Amorphous FePO₄/Carbon Nanotube Cathode Preparation via in Situ Nanoprecipitation and Coagulation in a Microreactor

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Supporting Information

ABSTRACT: In this article, nanostructured amorphous FePO₄ (a-FePO₄)–carbon nanotube (CNT) composites, with high purity of FePO₄ and a controllable FePO₄/C ratio, were directly synthesized by a fast nanoprecipitation process in a microreactor, using Fe(NO₃)₃ and (NH₄)₃PO₄ as precursors. Oxidized CNTs are well dispersed via strong electrostatic repulsion in a high pH solution system. Subsequently, a-FePO₄ nanoparticles are adhered onto CNTs just following the fast nanoprecipitation process; then, the precipitated composites are compacted by ball-milling, forming a compact conductive network with well dispersed and highly loaded active materials. As cathode materials for lithium-ion batteries, the composites exhibit a capacity of 175.8 mAh g⁻¹ at 0.1 C, close to the theoretical capacity (178 mAh g⁻¹), and a good cycle performance with a reversible capacity of 137.0 mAh g⁻¹ after 500 cycles at 5 C. Importantly, the enhanced micromixing enables fast nanoprecipitation in suspension and opens a shortcut for constructing nanostructured composites that have potential in functionalization and are easy to handle.

1. INTRODUCTION

Rechargeable batteries supply electrical energy source on demand for plenty of applications and have become an essential part of our modern world. Within the last two decades, the ever-growing demands for more effective batteries raised a strong growth in research focused on lithium-ion battery (LIB) technology principally. As a main component of LIBs, cathode materials have significant effects on their electrochemical performance.¹–³ Layered oxide LiCoO₂, spinel LiMn₂O₄, and polyanion-type phosphates⁴–⁸ are presently widely implemented in commercial LIBs.⁹ Among these promising cathode candidates, enormous amount of research and great expectations are settled on the olivine-type LiFePO₄ because of its abundant resources, high theoretical capacity, and increased safety.¹⁰¹¹ As an analogue of LiFePO₄, amorphous FePO₄ (a-FePO₄) possesses extra advantages. The a-FePO₄ can be prepared at air atmospheres and low temperatures, which determines its low cost. Besides, compared with the two-phase LiFePO₄–FePO₄ system like olivine LiFePO₄, a-FePO₄ is expected to stabilize a single-phase lithium-intercalation mechanism due to the notion of a one-dimensional (1D) Li channel being lost, which leads to a continuous charge/discharge voltage variation and enables the amount of lithium ions transferred in the charging and discharging process to be well tracked from the potential. Although FePO₄ cathode materials do not have Li ions in the structure, similar to the lithium predoping process in the lithium-ion capacitors, lithium predoping could be used to provide preliminary lithium-intercalation into the FePO₄ cathode using an auxiliary lithium metal electrode before charging of the FePO₄/graphite full-cell. From these viewpoints, a-FePO₄ has more advantages compared with LiFePO₄. However, it still suffers from poor ionic transport and electronic conductivity, causing reduced capacity utilization at high rates.¹²–¹⁵

Fast transportation of lithium ions and electrons is crucial to sustaining rapid charge and discharge processes in the LIBs. Several practical approaches have been applied to overcome the shortcoming of some active materials in this aspect, such as decreasing the particle size,¹⁶,¹⁷ mixing particles with conductive agents, and ion doping.¹⁴,¹⁸ Among them, the most common way to enhance the conductivity is to coat a carbon layer on the active particle surface. Unfortunately, the carbon coating method is not appropriate to improve the electrochemical performance of a-FePO₄ because of the phase transformation from the amorphous state to an electrochemically inert hexagonal system at 460 °C.¹⁷ As an alternative method, highly conductive carbon additives such as graphene, carbon nanotubes (CNTs), or carbon black are often applied to a-FePO₄ materials to improve the conductivity of the cathodes.¹⁹–²⁴

