

Full paper

In-situ self-polymerization restriction to form core-shell LiFePO₄/C nanocomposite with ultrafast rate capability for high-power Li-ion batteries



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ABSTRACT

Charging and discharging lithium ion batteries (LIBs) in a matter of seconds to tens of seconds rather than hours can potentially lead to technological breakthroughs and bring about lifestyle changes. This work aims to enable ultrafast Li-ions charge/discharge ability for LIBs by significantly accelerating the diffusion kinetics of Li⁺ ions and enhancing the electric conductivity in LiFePO₄ cathode material. An innovative method was developed to synthesize LiFePO₄/C nanocomposite with secondary particles structure containing uniform (20–50 nm) and highly crystalline LiFePO₄ single nanoparticles which are free from any anti-site defects (*e.g.* Fe_{Li}) and uniformly coated by a highly graphitized carbon-shell network with good electronic conduction. The LiFePO₄/C material was formed from a FePO₄·xH₂O/poly(furfuryl alcohol) nanocomposite, which was prepared through a self-regulated *in situ* polymerization restriction method, followed by a rapid wet-chemistry lithiation (H⁺/Li⁺ ion exchange) and subsequent calcination. Benefiting from the ultra-small size of the LiFePO₄ nanoparticles, absence of Fe_{Li} defects, and a continuous 3D carbon network, the LiFePO₄/C nanocomposite demonstrated ultrafast lithium-storage rates when used as a cathode material in lithium half-cells, which required only 21.6 s to reach a complete discharge at a rate of 150 C while still maintaining a high specific capacity of 95.4 mAh g⁻¹.

1. Introduction

Lithium ion batteries (LIBs), as one promising energy storage technology, have been widely deployed in many applications including electric vehicles (EV) [1,2] and large-scale energy backup systems [3–5], however, currently it takes hours to fully charge or discharge the LIBs. The performance of an LIB is limited largely by its electrode materials, in which olivine LiFePO₄ is superior as a common cathode material in terms of stability, natural abundance, cost, and environmental friendliness [1,6–8]. Unfortunately, the slow diffusion of Li⁺ ions and the poor electric conductivity of LiFePO₄ are inhibiting the raise of charging/discharging rates in LiFePO₄-based LIBs [1,2,7–9]. Reducing particle size, in conjunction with surface carbon coatings to form a LiFePO₄/C nanocomposite is acknowledged as the technology of choice to address this issue effectively [9–12]. However, it seems to be

inherently challenging to simultaneously achieve a high degree of crystallization, nanometer-sized particles, and a full surface coverage with highly-conductive carbon in LiFePO₄/C composite materials. Most previous studies [10,13] have focused upon only one or two structural preferences, rather than considering them all together. Moreover, once the particles size of LiFePO₄/C is down to the nanoscale, significant interfacial resistance originating from more soft contacts [14,15], reduced tap density, as well as poor processability often turns into new issues, which might be ameliorated by the secondary granulation technology [10].

In recent years, various wet-chemistry technologies including hydrothermal/solvothermal, sol-gel, co-precipitation methods have been successfully developed to synthesize LiFePO₄/C nanocomposite materials [9–13], in which *in situ* polymerization restriction methods based upon Fe³⁺-based FePO₄·xH₂O precipitation system were well

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established and widely perceived as a technology of choice to produce LiFePO_4/C nanocomposite materials with multiple structure advantages that are highly desired for fast lithium storage [10,16–18]. For instance, Zhou's group [16] creatively explored a method of such kind *via* a $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ /polyaniline system to prepare LiFePO_4/C nanomaterial with core-shell structure, formed from a highly crystalline LiFePO_4 “core” with grain sizes of 20–40 nm and a thin semi-graphitic carbon “shell” (thickness of 1–2 nm), using which as active electrode the power rate can reach up to 60 C with a high reversible capacity of 80 mAh g^{-1} . However, most previous attempts [16–18] to design such route relied on high temperature solid-state reaction for lithiation that entails tedious grinding or alternatively ball milling followed by long-term calcination cycles. Besides, additional organics, such as starch, sucrose, glucose, citric acid, and resin [10,16–18], need to be added during the procedure to ensure adequate carbon coatings. Thus exploiting an optimized preparative method that is simpler and more controllable to acquire superior LiFePO_4/C nanocomposite materials for fast lithium storage would be of great significance.

In this work, we propose a unique and controllable method for synthesizing LiFePO_4/C nanocomposite materials with appealing structural features to achieve ultrafast Li-storage capabilities. The synthesis can be divided into three easy steps, namely i) self-regulated *in situ* polymerization restriction, ii) H^+/Li^+ ion exchange, and iii) calcination, which does not include a tedious mixing step. The final LiFePO_4/C obtained is composed of single-particle LiFePO_4/C containing 20–50 nm highly crystalline LiFePO_4 “cores” which are free from any anti-site disorders (e.g. $\text{Fe}_{1-x}\text{Li}_x$) and fully coated by highly conductive thin carbon “shells” with typical thickness of 1.6–2.0 nm. These single LiFePO_4/C nanoparticles aggregated and tightly held together by the surface carbon to form porous secondary particles with a size up to several micrometers to tens of micrometers. Importantly, the LiFePO_4/C material was capable of reducing the polarization effect of electrode substantially and enabling a super-high charging/discharging rate of up to 150 C with a reversible capacity of 95.4 mAh g^{-1} . As a result, the material can afford a super-high power density of 64.5 kW kg^{-1} which is comparable to those in aqueous-based supercapacitors, yet with an energy density (261.3 Wh kg^{-1}) almost one order of magnitude higher.

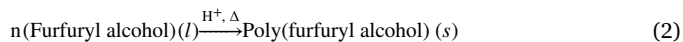
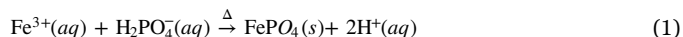
2. Results and discussion

2.1. Design process for the synthesis of LiFePO_4/C nanocomposite material

2.1.1. Self-regulated *in situ* polymerization restriction

As illustrated schematically in Fig. 1, the synthesis designed starts with a one-step process of spontaneous precipitation and *in situ*

polymerization reactions that proceed at a low temperature of 90°C (Fig. 1, Step I). The process involves the dropwise addition of Fe^{3+} ions and furfuryl alcohol (FA) monomers to a solution containing H_2PO_4^- ions, and the reactions can be summarized as follows:



