TOC Figure: We report on the synthesis, multifaceted characterization, and electrochemical activity of crystalline, chemically pure 200 nm lithium iron phosphate nanowires, mediated by using a seedless, surfactantless U-tube method.

Sentence summary of work: We have developed a novel ambient preparative method for the fabrication of chemically pure, highly crystalline 200 nm lithium iron phosphate nanowires.

**Ambient Synthesis, Characterization, and Electrochemical Activity
of LiFePO₄ Nanomaterials derived from Iron Phosphate Intermediates**

Jonathan M. Patete,^{1,⊥} Megan E. Scofield,^{1,⊥} Vyacheslav Volkov,²

Christopher Koenigsmann,¹ Yiman Zhang,¹ Amy C. Marschilok,^{1,3} Xiaoya Wang,^{1,4}

Jianming Bai,⁵ Jinkyu Han,² Lei Wang,¹ Feng Wang,⁴ Yimei Zhu,² Jason A. Graetz,^{4,#} and

Stanislaus S. Wong^{1,2,*}

Email: stanislaus.wong@stonybrook.edu; sswong@bnl.gov

¹Department of Chemistry, State University of New York at Stony Brook,

Stony Brook, NY 11794-3400

²Condensed Matter Physics and Materials Sciences Department, Building 480,

Brookhaven National Laboratory, Upton, NY 11973

³Department of Materials Science and Engineering,

State University of New York at Stony Brook, Stony Brook, NY 11794-2275

⁴Sustainable Energy Technologies Department, Building 815,

Brookhaven National Laboratory, Upton, NY 11973

⁵National Synchrotron Light Source II, Building 741,

Brookhaven National Laboratory, Upton, NY 11973

[#]Current address: Sensors and Materials Laboratory, HRL Laboratories, LLC,

3011 Malibu Canyon Road, Malibu, CA 90265-4797

[⊥]These authors contributed equally to this work.

*To whom correspondence should be addressed.

Abstract: LiFePO_4 materials have become increasingly popular as a cathode material due to the many benefits they possess including thermal stability, durability, low cost, and long life span. Nevertheless, to broaden the general appeal of this material for practical electrochemical applications, it would be useful to develop a relatively mild, reasonably simple synthesis method of this cathode material. Herein, we describe a generalizable, 2-step methodology of sustainably synthesizing LiFePO_4 by incorporating a template-based, ambient, surfactantless, seedless, U-tube protocol in order to generate size and morphologically tailored, crystalline, phase-pure nanowires. The purity, composition, crystallinity, and intrinsic quality of these wires were systematically assessed using TEM, HRTEM, SEM, XRD, SAED, EDAX, and high-resolution synchrotron XRD. From these techniques, we were able to determine that there is an absence of defects present in our wires, supporting the viability of our synthetic approach. Electrochemical analysis was also employed to assess their electrochemical activity. Although our nanowires do not contain any noticeable impurities, we attribute their less than optimal electrochemical rigor to differences in the chemical bonding between our LiFePO_4 nanowires and their bulk-like counterparts. Specifically, we demonstrate for the first time experimentally that the Fe-O3 chemical bond plays an important role in determining the overall conductivity of the material, an assertion which is further supported by recent first principle calculations. Nonetheless, our ambient, solution-based synthesis technique is capable of generating highly crystalline and phase-pure energy-storage-relevant nanowires that can be tailored so as to fabricate different sized materials of reproducible, reliable morphology.

Keywords: ambient synthesis; template synthesis; cathode material; lithium iron phosphate; nanostructures.