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To introduce a-FePO₄ into graphene and CNTs, which have attracted an extensive area of interest due to high electronic conductivity, excellent chemical stability, and large surface area, researchers usually synthesized a-FePO₄ in their suspensions. According to the method of a-FePO₄ synthesis, the approaches to preparing a-FePO₄/C composites can be classified into three categories: hydrothermal method, microemulsion method, and direct precipitation method. Wang et al. fabricated FePO₄/MWCNTs using pyrene to modify the graphene. This hybrid material exhibited high capacity up to 41.5 mAh g⁻¹ at the discharge rate of 20 C and a high capacity retention ratio up to 92% over 300 cycles at 0.5 C, but it suffers from a time-consuming synthesis process, including a hydrothermal treatment for 12 h and a morphology transformation period for 24 h. Wang et al. fabricated FePO₄/MWCNTs composites with a cylindrical core–shell structure via a microemulsion method, for which the capacity retention was around 100% after 200 cycles at 1 C. However, in the microemulsion system, the FePO₄ nucleation process has to be confined in the nanodroplets with CNTs inside to assure the adhesion of FePO₄ and CNTs after particle formation, and an aging process as long as 3 h was required to fulfill the adhesion. Fan et al. used rhodanineacetic acid–pyrene to modify the graphene, and then both FeSO₄ and NH₄H₂PO₄ solutions were added dropwise. The attraction between Fe²⁺ and the negatively charged graphene induced the precipitation of FePO₄ particles on the surface of graphene. However, the purity of a-FePO₄ was hard to be controlled precisely in the reaction system involving multicomponent coprecipitation processes, and dropwise feeding determined low productivity as well as difficulties in scale-up. Apart from these main approaches, other strategies ever reported include atomic-layer deposition, mechanochemical synthesis, etc. All in all, the synthesis of high-performance a-FePO₄-C materials still involves complicated and inefficient processes. Thus, it is highly desired to develop new strategies of manufacturing a-FePO₄-C materials with the characters of expedience in process and excellence in product application performance. To this end, we need to improve the preparation of a-FePO₄·2H₂O nanoparticles as well as the combination of a-FePO₄·2H₂O nanoparticles and carbon nanomaterials.

Recently, using a membrane dispersion microreactor, our group proposed a fast and simple approach of preparing a-FePO₄·2H₂O nanoparticles that have high purity and narrow size distribution via fast precipitation. By regulating the addition amount of phosphoric acid, the purity of a-FePO₄ could be well guaranteed under different reactant concentrations. More recently, we first conducted the surface modification of a-FePO₄·2H₂O nanoparticles and dispersed them in water and then synthesized the composite composed of a-FePO₄·2H₂O nanoparticles and carbon nanomaterials by fast suspension mixing and controlled sedimentation in sequence with the help of a micromixer. The reversible discharge capacity reached 119.5 mAh g⁻¹ at 5 C when FePO₄/CNT = 80:15, indicating the effectiveness of their composition. However, it needs to meet two criteria to assure that this strategy works well. The first is that the monodispersity of both CNTs and a-FePO₄·2H₂O nanoparticles ought to sustain in a relatively long term. Thus, surface modification is required for a-FePO₄·2H₂O nanoparticles. The second is that the micromixing of two suspensions ought to be enhanced as far as possible. Unfortunately, the mixing of two suspensions is more difficult than that of two fluids obviously. It was noticed that the preparation of a-FePO₄·2H₂O nanoparticles just relied on the enhanced micromixing of two fluids, and the as-prepared a-FePO₄·2H₂O nanoparticles were well dispersed in the mixture instantaneously. In addition, learning from using a T-junction micromixer to synthesize Fe₃O₄ nanoclusters with a narrow size distribution from Fe₃O₄ nanoparticles, we recognized the accessibility of controlled coagulation of nanoparticles in the microreactor. Naturally, we envision that the FePO₄·C nanocomposites might be synthesized via a one-step coprecipitation method, that is, the solutions containing iron source, phosphor source, and carbon nanomaterials are continuously mixed in the microreactor to carry out FePO₄·2H₂O microprecipitation together with the following FePO₄·C coagulation. This route would potentially skip the surface modification of a-FePO₄·2H₂O nanoparticles and improve the application performance of FePO₄·C nanocomposites substantially.