Here, the precipitation reaction between Fe^{3+} and H_2PO_4^- releases H^+ ions which act as an acid-catalyst for the polycondensation of furfuryl alcohol [19,20]. Detailed acid-catalyzed polycondensation mechanism can be described below Fig. S1. The precipitation reaction expressed in Eq. (1) occurs slightly prior to the polycondensation of furfuryl alcohol (i.e. Eq. (2)) due to a higher pH level of the initial solution. Visually, just a single white precipitate associated with $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ inorganics appears at the onset of dropping. As more $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ precipitates form, the pH value of the solution gradually decreases (Fig. S1), which in turn initiates the polycondensation of FA monomers into poly(furfuryl alcohol) (PFA) halfway through the dropping, resulting in a bluish-green and then yellowish-brown suspension. Given that the produced H^+ ions appear initially at the surface of the $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ precipitates, the primordial oligomer units of PFA polymer should form preferentially near the outer surface of these precipitates, and the newly-formed PFA polymers can easily anchor onto them through an electrostatic interaction and/or host-guest binding behavior. As thus, contact-induced growth of the existing $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ nanoparticles is regulated by the surface PFA coverage during dropping and aging. In a departure from the principle for Fe^{3+} -catalyzed polymerization of aniline [16], this acid-catalyzed polycondensation process can continue even when the outer surface of $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ precipitates has already been fully covered by a layer of PFA. This will ensure a sufficient loading of organics on the $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ host. To sum up, the PFA polymer *in situ* polymerized and particle-grown plays key roles in confining the $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ nanoparticles, separating them to each other to avoid particles growth, and also linking them together *via* the polymer network to form an assembled secondary particle.

2.1.2. Rapid wet-chemistry lithiation (H^+/Li^+ ion exchange)

The next step (Fig. 1, Step II) is to convert the FePO_4/PFA nanocomposite precursor into $\text{Li-FePO}_4/\text{PFA}$ by using a rapid wet-chemistry lithiation method (i.e. H^+/Li^+ exchange reaction) that proceeds in a lithium acetate ethanol solution (60°C) exposed to air [21]. Briefly speaking, the protons belonging to the $-\text{OH}$ and/or $-\text{OH}_2$ groups of amorphous $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ compound, under the specified non-aqueous condition, favor the exchange of Li^+ ions. The process was

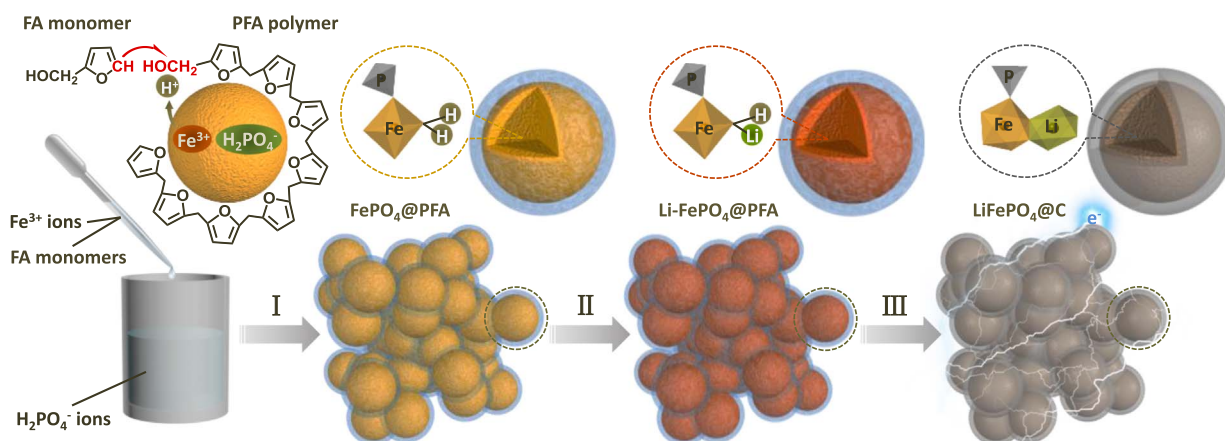


Fig. 1. Schematic illustration for the synthetic process of LiFePO_4/C nanocomposite material with ultrafast lithium-storage ability by using an amorphous $\text{FePO}_4 \cdot x\text{H}_2\text{O}/\text{PFA}$ nanocomposite prepared by a self-regulated *in situ* polymerization restriction method (Step I), in conjunction with a rapid H^+/Li^+ ion exchange reaction (Step II), followed by direct calcination (Step III).

proved by the comparisons of Gas chromatography/mass spectrometer (GC-MS) data between the liquid supernatant separated from the final lithiation product, and the initial lithium acetate ethanol solution, as shown in Fig. S2. It was found that detectable acetic acid emerges in the solution after the lithiation reaction, and the pH value is decreased with it from 8.3 to 6.0 (1 mL of the solution to be tested was diluted with 5 mL distilled water for pH detection), which indicates the H^+ ions are released to solution from the $FePO_4$ /PFA precursor by a H^+/Li^+ ions exchange process to form $Li-FePO_4$ /PFA. More proof for the reaction mechanism will be given in the following section.

2.1.3. Post-calcination treatment in an inert atmosphere

The final step (Fig. 1, Step III) is to convert the $Li-FePO_4$ /PFA nanocomposite intermediate into $LiFePO_4$ /C by direct calcination in an Ar atmosphere. During the calcination process, the isolated nanoparticles of inorganic $Li-FePO_4$ can crystallize into $LiFePO_4$ single nanocrystals, and meanwhile the surface PFA is pyrolyzed gradually into a highly conductive carbon shells network that *in situ* restricts the crystal growth of $LiFePO_4$ nanoparticles and assembles them together to form secondary composite particles at a micrometer scale.

2.2. Structure features of $FePO_4$ /PFA and $Li-FePO_4$ /PFA nanocomposite precursors

Fig. S3 shows the X-ray diffraction (XRD) patterns of $FePO_4$ /PFA and $Li-FePO_4$ /PFA, according to which we can determine that the two materials are completely amorphous. Based upon thermogravimetric analysis/differential scanning calorimetry (TG-DSC) data (Fig. S4), the chemical formula of the hydrated $FePO_4$ in $FePO_4$ /PFA nanocomposite can be roughly estimated to be $FePO_4 \cdot 2.7H_2O$. The successful loading of PFA polymer onto $FePO_4 \cdot xH_2O$ precipitates was verified by Fourier transform infrared spectroscopy (FTIR) as illustrated in Fig. 2A. Typically, the IR peak located at 793 cm^{-1} corresponds to the C-H out-of-plane bending of 2, 5-disubstituted furan rings, and the peaks attributed to carbonyl group ($C=O$) (typical characteristics for the acid-catalyzed ring opening of furan rings) are observed at 1713 and