1. Introduction

LiFePO₄ materials have become increasingly popular as a cathode material, due to the many benefits they possess including thermal stability, durability, low cost, and long life span. Nevertheless, to broaden the general appeal of this material for practical electrochemical applications, it would be useful to develop a relatively mild, reasonably simple synthesis method of this cathode material. Since the seminal work performed by Goodenough and co-workers,^{1, 2} olivine LiFePO₄ has attracted the most interest due to its low cost, low toxicity, high thermal stability, and excellent electrochemical properties. Specifically, LiFePO₄ exhibits a high, flat voltage profile, good cycle stability, and a high theoretical specific capacity (~170 mAh/g).^{3, 4} The material also possesses a relatively high lithium intercalation voltage of 3.5 V, relative to lithium metal.^{3, 5} Moreover, the lifetime of a LiFePO₄ battery has been estimated to extend to more than 2,000 cycles, which is key to producing commercial cells with high electrochemical durability and stability. As shown in Equation 1, the discharge of LiFePO₄ involves the intercalation of Li⁺ along with the uptake of an equivalent number of electrons:

The olivine crystal structure of LiFePO₄ possesses a slightly distorted hexagonal-close packed array of oxygen atoms, wherein 50% of the octahedral sites are occupied by Fe²⁺ and 12.5% are occupied by Li⁺.⁶ The FeO₆ octahedra are corner shared and the LiO₆ octahedra are edge shared with the Li⁺ ions, forming a continuous chain down the [010] crystallographic direction.^{6, 7} The olivine phase is uniquely advantageous, because the structural matrix formed by the iron-oxygen octahedral complex in LiFePO₄ does not change significantly upon delithiation.^{8, 9} By contrast, layered structures, such as LiCoO₂, undergo significant structural reconfiguration, when the lithium ion content is decreased below a certain amount.¹⁰ In essence,

the olivine structure is anticipated to be more robust for long-term applications in Li-ion batteries, because the relatively stable structure should promote increased reversibility of the lithiation/de-lithiation process.

Improvements to the lithium ion diffusion rate have also been successfully demonstrated by reducing the dimensions of the LiFePO_4 material to the nanoscale regime. For instance, a reduction in particle size from the bulk to the nanoscale would minimize the path length for Li^+ ion diffusion and facilitate electron transport through the material. It has also been suggested that nanoparticles maintain less mechanical strain, thereby enabling faster lithium ion diffusion into the material upon reversible intercalation, which would allow for improved cycle lifetimes.^{4, 7} Nanostructured LiFePO_4 also possesses increased surface area-to-volume ratios as compared with their bulk analogues, which facilitates electrochemical performance by increasing the interface between the metal oxide and the electrolyte.^{4, 6, 7} As such, there have been extensive reports regarding the preparation and characterization of LiFePO_4 nanostructures.¹¹⁻¹⁹ In particular, one-dimensional (1-D) nanomaterials, such as nanowires, nanotubes, nanorods, and nanoribbons, are expected to play a significant role in advancing LiFePO_4 battery performance, due to their uniquely advantageous structural and electronic properties.^{3, 4, 20-32}

For instance, computational analysis has shown that although there are three potential Li^+ ion diffusion pathways, the preferred pathway is oriented along the *b*-axis (0.55 eV), wherein the Li^+ ions form a continuous chain through the FePO_4 matrix.^{33, 34} Therefore, an increased rate performance can be achieved in a nanowire system by selectively growing the material such that either the *a*- or *c*-axis is oriented along the anisotropic growth direction of the nanowire. Preferential growth along either the *a*- or *c*-axis would also enable the selective orientation of the *b*-axis and the Li^+ ion channels along the radial aspect of the nanowire (*e.g.* parallel to the

diameter of the nanowire), which is confined to the nanoscale. This would effectively minimize the Li^+ ion diffusion length through the material and also promote better performance at high rates of charge and discharge.

Our synthesis method herein forms iron phosphate as the initial product, allowing for direct electrochemical evaluation of the FePO_4 moiety. Prior reports have indicated that success in the electrochemical lithiation of iron phosphate materials can be very sensitive to specific structural properties, depending on the crystallinity and the phase of the FePO_4 material. For example, a prior report yielded a cycle 2 specific discharge capacity of 76 mAh/g for an amorphous $\text{FePO}_4 \cdot 2 \text{H}_2\text{O}$ material, but only 18 mAh/g for a more crystalline hexagonal FePO_4 material prepared at 500°C .³⁵ Similarly, carbon nanotube-amorphous FePO_4 core-shell nanowires realized a specific capacity of 175 mAh/g in lithium batteries³⁶ and 120 mAh/g in sodium batteries,³⁷ respectively, but with ultra-thin amorphous coatings of FePO_4 comprising only a few nm in thickness. A limitation of these prior studies was a lack of discernible X-ray diffraction patterns in each case. By contrast, herein, through directed control of synthesis properties, we can tailor the aspect ratio and size of FePO_4 material, thereby providing for an opportunity to evaluate function with respect to electrochemical lithiation for nanowire FePO_4 material relative to bulk-type granular FePO_4 material.

