the first cycles at 0.1 C after the activation process (113.6 mAh g⁻¹). This may relate to an ongoing activating process, even during the high rate performance. Another possible explanation is that, at a higher C rate cycling, more electrons were quickly collected on the surface as a result of charge transfer. Once the C rate went back to 0.1 C, the slower current allowed for a longer relaxation, which contributed to a higher capacity.

The electronic conductivity and its changes during cycling of the NaFePO₄/CNF electrode were analyzed by EIS. The Nyquist plots in Figure 4d consist of a semicircle in the high
frequency range, which is due to the ohmic resistance and charge transfer resistance, and a short inclined line in the low frequency range, which stems from the ionic diffusion within the electrodes. The first parts of the semicircles from each cycle at high frequencies are overlapping, which can be caused by the solid electrolyte interface (SEI) formation within the first cycles. We can also observe that, in the Nyquist plots, the diameters of the semicircle of the electrodes decrease noticeably during cycling, which demonstrate that the charge transfer becomes faster and easier upon cycling within the first 10 cycles. The increasing conductivity also indicates an activation process of the electrodes upon charge–discharge. Furthermore, differential capacity diagrams (dQ/dV) shown in Figure 5 were plotted by processing the constant current charge–discharge data in the 1st, 2nd, 50th, 100th, 200th, and 300th cycles. In the initial cycles, no reduction/oxidation reaction peaks show up, indicative of a dominant capacitive behavior of the NaFePO₄/CNF electrode. Upon cycling, an increasing intensity of broad peaks at around 3 V can be observed, which agrees well with the gradual interaction of NaFePO₄ in the electrochemical behavior of the composite electrode, again confirming the gradual redox activation of Fe³⁺/Fe²⁺ in NaFePO₄. Moreover, the separation of oxidation/reduction peaks is reduced in the first 100 cycles, indicating a reduced polarization.

3.3. Ex Situ and Activation Studies. The activation of NaFePO₄ in NaFePO₄/CNF electrodes was further confirmed by ex situ analysis of the samples after cycling. The Mössbauer spectra shown in Figure 6 demonstrate distinguished phases or sites in the respective samples. The intensities of Fe²⁺ and Fe³⁺ doublets were fitted to estimate the amount of each oxidation state in the samples of first cycle start, first cycle charged, first cycle discharged, 100th cycle start, 100th cycle charged, and 100th cycle discharged electrodes. While the as prepared NaFePO₄ powder shows exclusively Fe²⁺ after synthesis, some amount of Fe³⁺ is observed in the electrodes at the beginning of the first cycle and 100th cycle with an area fraction of 35.2 and 37.8%, respectively. This partial oxidation occurs during the stabilization process of the fiber mats, which is in agreement with the results from HT XRD, showing an impurity phase of oxidized Fe³⁺ in Na₃Fe₂(PO₄)₃. A rise in Fe²⁺/Fe³⁺ content from 35.2 to 43.2% appears during charging in the first cycle, while an increase from 37.8 to 63.0% is observed in the 100th cycle. After 100 cycles, more Fe³⁺ species exist at the charged state, which clearly demonstrates an increased Fe³⁺/Fe²⁺ redox reaction upon extended cycling. This correlates with the results from Figure 3b, showing smaller b values of cycled NaFePO₄/CNF electrodes compared to those of non cycled NaFePO₄/CNF, demonstrating a more active Fe²⁺ ⇌ Fe³⁺ + e⁻ redox reaction along cycling.

Raman spectra shown in Figure 7a illustrate the structural changes before and after cycling with fitted D and G bands of carbon. The ratio between I_D and I_G is often used as an indication of the degree of disorder/defects in carbonaceous materials. In NaFePO₄/CNF, the intensity ratio of I_D/I_G decreased from 0.86 in the pristine state to 0.85 after 100 cycles. A significant structural change did not take place upon charge–discharge cycles, specifying a stable structure of the NaFePO₄/CNF electrode. The minor decrease of the I_D/I_G intensity correlates with the morphology observed by SEM in...
the cycled electrodes, as shown in Figure 8, with more cracks and partial defects allowing for more NaFePO$_4$ particles to become exposed and in contact with the electrolyte. Moreover, more defects allow for more Na$^+$ ion transfer channels for an increased electrochemical performance. Furthermore, as seen from the SEM images, nanoparticle clusters with clear crystalline boundaries can be observed in pristine electrodes before cycling. However, after cycling, the sharp boundaries of the crystalline particles disappeared and transform to an agglomerated morphology. This further proves the involvement of NaFePO$_4$ particles in the electrochemical activity. Amorphous phases are observed in the XRD patterns of the samples charged and discharged in the 100th cycle, as shown in Figure 7b: areas marked with orange and green dashed rectangles include reflections with decreasing intensities. By amplification of the reflections in the green marked area, we observe no shift of reflections in the cycled electrodes. A transformation of maricite NaFePO$_4$ into a completely amorphous phase has been observed from the XRD patterns of the electrodes charged up to 4.5 or 4.7 V$^{14,16}$ In our NaFePO$_4$/CNF composite, the gradual activation of NaFePO$_4$ should theoretically lead to a gradual structural change. This perfectly explains the incomplete amorphization with retention of a high intensity of crystalline reflections in the electrodes after 100 cycles.

To further demonstrate the difference before and after intense cycling, STEM−EDX elemental mapping was carried out on pristine and intensively cycled electrodes. As shown in Figure 9, the nanofiber as the pristine electrode has a rather smooth surface, which shows no defects or cracks with the NaFePO$_4$ particles located on the surface. In comparison, a large crack appears on the fiber shown in panel b from an intensively cycled electrode, leaving the NaFePO$_4$ particles exposed. Moreover, some nanosized pores can also be observed on the surface of the intensively cycled electrode. By comparison of the electrodes before and after cycling, we were able to observe the gradual changes in the activity of Fe$^{2+} \rightleftharpoons$ Fe$^{3+}$ + e$^-$ redox reactions and the structures of both the carbon fiber and the maricite NaFePO$_4$ particles by various experimental methods. These ex situ results confirm an activation process of maricite NaFePO$_4$ involving the electrochemical behavior with slight mechanical breakdown and
defect formation of the carbon nanofibers. The activation process corresponds to an increased capacity appearing in the charge−discharge performance of NaFePO₄/CNF, which provides insight into the mechanism and the unique behavior of such self standing carbon integrated maricite NaFePO₄ electrodes.

4. CONCLUSION
Although maricite NaFePO₄ is considered as electrochemically inactive, the addition of an electrically conductive carbon nanofiber network results in a long term cycling stability of NaFePO₄. With the help of electrospinning, a self standing, collector free, and binder free maricite NaFePO₄/carbon nanofiber composite electrode was successfully prepared. A hybrid electrochemical mechanism of capacitive charge storage and intercalation based redox reaction of $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{e}^{-}$ was confirmed by cyclic voltammograms at different scan rates. The phenomenon of an initially increasing capacity was explained along with ex situ measurements, demonstrating an activation process of NaFePO₄ particles in such composite electrodes. Even though a very high capacity was not delivered, this work presents a comprehensive study of such hybrid NaFePO₄ electrodes for the first time and enlightens the potential of self standing electrodes in future applications.

Figure 9. STEM−HAADF images of (a) pristine electrodes and (b) intensely cycled NaFePO₄/CNF electrodes.

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