1768 cm^{-1} [22]. By contrasting the two FTIR spectra carefully, one can notice that the cation exchange process has subjected initial $FePO_4$ /PFA precursor to partial curve changes, as labeled by the black dotted lines. According to our earlier study [21], the marked changes including the weakening of O-H characteristic peak around 3205 cm^{-1} and the appearance of a new band at 495 cm^{-1} should be ascribed to the formation of Li-O units by partial substitution of framework protons with Li^+ ions. The conclusion can be further supported by the X-ray photoelectron spectroscopy (XPS) analysis of the two samples (Fig. S5). Calcination in an inert atmosphere can lead to the direct conversion of $Li-FePO_4$ /PFA into $LiFePO_4$ /C nanocomposite (named as PreLFP). Fig. 2B shows the *in situ* XRD data showing the evolution of $Li-FePO_4$ /PFA to $LiFePO_4$ /C during temperature ramping. As it can be seen, just a single crystalline phase associated with orthorhombic $LiFePO_4$ emerges initially at $\sim 400^\circ\text{C}$ without undergoing any transient crystalline phases, and the degree of crystallization increases as the temperature increases, which matches well with that of quasi *in situ* FTIR test, as shown in Fig. S6.

Morphological details of $FePO_4$ /PFA and $Li-FePO_4$ /PFA precursors were first visualized by scanning electron microscopy (SEM) (Fig. S7), from which we can clearly observe that both of the nanocomposites present a porous agglomerate structure assembled by a large number of nanoparticles. No significant difference in the morphology can be identified. Further studies by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) (Fig. 2(C) and (D)) reveal that these nanoparticles are completely amorphous, in good agreement with the XRD analysis, and take on a spherical appearance with tens of nanometers in dimension, which are solidly connected together by the surface PFA polymer forming a porous architecture. Bright-field scanning TEM (STEM) technique is a general tool for the characterization of nanostructures with complex compositions [23]. The outer “shells” with brighter contrast observable in the STEM images of both $FePO_4$ /PFA and $Li-FePO_4$ /PFA composites (Fig. 2(E) and (F)) can be assigned to PFA polymer, whereas the darker “cores” inside should belong to the inorganic components chiefly made up of heavier elements (*e.g.* Fe, P in $FePO_4$ and $Li-FePO_4$ compounds).

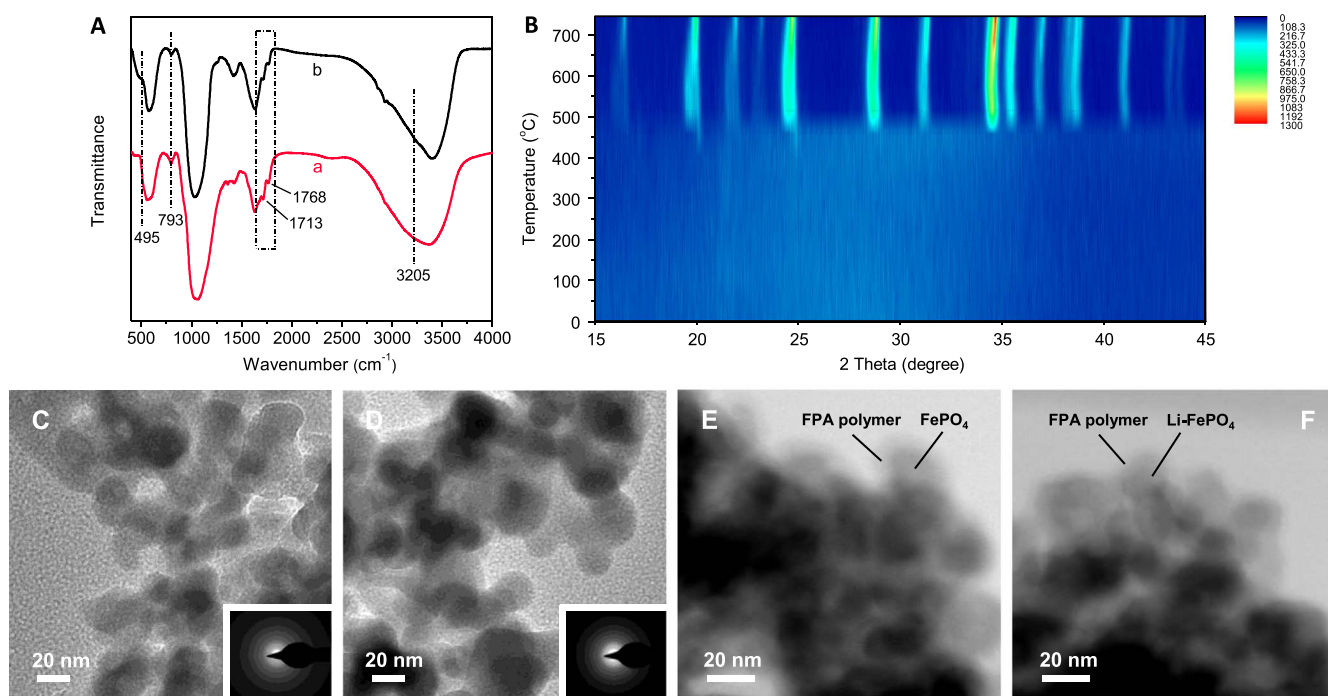


Fig. 2. (A) Typical FTIR spectra of a) $FePO_4$ /PFA and b) $Li-FePO_4$ /PFA. (B) *In situ* high temperature XRD analysis of $Li-FePO_4$ /PFA intermediate under an inert atmosphere at controlled temperatures (25–700 $^\circ\text{C}$, heating rate of 5°C min^{-1}) with 15 min for each collection. TEM images of (C) $FePO_4$ /PFA and (D) $Li-FePO_4$ /PFA. Bright-field scanning TEM images of (E) $FePO_4$ /PFA and (F) $Li-FePO_4$ /PFA. Insets in Fig. 2(C) and (D) show the corresponding SAED patterns.