Recently, there have been a number of successful reports generating 1-D LiFePO_4 nanomaterials primarily through hydrothermal and electrospinning-based techniques.^{3, 4, 21-23} By contrast, template-directed methods represent a conceptually straightforward approach for the synthesis of 1-D nanostructures.³⁸ In general, the template acts as a structural framework for the nucleation and growth of materials within a confined space. The scaffold restricts and spatially directs the formation of the material, such that the product morphology mimics the underlying

size and shape of the originating template. The most popular commercial template materials for the production of 1-D metal oxide nanostructures are porous anodic alumina and polycarbonate membranes.³⁸ In particular, these templates feature a high density array of parallel, straight, cylindrical pores with uniform diameters. This methodology offers a great deal of flexibility, as the diameter of the resulting 1-D material may be tuned by appropriately varying the corresponding pore size of the commercially available templates from whence it is generated. Another advantage of this latter approach is our ability to isolate products with sufficient order for subsequent characterization by X-ray diffraction and related techniques.

Within our group, we have typically prepared nanowires from templates with pore diameters as small as 15 nm and as large as 200 nm.^{25, 29, 31, 32, 39-42} It has also been shown that arrays of 1-D nanomaterials can be obtained by selectively etching the template during the isolation process.^{29, 31, 38} Interestingly, arrays of LiFePO_4 nanorods have been obtained by incorporating an anodic alumina (AAO) template into the hydrothermal reaction scheme. Nanoscale arrays are expected to exhibit large surface areas within a relatively confined space, reduced internal resistance, and high tolerance for volume change.⁴³ By filling the pores of an AAO template with a sol-gel precursor system, Yang et al. were able to produce LiFePO_4 nanotubes after a calcination process at 550°C for 2 hours in a 5%/95% H_2/Ar atmosphere.⁴⁴ Also, in a separate study, nanowires were obtained by immersing a PC template in an aqueous precursor solution, consisting of ferric nitrate, lithium hydroxide, phosphoric acid, ascorbic acid, and ammonium hydroxide for 24 hours.⁴⁵ The as-synthesized electrodes exhibited excellent battery performance, providing for a specific capacity of 165 mAh/g at the 3C discharge rate.

In our synthesis scheme herein, the membranous template is wedged between two half-cells of the so-called “U-tube device”, which is a U-shaped tube. The addition of precursor

solutions to the two half-cells of the device enables the “double-diffusion” of precursors into the porous channels. Subsequently, the precursors meet within the spatial confines of the polycarbonate membrane and react within the confined 1D pore space, thereby forming the desired product. This synthetic technique has been extensively developed by our research group to generate a wide range of materials including but not limited to metals, metal oxides, phosphates, sulfides, and fluorides.^{3, 20, 22, 25, 28, 29, 31, 38, 41, 42, 46-51} The template-assisted U-tube method offers many advantages for the synthesis of 1D nanostructures, since it is a simple and flexible methodology, often operating in aqueous media and yielding high-quality single-crystalline nanomaterials with high yield and with reliable control over composition, size, and shape. Additionally, the method is compatible with a wide range of relatively benign, sustainable precursor systems, and typically involves rather short reaction times under ambient conditions.

In this paper, we explore the synthesis and corresponding characterization of 1-D LiFePO_4 nanostructures, prepared with our relatively mild template-assisted U-tube method. Specifically, we are able to reliably synthesize amorphous ‘precursor’ FePO_4 nanowires by the co-precipitation of Fe^{3+} and PO_4^{3-} ions within the confines of a commercial PC template. The diameter of the amorphous ‘precursor’ FePO_4 nanowires was readily controlled by rationally varying the nominal pore size of the template, and hence, nanowires with average diameters of 185 ± 35 nm and 63 ± 14 nm were prepared from templates, maintaining pore sizes of 200 nm and 50 nm, respectively. In addition, a bulk sample was also produced by reacting the Fe^{3+} and PO_4^{3-} precursors in the absence of the PC template.