Accordingly, in this work, we developed a new facile and fast synthesis approach of nanostructured a-FePO₄-CNT composites via fast precipitation in a microreactor followed by the ball-milling process. In detail, the CNT was dispersed in a (NH₄)₃PO₄ solution; after that the obtained suspension was used as a continuous fluid. The Fe(NO₃)₃ solution was selected as the dispersed fluid. They were mixed continuously to generate the clusters composed of nanosized FePO₄ and CNTs directly. By the utilization of this methodology, the synthesis process can be achieved within seconds instead of hours (Table S1) due to the extremely small mixing scale enabled in the microreactor. Meanwhile, it could guarantee the high purity of FePO₄ and adapt the high ratio of FePO₄. The electrochemical performance of the composites as cathodes was further enhanced by mechanical ball-milling, improving the contact between a-FePO₄ and CNT. The factors involved in the preparation process were thoroughly investigated to understand their influences on the electrochemical performance of a-FePO₄-CNT composites. The optimizations on procedures and recipes were conducted and further discussed regarding the dispersion and contact status of a-FePO₄ nanoparticles and CNTs. Optimally, the discharge specific capacities of the cathode reached 175.8 mAh g⁻¹ at 0.1 C and 137.0 mAh g⁻¹ at 5 C and almost did not exhibit capacity fading over 500 cycles at 5 C, demonstrating the effectiveness of our approach.

2. RESULTS AND DISCUSSION

2.1. Proposed Mechanism To Prepare High-Performance a-FePO₄-CNT Composites. We developed the high-performance a-FePO₄-CNT composites with the following features: (1) the a-FePO₄ is composed of nanoparticles; (2) both a-FePO₄ nanoparticles and CNTs are well dispersed; and (3) there exist abundant, uniform, and compact contact sites between a-FePO₄ nanoparticles and CNTs. Accordingly, we proposed a mechanism as shown in Figure 1. In details, CNTs were dispersed into one of the reactant solutions (containing (NH₄)₃PO₄ or Fe(NO₃)₃), producing a high-dispersed CNT suspension via electrostatic repulsion among charged functional groups (e.g., carboxyl) on the surface of CNTs. The other reactant solution was introduced into the suspension by a membrane dispersion microreactor, allowing the fast mixing and reaction between Fe²⁺ and HPO₄²⁻ to generate a-FePO₄ nanoparticles in the mixture. The a-FePO₄ nanoparticles were...
precipitated and then interacted with surrounding CNTs by electrostatic attraction to generate a-FePO4-CNT aggregates, which were easily separated out as microsized precipitates. The a-FePO4-CNT aggregates were dried and then ball-milled to improve the contact between FePO4 nanoparticles and CNTs.

2.2. Dispersion of CNTs in Reactant Solution. In the stage of making up the CNTs suspension containing the reactant, the dispersion state of CNTs is a crucial concern since it determines the performance of the interconnecting network, which provides fast electronic conduction pathways between the segregated FePO4 nanoparticles. Nanosized CNTs can offer almost 100% utilization of the whole carbon network to electron transport among individual FePO4 particles. However, the utilization will be restricted if CNTs are agglomerated. Thus, it is necessary to prevent CNTs from forming huge bundles. In our approach, high dispersion of CNTs was ensured by chemical functional groups on the surface of CNTs, like carboxylates, which convey negative charges and, thus, provide the electrostatic stability that a colloidal dispersion needs. ζ-potential on a surface is the direct indicator of electrostatic interaction. As seen in Figure 2a, the ζ-potential ranges from 21.1 to −28.0 mV for FePO4 particles, which is dependent on the pH value. Correspondingly, the ζ-potential ranges from 1.8 mV to −73.3 mV for oxidized CNTs. When the pH is higher than 8, the ζ-potential of the CNT suspension reaches the largest value, and the electrostatic repulsion among CNTs could increase to the maximum as well. Otherwise, when the pH decreases to 2, the ζ-potential of CNT is almost zero and the suspension will lose the stability. To investigate the influence of ζ-potential on the dispersion state of CNTs, dynamic light scattering measurements of suspensions were conducted, and the results are exhibited in Figure 2b. As seen, it is easily found that the unimodal peak originated from the CNTs. The CNTs dispersed in the (NH4)3PO4 solution had the size distribution around 142 nm, and the CNTs dispersed in the Fe(NO3)3 solution had the size distribution around 712 nm. It indicates that CNTs are aggregated at a lower pH. For the obtained cathodes, the positive influence of a better dispersion state of CNTs was to decrease the charge-transfer resistance (Rct) of the cathode, as confirmed in Figure S2.