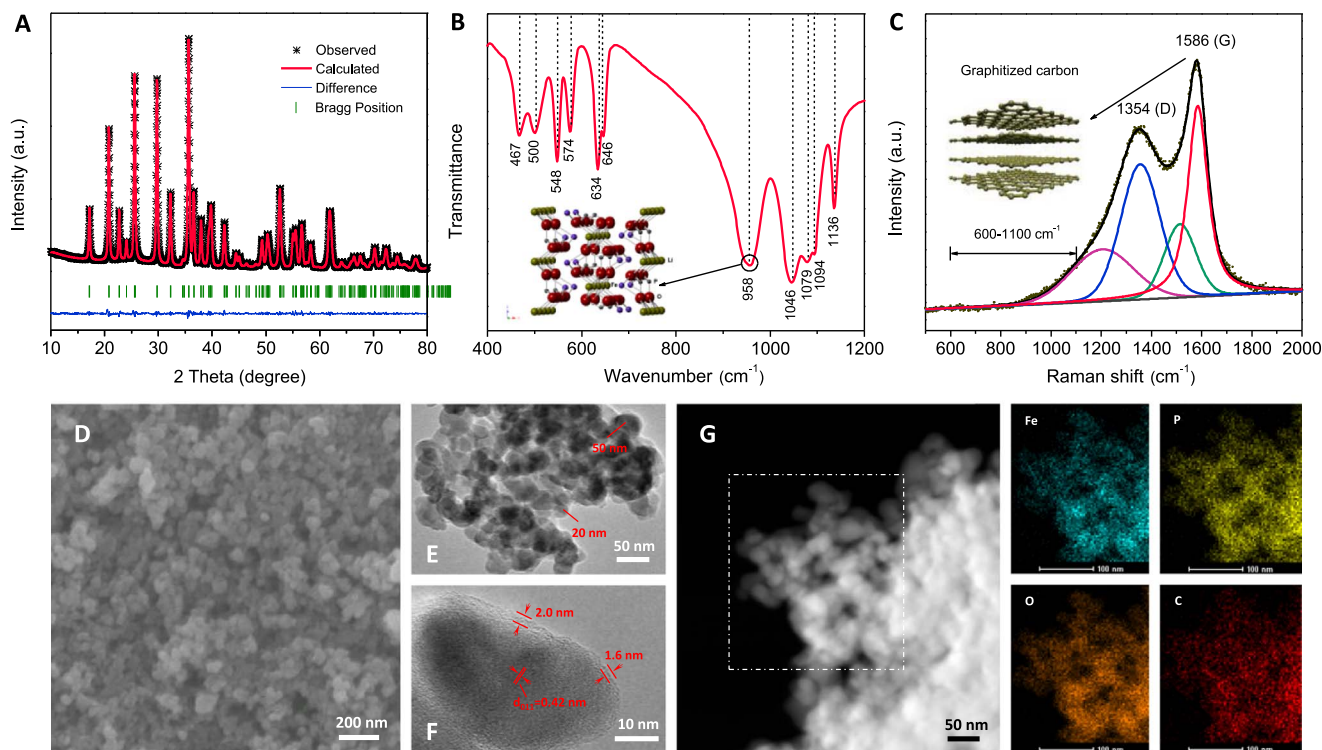


Fig. 3. (A) XRD powder pattern (black points) and Rietveld fit (red lines) of PrePLFP. Blue curve shows the difference between them. R factors are $R_{wp} = 3.08\%$, $R_p = 2.30\%$, $R_{exp} = 2.00\%$, and $GoF = R_{wp}/R_{exp} = 1.54$, respectively. (B) FTIR spectrum of PrePLFP recorded in the wavenumber region of 400–1200 cm^{-1} . (C) Raman spectrum of PrePLFP fitted by a Gaussian-Lorentzian mixing model. I_G/I_D values are estimated to be 0.95 for peak area ratio and 1.4 for peak height ratio. Typical (D) SEM image, (E) low-resolution TEM image, and (F) high-resolution TEM image of PrePLFP. (G) Scanning TEM (STEM) image of PrePLFP and the corresponding EDS mapping images of Fe, P, O, and C elements, respectively.

Moreover, STEM-energy dispersive spectroscopy (STEM-EDS) mapping images show clearly that both the composites contain Fe, P, O, and C distributing evenly over the particle aggregates (Fig. S8). STEM images, in conjunction with STEM-EDS mapping images can be indicative of a continuous and integrated surface loadings of PFA polymer on the $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ particles, which remains barely changed over the H^+/Li^+ ion exchange process. Further evidence for the structural similarity is provided by N_2 adsorption-desorption data (Fig. S9), which show almost identical porosity parameters in terms of BET surface area (57.2 vs. 59.1 $\text{m}^2 \text{g}^{-1}$) and pore size distribution (inset in Fig. S9).

2.3. Structure features of LiFePO_4/C nanocomposite material

XPS spectra (Fig. S10) of as-prepared LiFePO_4/C nanocomposite material (PrePLFP) clearly evidences the iron species in PrePLFP are all at Fe (II) oxidation state [24,25]. The phase structure of PrePLFP is characterized by XRD analysis, as shown in Fig. 3A. All of the Bragg reflections can be well indexed to the standard orthorhombic structure of LiFePO_4 (JCPDS No. 81–1173) with no other discernible impurities. According to Rietveld refinement based on the structural model provided by Yakubovich *et al.* [26], the lattice constants of the material can be determined to be $a = 10.32499(4) \text{ \AA}$, $b = 6.007608 \text{ \AA}$, $c = 4.694038 \text{ \AA}$, $V = 291.1642 \text{ \AA}^3$, similar to the single crystal values reported previously ($a = 10.332(4) \text{ \AA}$, $b = 6.010(5) \text{ \AA}$, $c = 4.692(2) \text{ \AA}$, $V = 291.4(3) \text{ \AA}^3$) [26,27]. Fe_{Li} anti-site defect, namely Fe^{2+} ions on the Li^+ sites, is a type of lattice defect commonly observable in LiFePO_4 crystals, and it is proven undesirable due to the blocking of the Li^+ ions diffusion pathway [25,28,29]. The level of Fe_{Li} disorder in LiFePO_4 can be easily identified from FTIR spectroscopy [30]. In theory, infrared absorption peak concerning to the P–O symmetric stretching vibration of PO_4 tetrahedron in Fe_{Li} defect-free LiFePO_4 should emerge at 957 cm^{-1} , which is to shift towards a higher wavenumber region with raising amount of Fe_{Li} anti-site defects. For PrePLFP, the characteristic