Subsequently, we prepared crystalline LiFePO_4 nanowire motifs and bulk particles with the desired olivine structure by utilizing a simple two-step protocol. In the first step, the amorphous FePO_4 is chemically lithiated by reacting the as-prepared powder with LiI. The

reduction and crystallization of the lithiated amorphous product are subsequently accomplished by a heat treatment under a reducing atmosphere. The quality and purity of the nanowire structure can then be characterized during the lithiation and crystallization steps by utilizing a suite of complementary techniques including SEM, TEM, XRD (including synchrotron XRD), EDAX, HRTEM, and SAED. Interestingly, we demonstrated that the desirable 1-D morphology is maintained after crystallization, which results in a nearly single-crystalline product. In addition, the electrochemical performance of the nanowire sample has been investigated to demonstrate its inherent electrochemical activity.

2. Experimental.

2.1. Synthesis of Amorphous Iron Phosphate Nanostructures and Bulk Materials

The morphology-controlled preparation of amorphous FePO_4 was achieved through a precipitation reaction between Fe^{3+} and PO_4^{3-} precursor solutions. Specifically, the iron precursor solution was prepared by dissolving anhydrous ferric chloride, FeCl_3 (EM Science, 98%), in a 0.1 M aqueous solution of HCl (EMD, 38%), such that the concentration of Fe^{3+} was 0.05 M. The excess acid was added to the precursor solution with the goal of enhancing the solubility of the FeCl_3 as well as inhibiting the precipitation of any potential $\text{Fe}(\text{OH})_x$ impurities. The formation of $\text{Fe}(\text{OH})_x$ is undesirable, as it is expected to decompose into iron oxide during the crystallization step. The phosphate precursor was prepared separately by dissolving sodium phosphate dodecahydrate, tribasic (Acros Organics, 98%) in distilled water, with a final concentration of 0.05 M PO_4^{3-} .

Nanowires of amorphous FePO_4 were synthesized by the U-tube method. A polycarbonate track-etched Nucleopore membrane (Whatman Co., U.K.), possessing nominal

pore size diameters of either 50 or 200 nm, was immersed and sonicated in distilled, deionized water, so that the internal channels of the membrane would be wetted, while removing any air bubbles present either in the pores or on the surface. The template was then mounted between the two half-cells of the glass U-tube apparatus. The Fe^{3+} precursor solution was deposited into one side of the reaction vessel, while the PO_4^{3-} solution was simultaneously poured into the other half cell, so that the solution level was consistent on both sides of the template. This careful degree of control allows for the diffusion of precursor into the pores to begin at approximately the same time on both sides of the membrane. The two solutions converge within the porous channels of the membrane, wherein the nucleation and growth of the precipitated FePO_4 are expected to be spatially confined to and maintained within the template material, thereby forming 1-D nanostructures with diameters that are commensurate with the originating pore size of the commercially available membrane. After the reaction has proceeded for 24 hours, the remaining solutions are removed from the arms of the U-tube, and the template, now impregnated with our product, is taken out from the apparatus.

Over the course of the reaction, excess amorphous material typically forms on the outer surface of the membrane, generating a thin layer of material, which was subsequently removed by simply abrading the outer surface of the template. Additionally, the production of orange-colored material, formed within the template, is indicative of some $\text{Fe}(\text{OH})_x$ impurity. These areas of the template were excised with a scissor to ensure the desired purity of our as-prepared product. The amorphous FePO_4 nanowires could then be subsequently isolated by dissolving the polycarbonate template in CH_2Cl_2 (Acros, 99.5%). The amorphous product was later washed in CH_2Cl_2 several times by centrifugation and decantation, and ultimately dispersed in ethanol. Prior to chemical lithiation and crystallization, the nanowires were oven dried at 80°C overnight.