2.3. Nanoprecipitation of a-FePO4 and Aggregation of a-FePO4-CNTs. In the stage of a-FePO4 nanoprecipitation followed by a-FePO4-CNTs aggregation, the nucleation and growth of FePO4 can take place throughout the bulk solution once two reactant solutions are mixed. Consequently, FePO4 particles might generate either close to the CNTs network, being able to effectively interact with CNTs, or far away from the network, being prone to agglomerating to larger clusters. Enhancing the micromixing of two reactant fluids could offset the difference of CNTs and reactants in the transport property and inhibit the occurrence of the latter case. Besides, it is obvious that promoting the nucleation of FePO4 close to CNTs is helpful for building a more efficient conductive structure, which could be achieved by increasing the content of CNTs in suspension in our approach. For a nanoprecipitation process, increasing the concentrations of reactants usually leads to the decrease of particle size. Thus, our approach has the potential of providing improved productivity and product performance simultaneously as long as the good dispersion state of the CNT suspension and good micromixing performance can be guaranteed.

Figure 3a shows the X-ray diffraction (XRD) patterns of the a-FePO4-CNT composites under 0.1 M ((NH4)3PO4 and Fe(NO3)3) concentration, FePO4/CNT = 8:1.5) and pure a-FePO4. Both exhibit no obvious peak, indicating that FePO4 kept the amorphous structure after adding CNTs. To further inspect the purity of a-FePO4-CNT composites, the XRD patterns and inductively coupled plasma optical emission spectrometry (ICP-OES) results of composites after 800 °C calcination are supplied in Figure 3b and Table S2. In comparison with the diffraction peaks of pure FePO4 indexed from the standard JCPDS data file no. 29-0715 (green triangle), the XRD patterns of the composites after calcination show that the crystal structure of composites was in a...
hexagonal system with space group P321 (150). In the meantime, diffraction peaks that are relevant to impurity are not found in the XRD patterns, confirming the excellent purity of the product. According to the ICP-OES result (Table S2), the P/Fe mole ratio of the composites was highly close to the stoichiometry of FePO₄ (1.00), implying that the composites contained FePO₄ with high purity. Figure 3c exhibits the thermogravimetric analysis–differential scanning calorimetry (TGA–DSC) curve of α-FePO₄-CNT composites. Two stages of mass loss are observed at about 150 and 600 °C, which correspond to the dehydration process and CNTs oxidation. The whole weight loss is measured to be about 19.0%. The mass loss of CNTs oxidation is about 14.7%, which is close to the ratio in feedstock (15 wt %). The small weight difference may arise from water taken in during weighting. Herein, we used the content of CNTs added originally to calculate the specific capacity.

The transmission electron microscopy (TEM) image of pure α-FePO₄, without CNT addition, is displayed in Figure 4a. It exhibits near-spherical morphology and an average size of about 20 nm. According to the TEM image (Figure 4b), the surface oxidation could exfoliate well-dispersed CNTs from their bundles. Figure 4c,d displays different visions of the as-prepared α-FePO₄-CNT nanocomposites under TEM. Apparently, the α-FePO₄ nanoparticles precipitated uniformly on the CNTs to construct nanocomposites. To further recognize the structure of the α-FePO₄-CNT nanocomposites, the scanning electron microscopy (SEM) image is demonstrated in Figure 4e. We can find out that α-FePO₄ nanoparticles were in close contact with CNTs, which represents the same morphology as indicated in the TEM images. To further testify the existence of CNTs, the elementary analysis of the composites was carried out by energy-dispersive spectrometry (EDS), and a typical result is shown in Figure 4f. As seen, the mole ratio of Fe/P is close to 1:1, and the content of CNT is 15.57 wt %, very close to the TGA result noted previously. In summary, α-FePO₄-CNT composites with close contact between FePO₄ and CNTs as well as uniform particle size distribution have been successfully prepared by a fast precipitation method. The contents of FePO₄ and CNTs were almost the same as materials added originally, proving a controllable FePO₄/C ratio.