peak is found to appear at 958 cm^{-1} (shown in Fig. 3B), that is, almost identical to the theoretical value of Fe_{Li} defect-free LiFePO_4 , illustrating extremely few Fe_{Li} defects in PrePLFP. The conclusion can be further evidenced by the crystallography data acquired from Rietveld refinement of the XRD pattern. As illustrated in Table S1, PrePLFP can be precisely refined to the ideal atomic distributions of orthorhombic LiFePO_4 under the space group $Pnma$ free from any atomic disorder, similar to the values reported [26,27]. By using Scherrer's formula ($d = 0.89\lambda/\beta\cos\theta$), the average particle sizes of LiFePO_4 nanocrystals can be calculated to be 43 nm. From SEM and TEM images (shown in Fig. 3(D) and (E)), we can clearly visualize that the primary particles of PrePLFP are quite uniform in size, typically in a narrow range of 20–50 nm, which are connected together by the surface carbon forming bulky porous secondary particles with sizes up to several micrometers to tens of micrometers (Fig. S11). Such kind of porous particles assembly is capable of establishing a continuous 3D electronic transfer network from active iron redox sites of LiFePO_4 to the conductive additives and/or the current collector and reducing the concentration polarization effectively to enhance the charging/discharging rate performance (*i.e.* depolarization effect) [12,14,15], and also bringing potential benefits for the volumetric energy density and processability of the electrodes [10,13,16,21]. STEM-EDS mapping images (see Fig. 3G) further confirm that PrePLFP contains elements of Fe, P, O, and C, all of which are well-distributed over the entire scanning region. High resolution TEM (HRTEM) image, shown in Fig. 3F, reveals that the visible lattice fringes correspond to a spacing of $\sim 0.42 \text{ nm}$, which matches well with the expected d spacing for (011) plane of olivine LiFePO_4 . One can also find that the LiFePO_4 nanocrystal is fully wrapped by a non-crystalline carbon layer with a thickness of 1.6–2.0 nm. It is believed that the kinetic barrier for Li^+ ions to diffuse through such a thin carbon layer can be negligible when compared with other diffusion limitations upon (de)lithiation [10,31]. The surface residual carbon was quantified by TGA, as illustrated in Fig. S12. By taking the theoretical weight gain (5.07 wt%) of pure LiFePO_4 during

TGA into account [32], the content of carbon in PrepLFP was calculated to be ~9.96 wt%. Detailed structure information on the surface residual carbon was further provided by Raman spectrum (Fig. 3C) [2,21,32], which shows two conjoint peaks for PrepLFP over a range of 500–2000 cm^{-1} . Using a Gaussian-Lorentzian mixing model, the spectrum can be divided into four peaks, in which the peaks at 1354 and 1586 cm^{-1} are ascribed to the D band (disordered carbon, sp^3) and G band (graphite, sp^2) of Raman vibration modes for amorphous carbon, respectively [21]. According to the fitting result, the peak intensity ratio (I_G/I_D) of PrepLFP can be estimated to be 0.95 for peak area ratio (1.4 for peak height ratio), which is found higher than those of most LiFePO_4/C hybrid materials reported [10,32], implying that the residual carbon pyrolyzed *in situ* from a mixture of PFA polymer and Li-FePO_4 inorganics is more graphitized and capable of providing a better electronic conductive network. The high degree of graphitization can be interpreted largely from two contributing factors. For one, the calcination temperature (700 °C) is adequate when using PFA polymer as a carbon precursor [33,34]. For the other, the ferric oxides in $\text{Li-FePO}_4/\text{PFA}$ precursor can catalyze the graphitization process of the surface carbon upon calcination [33]. Earlier study revealed that the electric conductivity of pyrolytic carbon produced by thermally carbonizing PFA polymer under 700 °C in the presence of ferrocene can reach up to metallic type ($\sim 1.9 \text{ S cm}^{-1}$), which turns out to be two orders of magnitude higher than that of the pyrolyzed carbon ($\sim 2.2 \times 10^{-2} \text{ S cm}^{-1}$) produced from single PFA polymer under otherwise identical conditions [33]. In addition, a total lack of LiFePO_4 Raman response in the range of 600–1100 cm^{-1} illustrates that the surface carbon coatings on LiFePO_4 particles is fairly complete [21,32], well consistent with the HRTEM observations.

2.4. LIBs performances of LiFePO_4/C nanocomposite as a cathode material

As a proof of concept, coin cells with a metallic Li anode were assembled to evaluate the performance of PrepLFP in LIBs. Charge and discharge characteristics were evaluated by a galvanostatic testing model, and 1 C rate equals to a current density of 170 mA g^{-1} . As displayed in Fig. 4A, the material can discharge to an initial specific capacity of 156.2 mAh g^{-1} at 0.5 C rate, which slightly exceeds the theoretical value of 153.1 mAh g^{-1} , estimated by considering a mixture of LiFePO_4 and 9.96 wt% carbon. This phenomenon is very common in hybrid electrodes with nanometric and hierarchical architectures [28,35,36], and the capacities exceeded can be attributed to the surface and/or interface lithium storage (*e.g.* pseudocapacitive effects). The material also delivers a discharge capacity of 145.7 mAh g^{-1} at a higher rate of 10 C, and the capacities keep as high as 134.9 and 123.0 mAh g^{-1} when cycled at 30 C and 60 C rates. More excitingly, even when the rates are up to 100 C (32.4 s to full discharge) and 150 C (21.6 s to full discharge), the capacities can still remain at 109.6 and 95.4 mAh g^{-1} , respectively. The result is significantly better than that of commercial LiFePO_4/C (CommLFP), and superior to the LiFePO_4/C nanomaterial (PrevLFP) prepared by our group previously *via* partially *in situ* carbon coatings [21], as is also the case for most core-shell LiFePO_4/C nanocomposite materials available in previous literatures [16,37–40], as illustrated in Fig. S13 and Table S2. After a series of creep test at varying rates, the reversible capacities almost return to the initial values of 123.5, 145.6 and 156.4 mAh g^{-1} as the discharging rate changes back to 60 C, 10 C and 0.5 C successively (see Fig. 4B). It thus follows that our PrepLFP has the ability to sustain a high capacity at a super-high charge/discharge rate of up to 150 C, or a current density of 25.5 A g^{-1} . The discernible capacity decay at higher rates can be attributed to the electrode polarization related to the diffusion-limited transfer of Li^+ ions near the two-phase interface. The fact that the primary particles of PrepLFP are nanometer-sized and fully covered with a thin conductive carbon definitely contributes to the super-high power rates, but the performance is substantially better than those of

reported LiFePO_4/C materials with particles of similar size [16], suggesting that some unique features of our PrepLFP might be critical. From a topological point of view, the outstanding battery properties of PrepLFP can be derived from the unique inorganic-organic hybrid structure of the $\text{Li-FePO}_4/\text{PFA}$ intermediate, which is formed from fully sealed PFA polymer “shells” with a 3D-connected network and amorphous inorganic framework “cores” wherein ideal constituent elements involving Li, Fe, P, and O are evenly distributed almost at the atomic level, thus capable of minimizing the inclusions of unwanted impurities and lattice defects (*e.g.* Fe_{Li} disorder) for LiFePO_4 finally formed due to the absence of complex crystallographic phase transition and solid-solid mass transfer upon crystallization at elevated temperatures (as confirmed by Fig. 2B and Fig. S6) [41], and also in favor of establishing, in the true sense, an integrated and high-quality 3D electronic transfer network from active iron redox sites of LiFePO_4 to the conductive additives and/or the current collectors (*i.e.* depolarization effect) after calcination while remaining an open Li^+ ions transport pathway [14,15].