An analogous bulk sample was prepared by mixing an equal volume of the same two precursor solutions in a beaker, without the use of any shape-directing agent. The mixture was stirred under ambient conditions and allowed to react for 1 hour. The particles were isolated and washed with distilled water by centrifugation and decantation. The amorphous bulk FePO_4 was finally dispersed in ethanol for storage, but was similarly dried in an oven at 80°C over night, prior to the chemical lithiation step.

2.2. Conversion of Amorphous FePO_4 to Crystalline Lithium Iron Phosphate

The amorphous iron phosphate precursors, with predetermined size and morphology, are chemically lithiated by a previously established protocol.^{41, 52} Specifically, the as-prepared powders are dispersed into a 1 M solution of lithium iodide (Aldrich, 99.9%) in acetonitrile (EMD, 99.8%), such that the ratio of FePO_4 : Li is 1: 3. The mixture is then handled under an inert nitrogen atmosphere using Schlenk conditions and stirred for 24 hours. The still amorphous products are subsequently washed in acetonitrile by centrifugation and decantation several times, until the washing solution turns clear. Finally, the chemically lithiated products are placed in a porcelain-coated ceramic crucible and annealed in a tube furnace at 550°C for 5 hours in a flowing 5% H_2 / Ar atmosphere. The crystallized products are then dispersed from the crucible into distilled water with sonication. The samples are later washed several times in distilled water, and finally dispersed in ethanol to facilitate the preparation of samples for characterization.

2.3. Characterization Methods

To investigate the size and morphology of our as-prepared samples, the product was dispersed in ethanol, sonicated, drop cast onto a clean silicon wafer, and characterized with a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM), operating at an accelerating voltage of 5 kV. Energy dispersive X-ray spectroscopy (EDAX) was performed on a

Leo 1550 FE-SEM instrument, operating at an accelerating voltage of 20 kV. The same preparation technique was also used to deposit samples onto a lacey carbon-coated copper grid for investigation with a FEI Tecnai12 BioTwinG² transmission electron microscope (TEM), equipped with an AMT XR-60 CCD digital camera system. Low-magnification TEM images were obtained at an accelerating voltage of 80 kV. High-resolution TEM (HRTEM) experiments, the acquisition of selected area electron diffraction (SAED), high angle annular dark field (HAADF) imaging, and the collection of defocused diffraction patterns were carried out with a JEOL 3000F microscope, equipped with a field-emission gun operating at an accelerating voltage of 300 kV.

The crystallinity of the products was determined using HRTEM, powder X-ray diffraction (XRD), as well as high-resolution synchrotron powder XRD. To obtain the powder XRD patterns, a concentrated slurry of the product in ethanol was sonicated and subsequently deposited onto an amorphous glass microscope slide, such that the ethanol would evaporate, thereby forming a homogeneous film of the as-prepared product. Diffraction patterns were initially obtained on a Scintag diffractometer, operating in the Bragg-Bretano configuration using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) with a range, encompassing 10 to 70° at a scanning rate of 0.25° per minute. High-resolution XRD data were acquired using the X14A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. This station is equipped with a position-sensitive silicon strip detector, located at a distance of 1433 mm from the sample and operating at a wavelength of 0.7788 Å. Structural and compositional information were derived by Rietveld refinements of the XRD patterns using the TOPAS 4.1 program.

2.4. Evaluating the Electrochemical Performance of the LiFePO₄ Battery System

The electrochemical performance of the 200 nm diameter LiFePO_4 nanowires was measured on an Arbin BT-2000 test station. Both the bulk-like particles as well as the 200 nm nanowires were electrochemically assessed by investigating their capacity as a function of cycle number. Moreover, the cycling ability of the 200 nm diameter nanowires was specifically evaluated. For electrochemical studies, to prepare the electrode using a ‘recipe’^{53, 54} specifically chosen to take into account of the relatively small amount of nanoscale LiFePO_4 we were able to form ambiently, the LiFePO_4 was mixed with 10 weight % carbon black and 10 weight % Teflon (PTFE) powder. The mixture was ground in a mortar and pestle for approximately 30 min into a wafer. The wafer was then rolled out and placed in a drying oven under vacuum at 80°C for 24 h to ensure removal of hydration from the electrode. A coin cell configuration was used with pure lithium foil as the anode; 1.0 M LiPF_6 dissolved in EC/DMC (1:1) solution was utilized as the electrolyte, in addition to a separator for the cell. Specifically, under an inert argon atmosphere within a glove box environment, the electrodes were placed in the bottom terminal of a 2032 coin cell configuration to which electrolyte was added. An insulating polymer membrane was then placed over the electrode and a gasket was introduced to completely seal the cathode half-cell itself. A piece of lithium metal ribbon was layered on top of the separator, followed by a metal plate collector. Finally, a spring was placed on top of the collector to hold the components in place, and the top terminal of the coin cell was subsequently pressed into the setup to seal the cell. The assembled battery was then cycled between 2.0 V and 3.6 V at room temperature.