As we previously expected, higher CNT concentration might enable the fast precipitation to generate more primary FePO₄ particles attached on CNTs and strengthen the contact between FePO₄ and CNTs. To prove that, we conducted a series of syntheses of α-FePO₄-CNT composites under various reactant concentrations as listed in Table S3 and then determined the surface area of samples by measuring the
adsorption and desorption isotherms of α-FePO₄-CNT composites. All of the adsorption isotherm curves shown in Figure 5a display type IV isotherms with H3 hysteresis loops, indicating that both samples were typical mesoporous materials. Calculated from the N₂ adsorption isotherm curves, the Brunauer–Emmett–Teller (BET) surface areas of the samples precipitated under 0.025, 0.05, and 0.1 M ((NH₄)₃PO₄ and Fe(NO₃)₃ concentration, FePO₄/CNT = 8:1.5) are 89.3, 138.1, and 153.9 m² g⁻¹, respectively. In addition, the average size of FePO₄ particles was almost constant under different concentrations (Figure 5b), indicating that the change of surface area does not result from the variances of particle size. Therefore, the smaller BET surface area of the sample with higher CNT concentration was probably due to the tight contact between FePO₄ and CNTs. Furthermore, tight contact also led to higher tap density as well as less interspace existing in the structure of composites (Figure 5b).

The increased contact sites between FePO₄ and CNTs explain the improved electronic conductivity, which could be further investigated by their EIS measurements. Figure 5c shows the Nyquist curves for all of the cathodes, which show a straight line at low frequency, and a semicircle ranging in high and middle frequencies. The straight line and semicircle represent the diffusion of lithium ions in the electrode and charge transfer on the cathode surface, respectively. The corresponding equivalent circuit model is shown in Figure 5c as well. As observed in Table S4, the Rct value of the cathode was much lower than the other two, revealing a better conductive network for individual FePO₄ particles. This result also demonstrates that the electronic conductivity of the α-FePO₄ cathode was significantly improved by increasing amount of FePO₄ particles adhered to CNTs. For lithium battery cathodes, the ambipolar diffusion can only start at the vicinity of the point contact between active particles and carbon conductive agents, which leads to a constrained electric field around this point. When more contacting points were
created, the area for lithiation reaction increased as well, reflecting a higher apparent lithium diffusion coefficient, which also can be concluded from the higher and sharper redox peaks in CV curves. As illustrated in Figure 5d, all CV curves display only one pair of current peaks located near 3 V, which is in good agreement with the redox of Fe(III)/Fe(II). The broad redox peaks also prove that the process of lithiation/delithiation is a continuous, single-phase redox reaction. For the sample with higher CNT concentration, the redox peaks were higher and sharper, and the redox interval potential was smaller, compared with the other two samples, demonstrating the enhanced lithiation kinetics in the cathode having more FePO₄ particles adhered to CNTs.

Apart from the charge-transfer resistance, the apparent lithium diffusion coefficient (D) could also be calculated with the EIS measurement. The lithium diffusion coefficient was calculated in Table S5 by using the following equation17

\[ D = R^2T^2/(2A^nF^4C^2\sigma^2) \]  

(1)

Herein, σ is the Warburg factor, C is the lithium-ion concentration in the cathode, F is the Faraday constant, n is the amount of electrons transferred per molecule redox reaction, A is surface area of the electrode, T is the respective absolute temperature, and R is the universal gas constant. As shown in Figure 5c, a distinctly linear relationship between Zre and \( \omega^{-0.5} \) is exhibited. These slopes of lines were used to compare the diffusion coefficients. The results (Table S6) reveal that the apparent lithium diffusion coefficient in the 0.1 M sample was 1.6 times of that of the 0.05 M sample and 3.3 times of that of the 0.025 M sample, indicating that a significant increment in the diffusion coefficient could be achieved when more FePO₄ particles adhered to CNTs. Combined with the improved charge-transfer ability, an excellent electrochemical performance could be expected for the obtained composites. As seen in Figure S4, the cathode with 0.1 M reactants concentrations exhibits a specific capacity of 127.3 mAh g⁻¹ at 5 C, which was much higher than that of the cathode with 0.05 M (96.3 mAh g⁻¹) and 0.025 M (81.6 mAh g⁻¹) reactant concentrations at the same discharge rate.

### 2.4. Ball-Milling Treatment of a-FePO₄-CNTs

After precipitation, the aggregates are not compact enough to form a firm structure. In the macro level, the loose microstructure affects the volumetric energy density and tap density of the aggregates adversely. In the micro level, the loose microstructure implies unstable composite structures. Thus, the final composites with a compact structure are highly desired for manufacturing high-performance cathodes with good conductivity and high tap density. In our approach, ball-milling treatment was conducted for the precipitation aggregates. Since it did not require pulverization in the ball-milling process, the operation time could be comparatively short, like 5 h in our work.