Energy density (E) and power density (P) are two key factors for evaluating the high power applications of an electrical storage device. Fig. 4C shows the Ragone plots of PrepLFP with power density as a function of energy density, which are estimated from the discharging profiles by area integration. Typically, the material can deliver a super-high power density of up to $\sim 64.5 \text{ kW kg}^{-1}$ with an energy density of $\sim 261.3 \text{ Wh kg}^{-1}$ in a lithium half-cell, exceeding those of CommLFP and PrevLFP. Excitingly, the power density is similar to or even higher than those of aqueous supercapacitors [42–45], yet with an energy density almost one order of magnitude higher. For instance, the electrodes used for aqueous supercapacitors in previous literatures, such as Ni(OH)_2 thin film [42], MnO_2/CNT sponge [43], graphene/CNTs hybrid [44], and 3D V_2O_5 nanosheets [45] can just achieve the energy densities of 6.5, 31, 21.74, and 43.2 Wh kg^{-1} at the highest given power densities of 44, 63, 78.29, and 39.9 kW kg^{-1} , respectively. Inspired by these comparisons, we conjecture that the Li-ions batteries using PrepLFP or the materials of such kind as electrodes may have the potential to replace supercapacitors such as those planned for hybrid or all-electric vehicles.

We also evaluated the long-term cycling stability of PrepLFP by repeated cycles at a fixed rate of 10 C. As can be seen from Fig. 4D, despite the ultra-small primary particles (20–50 nm), PrepLFP exhibits an extremely good cyclability with less than 2% of capacity loss over 1000 cycles. Upon cycling, the Coulombic efficiency calculated from the ratio of discharging to charging capacity stays consistently at nearly 100% (inset in Fig. 4D). According to the XRD (Fig. S14) and XPS (Fig. S15) analysis, the bulk structure and near-surface region of active LiFePO_4 remained well after long-term cycles, confirming a high electrochemical stability of the material. In addition to the contributions from the stable LiFePO_4 nanocrystals and full surface carbon coatings, the elastic 3D carbon shell network formed *in situ* on the surface of LiFePO_4 nanocrystals is also supposed to play a positive role in the appealing cycling reversibility by relaxing the strain energy of entire electrode effectively upon (de)intercalation.

3. Conclusion

In summary, the principal merit of the research work is to establish a general and controllable method to synthesize LiFePO_4/C nanocomposite materials for ultrafast lithium storage by using polymer-rich amorphous $\text{FePO}_4 \cdot x\text{H}_2\text{O}$, typically rationally designed $\text{FePO}_4 \cdot x\text{H}_2\text{O}/\text{PFA}$ nanocomposites achieved by a self-regulated *in situ* polymerization restriction method, in conjunction with a rapid H^+/Li^+ ion exchange process, followed by direct calcinations. The final LiFePO_4/C obtained is structurally composed of uniform (20–50 nm in size) and highly crystalline LiFePO_4 single “cores” which are free from any anti-site disorder (*e.g.* Fe_{Li}) and are fully coated by highly conductive thin carbon “shells” (thickness of 1.6–2.0 nm). These LiFePO_4/C nanopar-

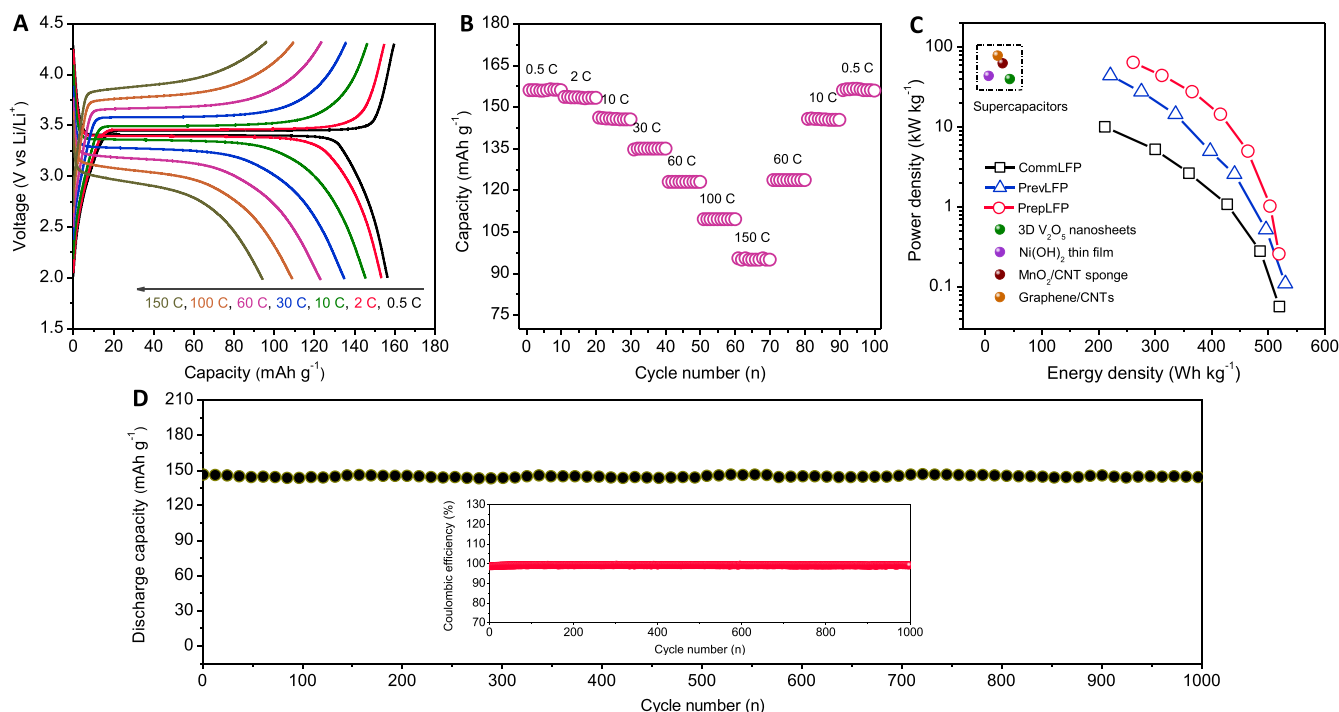


Fig. 4. (A) Typical charge/discharge curves of PrepLFP measured by a galvanostatic testing model with rates from 0.5 C up to 150 C. 1 C rate equals to 170 mA g⁻¹. (B) Rate-varying cycle stability of PrepLFP evaluated by raising the rate continuously from 0.5 C up to 150 C, and then back to 0.5 C with ten cycles for each rate. (C) Ragone plots of power density (P) as a function of energy density (E) for PrepLFP, PrevLFP, CommLFP, and several electrode materials used for aqueous-based supercapacitors [42–45]. (D) Long-term cycling stability of PrepLFP evaluated by repeatedly charging and discharging the cell at a constant rate of 10 C for 1000 cycles. Inset shows the corresponding Coulombic efficiency.

ticles are tightly held together by the surface carbon to form bulky porous architectures with secondary particles size up to several micrometers to tens of micrometers, thus in favor of effective depolarization at high power rates. The ideal structural features of LiFePO₄/C can be attributed to the unique inorganic-organic hybrid structure of the Li-FePO₄/PFA intermediate, formed from fully sealed PFA polymer “shells” with a 3D-connected network and amorphous inorganic “cores” wherein Li, Fe, P, and O are evenly distributed almost at the atomic level. In lithium half-cells, the LiFePO₄/C material can achieve a super-high power rate of up to 150 C with a reversible capacity of 95.4 mAh g⁻¹, which is equivalent to a high power density (64.5 kW kg⁻¹) comparable to those of aqueous-based supercapacitors yet with an energy density (261.3 Wh kg⁻¹) almost one order of magnitude higher. In view of the superiorities in other respects such as processibility, cost, safety, etc., the method developed here may provide us an opportunity to realize scale-up synthesis of LiFePO₄/C nanocomposite materials with ideal structures for use in ultrafast energy storage. We also hope the synthesis mentality established could inspire new ideas and concepts for rational design of all sorts of Li-contained electrodes, including but not limited to LiFePO₄/C nanomaterials, for high power battery applications or other else.

4. Experimental section

4.1. Materials synthesis

FePO₄/poly(furfuryl alcohol) (FePO₄/PFA) was synthesized through a novel self-regulated *in situ* polymerization restriction method. Typically, 50 mL of 0.2 M FeCl₃·6H₂O aqueous solution containing 0.8 mL furfuryl alcohol was added dropwise, with stirring, to 100 mL of 0.1 M NH₄H₂PO₄ aqueous solution that had been pre-heated for several minutes at 90 °C. After stirring the mixture for another 6 h (90 °C), a yellowish-brown suspension was formed. The solid precipitate was collected by filtration and then washed several times with distilled water before being dried off. Li-FePO₄/poly(furfur-

yl alcohol) (Li-FePO₄/PFA) was prepared with the aid of a facile chemical lithiation reaction (H⁺/Li⁺ ion exchange) that proceeded in a nonaqueous medium exposed to air [21]. In a typical run, 0.3 g of as-obtained FePO₄/PFA powder was suspended in 10 mL of 0.6 M lithium acetate alcohol solution. The temperature was then raised to 60 °C and kept for 1.5 h under stirring. After cooling down naturally, the precipitate was filtered, washed with alcohol and dried under 60 °C. LiFePO₄/C nanocomposite material (PrepLFP) was prepared by directly calcining the Li-FePO₄/PFA powder at 700 °C for 6 h under a flowing Ar atmosphere.

4.2. Materials characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2550 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) at 50 kV and 200 mA. Fourier transform infrared spectrometer (FTIR) spectra were collected by a Bruker IFS-66V/S spectrometer. X-ray photoelectron spectroscopy (XPS) analyses were performed on an ESCA LAB MARKII spectrometer. N₂ adsorption-desorption analyses were carried out on a Micromeritics ASAP 2020 M instrument. Specific surface areas were calculated on the basis of Brunauer-Emmett-Teller (BET) equation, and the pore size distributions were determined by the Barrett-Joyner-Halenda (BJH) model. Morphological details were examined by using JEOL JSM-6700F scanning electron microscope (SEM) and JEOL JSM-3010 transmission electron microscopy (TEM). Raman spectrum was collected with a Renishaw inVia Raman microscope and fitted by a Gaussian-Lorentzian mixing model. Thermogravimetric analysis (TGA) was conducted by a Perkin-Elmer TGA 7 TG analyzer under flowing air from ambient temperature up to 800 °C at a heating rate of 5 °C min⁻¹.

4.3. Electrochemistry tests

For electrochemical tests, LiFePO₄/C active material (80 wt%) was firstly mixed with 12 wt% of acetylene black (AB) and 8 wt% of

polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidinone (NMP). The mixture was then cast on an Al foil current collector and vacuum dried for > 10 h at 110 °C. The electrode sheet was tailored into disks of 10 mm, thus forming the cathodes. Generally, a mass loading of 1.5–2.0 mg of the active material was used for each electrode (geometric area of 0.785 cm²). CR2032 coin cells consisting of the cathode, metallic lithium anode, Celgard 2400 separator, and organic electrolyte were assembled in a glovebox filled with high-purity argon. The electrolyte used was a 1:1:1 (v/v) solvent mixture of ethylene carbonate (EC), ethylmethyl carbonate (EMC), and dimethyl carbonate (DMC) containing 1.0 M LiPF₆. The fresh cells were all aged for 6 h before electrochemical tests. Galvanostatic charge/discharge tests were performed by using Land battery test systems (CT2001A) over a potential range of 2.0–4.3 V (vs. Li/Li⁺). All the battery tests were operated at ambient temperature (~25 °C).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.07.001.