Figure 6a illustrates the comparative EIS results of a-FePO₄-CNT composites before and after ball-milling. The Rₓ value of the cathode after ball-milling treatment is 66.0 Ω, which was far less than that of the cathode without ball-milling treatment (Table S4). Since these two cathodes were identical in composition, we could confirm that the application of ball-milling improves the electron transport performance. Benefiting from the ball-milling treatment, the aggregates could be compacted firmly, indicating a comparatively high tap density of 1.05 g cm⁻³, far larger than that of 0.67 g cm⁻³ without ball-milling treatment. The rate performance of the cathodes at various discharge rates (increasing from 0.1 to 5 C gradually and recovering to 0.1 C) is represented in Figure S5. The cathode after ball-milling treatment displays a specific capacity of 137.0 mAh g⁻¹ at 5 C, which is larger than that of the cathode without ball-milling treatment (127.4 mAh g⁻¹) at the same rate. The result suggests that the ball-milling treatment significantly improved the utilization of the cathode active materials.

### 2.5. Comparison of Various a-FePO₄-C Cathodes in Electrochemical Performance

Finally, after taking the above three stages into consideration, the final composites were obtained optimally, which present high specific capacity as displayed in Figure 6b. The charge/discharge curves of a-FePO₄-CNT composites correspond to the discharge capacities of 175.8, 173.2, 165.8, 155.8, and 137.0 mAh g⁻¹ at rates of 0.1, 0.5, 1, 2, and 5 C, respectively. For comparison, pristine a-FePO₄ cathodes, mixed with CNTs or carbon blacks by ball-milling for 5 h, were obtained. As shown in Figure S6, compared to the above results, the marked decrease in the rate performance indicates a poor dispersion status of the a-FePO₄ and carbon conductive agents and proves that directly
3. CONCLUSIONS

In summary, nanostructured a-FePO4-CNT composites, as a cathode material for LIBs, were directly synthesized by a fast precipitation technique in a membrane dispersion microreactor. The prepared alkaline environment made CNTs distribution uniform, and FePO4 nanoparticles adhered successfully to CNTs by fast nucleation due to the dense CNTs network in the suspension. Then, a compact structure of the composites was formed by ball-milling treatment. It is found that the dispersion state and concentration of CNTs play crucial roles in the formation of the good conductive network for a-FePO4 cathodes. With the help of the CNTs conductive network, the prepared composites show low charge-transfer resistance and high lithium-ion diffusion ability. High tap density was obtained through ball-milling as well. Benefited by the excellent properties of the cathode structure, the as-prepared a-FePO4-CNT composites performed very well in terms of specific capacity and capacity retention, which were up to 175.8 mAh g⁻¹ at 0.1 C and 137.0 mAh g⁻¹ at 5 C, and kept stable at 5 C over 500 cycles without obvious capacity fading. Furthermore, compared with conventional methods used to synthesize a-FePO4 in the carbon material suspension, our approach is flexible to control the ratio of FePO4 to carbon and ensure the high purity of FePO4 without additional reagent requirement. Importantly, the enhanced micromixing enables fast nanoprecipitation in the suspension and opens a shortcut for constructing nanostructured composites, which have potential in functionalization and are easy to handle.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Materials. Ammonium phosphate ((NH₄)₃PO₄·3H₂O, ≥95%) and ferric nitrate (Fe(NO₃)₃·9H₂O, ≥98.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Nitric acid (HNO₃, 65–68%), sulfuric acid (H₂SO₄, 95–98%), and phosphoric acid (H₃PO₄, 85%) were obtained from Beijing Chemical Works. All of the chemicals were used as received. Carbon nanotubes (CNTs, FT9101) were obtained from Cnano Technology Co., Ltd.

The membrane dispersion microreactor device mainly comprised two stainless steel sample plates (50 mm × 50 mm × 18 mm) and a stainless steel microfiltration membrane. The membrane with a pore size of 5 μm was used in the microreactor as the dispersion medium. The active area of the microporous membrane was 12.56 mm², and the geometric
size of the microchannel was 15 mm × 0.5 mm × 0.5 mm (length × width × height).

4.2. Surface Oxidation of CNTs. First, 0.35 g of MWNTs was added in 100 mL of the mixture of H2SO4 and HNO3 (3:1, v/v). After 10 min of sonification treatment and stirring at 90 °C for 3 h, the suspension was diluted with water carefully, filtered out, and washed to be neutral with deionized water.

4.3. Preparation and Application of a-FePO4-CNT Nanocomposites. As shown in Figure 7, a microreactor was used to prepare the a-FePO4-CNT nanocomposites via the precipitation process. First, the oxidized CNTs were dispersed in 0.1 M (NH4)3PO4 solution by ultrasound treatment for 20 min to obtain the CNT suspension as the continuous fluid. The mass ratio of theoretical FePO4 yield to added CNTs was fixed at 80:15. The dispersed fluid was the aqueous solution containing 0.1 M Fe(NO3)3 and 0.02 M H3PO4. Other conditions with different reactant concentrations are referred to in Table S3. The flow rates of both these fluids were set at 50 mL min⁻¹. The as-prepared nanoparticles in the effluent were filtered, washed by water, dried, and transferred for ball-milling, in which N-methyl pyrrolidone was added and the nanoparticles were ball-milled for 5 h. Then, after annealing at 350 °C for 2 h to remove N-methyl pyrrolidone and crystal water, the a-FePO4-CNT composites was finally obtained. They were used to construct the cathode. In detail, they were mixed with poly(vinyl difluoride) (5 wt %) as the binder, coated on aluminum foils, and vacuum-dried at 120 °C for 12 h to become the final working electrode.

4.4. Characterization. The particle size distribution and ζ potential were characterized by a laser scattering particle analyzer (ZS-90, Malvern). The X-ray diffraction (XRD) patterns were collected on an X-ray powder diffractometer (D8 Advance) using Cu Kα radiation at a scanning rate of 5° min⁻¹. The Simultaneous Thermal Analyzer (NETZSCH STA 409 PC/PG) was exploited to conduct thermogravimetric analysis under an air atmosphere. ICP-OES spectrometry (IRIS Intrepid II XSP) with a plasma power of 1150 W and a peristaltic pump rotating at 100 rpm was used to determine elementary composition of the samples (i.e., iron and phosphorous). A transmission electron microscope (TEM, JEOL JEM2010, 120 kV) and a scanning electron microscope (SEM, JEOL JSM7401, 10 kV) with an energy-dispersive spectrometer (EDS, HORIBA X-man) were exploited to observe morphologies of the a-FePO4 particles, CNTs, and the composites. A Quantachrome Autosorb-1-C chemisorption/ physisorption analyzer was exploited to measure nitrogen sorption isotherms at 77 K. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. To measure the tap density, we placed the cathode material in a cylinder and then tapped it at least 50 times by hand. The ratio of the mass and the volume of the tapped powder was denoted the tap density.

To determine electrochemical performances, we assembled CR2025 coin-type cells in an argon-filled glovebox with a Celgard 2400 microporous membrane (polypropylene) as the separator and lithium foil as the counter electrode. The electrolyte was the mixture of dimethyl carbonate/diethyl carbonate/ethylene carbonate (1:1:1, v/v/v) containing 1 M LiPF6. Using a LAND CT2001A Battery Analyzer, charge-discharge measurements were performed in the voltage range of 2.0–4.2 V (vs Li/Li⁺) at room temperature (25 °C). The mass of the active material was set as the reference to calculate the capacity. An electrochemical workstation (VSP, BioLogic) was used to perform electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements. For the EIS measurement, the frequency range was from 10⁶ to 10⁻² Hz. For the CV measurement, the scanning rate was 0.1 mV s⁻¹.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01343.

Calculated distributions of iron species and phosphorus species under various pH values, EIS spectra of a-FePO4-CNT composites synthesized with CNTs dispersed in Fe(NO3)3 and (NH4)3PO4 solutions, XRD patterns (after calcination) and rate capacities of a-FePO4-CNT composites prepared under different CNT concentrations, rate capacities of a-FePO4-CNT composites before and after ball-milling and pristine a-FePO4 cathodes, FTIR spectra of FePO4 mixed with CNTs, and FePO4-CNT composite, contrast of various techniques for nano-FePO4 preparation, P/Fe molar ratios of composites after calcination, experimental conditions of samples under different CNT concentrations, fitted EIS parameters of all cathodes listed above, σ values and the apparent diffusion coefficients of the lithium ion and linear fitting results between Zrc and ω⁻⁰·⁵ of samples under different CNT concentrations (PDF)

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