References

- [1] J. Lu, Z. Chen, Z. Ma, F. Pan, L.A. Curtiss, K. Amine, *Nat. Nanotech.* 11 (2016) 1031–1038.
- [2] B. Kang, G. Ceder, *Nature* 458 (2009) 190–193.
- [3] B. Dunn, H. Kamath, J.-M. Tarascon, *Science* 334 (2011) 928–935.
- [4] D. Larcher, J.-M. Tarascon, *Nat. Chem.* 7 (2015) 19–29.
- [5] M. Armand, J.-M. Tarascon, *Nature* 451 (2008) 652–657.
- [6] J. Zheng, T. Liu, Z. Hu, Y. Wei, X. Song, Y. Ren, W. Wang, M. Rao, Y. Lin, Z. Chen, J. Lu, C. Wang, K. Amine, F. Pan, *J. Am. Chem. Soc.* 138 (2016) 13326–13334.
- [7] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188–1194.
- [8] J.B. Goodenough, Y. Kim, *J. Power Sources* 196 (2011) 6688–6694.
- [9] M.S. Whittingham, *Chem. Rev.* 104 (2004) 4271–4301.
- [10] J. Wang, X. Sun, *Energy Environ. Sci.* 5 (2012) 5163–5185.
- [11] J. Hu, W. Li, Y. Duan, S. Cui, X. Song, Y. Liu, J. Zheng, Y. Lin, F. Pan, *Adv. Energy Mater.* 7 (2016) 1601894.
- [12] J. Hu, Y. Jiang, S. Cui, Y. Duan, T. Liu, H. Guo, L. Lin, Y. Lin, J. Zheng, K. Amine, F. Pan, *Adv. Energy Mater.* 6 (2016) 1600856.
- [13] J. Wang, X. Sun, *Energy Environ. Sci.* 8 (2015) 1110–1138.
- [14] J. Zheng, J. Lu, K. Amine, F. Pan, *Nano Energy* 33 (2017) 497–507.
- [15] W. Ren, K. Wang, J. Yang, R. Tan, J. Hu, H. Guo, Y. Duan, J. Zheng, Y. Lin, F. Pan, *J. Power Sources* 331 (2016) 232–239.
- [16] Y. Wang, Y. Wang, E. Hosono, K. Wang, H. Zhou, *Angew. Chem. Int. Ed.* 47 (2008) 7461–7465.
- [17] J.P. Zhou, J.P. Tu, L.J. Cheng, S.J. Shi, Y.Q. Qiao, W.L. Liu, X.L. Wang, C.D. Gu, *J. Electrochem. Soc.* 158 (2011) A1237–A1242.
- [18] J. Liu, G. Yang, X. Zhang, J. Wang, R. Wang, *J. Power Sources* 197 (2012) 253–259.
- [19] T. Kim, R.S. Assary, H. Kim, C.L. Marshall, D.J. Gosztola, L.A. Curtiss, P.C. Stair, *Catal. Today* 205 (2013) 60–66.
- [20] M. Choura, N.M. Belgacem, A. Gandini, *Macromolecules* 29 (1996) 3839–3850.
- [21] H. Wang, L. Liu, R. Wang, D. Zhang, L. Zhu, S. Qiu, Y. Wei, X. Jin, Z. Zhang, *J. Mater. Chem. A* 3 (2015) 8062–8069.
- [22] H. Ünver, Z. Öktem, *Eur. Polym. J.* 49 (2013) 1023–1030.
- [23] W. Zhou, Z.L. Wang, *Scanning Microscopy for Nanotechnology: Techniques and Applications*, Springer, New York, 2007.
- [24] L. Castro, R. Dedryvère, M.E. Khalifi, P.-E. Lippens, J. Bréger, C. Tessier, D. Gonbeau, *J. Phys. Chem. C* 114 (2010) 17995–18000.
- [25] A. Paoletta, G. Bertoni, P. Hovington, Z. Feng, R. Flacau, M. Prato, M. Colombo, S. Marras, L. Manna, S. Turner, G.V. Tendeloo, A. Guerfi, G.P. Demopoulos, K. Zaghbi, *Nano Energy* 16 (2015) 256–267.
- [26] O.V. Yakubovich, O.V. Simonov, N.V. Belov, *Sov. Phys. Dokl.* 22 (1977) 347–348.
- [27] V.A. Streltsov, E.L. Belokoneva, V.G. Tsirelson, N.K. Hansen, *Acta Cryst. B49* (1993) 147–153.
- [28] Y. Zhao, L. Peng, B. Liu, G. Yu, *Nano Lett.* 14 (2014) 2849–2853.
- [29] D. Morgan, A.V. der Ven, G. Ceder, *Electrochem. Solid-State Lett.* 7 (2004) A30–A32.
- [30] X. Qin, J. Wang, J. Xie, F. Li, L. Wen, X. Wang, *Phys. Chem. Chem. Phys.* 14 (2012) 2669–2677.
- [31] R. Dominko, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel, S. Pejovnik, J. Jamnik, *J. Electrochem. Soc.* 152 (2005) A607–A610.
- [32] J. Qian, M. Zhou, Y. Cao, X. Ai, H. Yang, *J. Phys. Chem. C* 114 (2010) 3477–3482.
- [33] J.-i. Ozaki, M. Mitsui, Y. Nishiyama, J.D. Cashion, L.J. Brown, *Chem. Mater.* 10 (1998) 3386–3392.
- [34] T. Vergunst, F. Kapteijn, J.A. Moulijn, *Carbon* 40 (2002) 1891–1902.
- [35] J. Liu, X.-W. Liu, *Adv. Mater.* 24 (2012) 4097–4111.
- [36] M. Winter, R.J. Brodd, *Chem. Rev.* 104 (2004) 4245–4269.
- [37] L.-B. Kong, P. Zhang, M.-C. Liu, H. Liu, Y.-C. Luo, L. Kang, *Electrochim. Acta* 70 (2012) 19–24.
- [38] S.H. Ha, Y.J. Lee, *Chem. Eur. J.* 21 (2015) 2132–2138.
- [39] J. Yang, J. Wang, Y. Tang, D. Wang, B. Xiao, X. Li, R. Li, G. Liang, T.-K. Sham, X. Sun, *J. Mater. Chem. A* 1 (2013) 7306–7311.
- [40] G. Xu, F. Li, Z. Tao, X. Wei, Y. Liu, X. Li, Z. Ren, G. Shen, G. Han, *J. Power Sources* 246 (2014) 696–702.
- [41] Y. Jiang, H. Zhuang, D. Pan, Z. Jiao, X. Que, X. Ling, M. Zhong, Y. Chu, B. Zhao, *J. Appl. Electrochem.* 43 (2013) 611–617.
- [42] Y. Yang, L. Li, G. Ruan, H. Fei, C. Xiang, X. Fan, J.M. Tour, *ACS Nano* 8 (2014) 9622–9628.
- [43] W. Chen, R.B. Rakhi, L. Hu, X. Xie, Y. Cui, H.N. Alshareef, *Nano Lett.* 11 (2011) 5165–5172.
- [44] S.-Y. Yang, K.-H. Chang, H.-W. Tien, Y.-F. Lee, S.-M. Li, Y.-S. Wang, J.-Y. Wang, C.-C. Ma, C.-C. Hu, *J. Mater. Chem.* 21 (2011) 2374–2380.
- [45] J. Zhu, L. Cao, Y. Wu, Y. Gong, Z. Liu, H.E. Hoster, Y. Zhang, S. Zhang, S. Yang, Q. Yan, P.M. Ajayan, R. Vajtai, *Nano Lett.* 13 (2013) 5408–5413.



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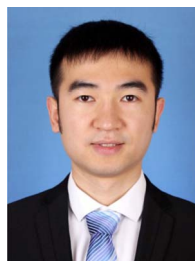
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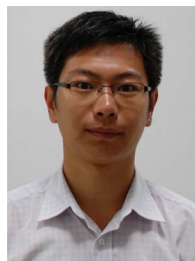
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