Electrodes containing iron phosphate were prepared using commercial and synthesized samples of FePO_4 . The commercial samples were obtained from Aldrich (iron (III) phosphate dihydrate, Fe content of 29%) and prepared by drying at 500°C (with purity determined by thermogravimetric analysis) to remove the water, prior to electrochemical evaluation. The as-

synthesized FePO_4 nanowire samples were prepared by the U-tube method, as described above in Section 2.1.

Electrodes consisting of FePO_4 (85%), carbon black (5%), graphite (5%), and polyvinylidene difluoride (5%) on battery grade aluminum foil were prepared using the standard doctor blade method. Two electrode cells were prepared versus lithium metal electrodes with an electrolyte of 1 M LiPF_6 in the presence of 1:1 ethylene carbonate: dimethylcarbonate. The cells were cycled at 30°C under voltage ranges of 2.0 – 3.6 V and 1.5 - 4.0 V at 0.18 or 0.018 mA/cm^2 rates, as described in the Results and Discussion section below.

3. Results and Discussion

3.1. Mechanism of Morphology-Controlled Synthesis of Amorphous FePO_4

In this work, we utilized the spontaneous precipitation of amorphous FePO_4 from the chemical reaction between aqueous Fe^{3+} ions and PO_4^{3-} anions as a pathway towards LiFePO_4 . Building on previously reported experiments,^{28, 29, 55-57} we selected ferric chloride as the iron source, because this precursor exhibits high solubility in aqueous solutions (74.4 g/100mL at 0°C)⁵⁶ and already maintains the 3+ oxidation state that is desired in the product. We found that the addition of hydrochloric acid assisted in dissolving the ferric chloride and maintaining stability over the course of the reaction. The low pH also helped to prevent the undesired hydrolysis of Fe^{3+} , which would precipitate into $\text{Fe}(\text{OH})_x$ impurities.⁵⁸ Tribasic sodium phosphate was employed as the phosphate anion source.

As an initial proof of concept, equal volumes of the ferric chloride and sodium phosphate precursor solutions were mixed in a beaker, without the addition of any shape-controlling agent, such as a surfactant. As the free Fe^{3+} ions encountered the dissolved PO_4^{3-} ions in the mixed

solution, an insoluble FePO_4 product is formed. The initial precursor interactions subsequently serve as nucleation sites for the continuous growth of amorphous FePO_4 particles in a manner that is limited only by ion availability. Again, the purpose of the template is to spatially direct the growth of this material within the channels of a porous membrane so as not only to control morphology but also diameter, as well. The immediate formation of a cream-colored precipitate was observed, and the solid product was subsequently isolated and collected by washing with distilled water, using centrifugation and decantation. The size and morphology of the as-obtained amorphous particles were determined by SEM, and a representative image is shown in Figure S1A. These bulk-like structures spanning several microns are in fact agglomerates of small spherical nanoparticles measuring about 31 ± 10 nm in diameter. In the absence of any shape-directing agent, it is not surprising that the material forms spherical structures, which are allowed to subsequently aggregate into bulk-sized structures of random shapes and sizes. Analysis by EDAX, shown in Figure S1B, indicates that the amorphous sample contains the target iron phosphate material, exhibiting peaks that are consistent with the presence of iron, phosphorous, and oxygen. Additional peaks, corresponding to Si and C, arise from the Si support substrate and carbon impurities, respectively, presumably present within the SEM chamber.

The synthesis of 1-D nanowires could therefore be achieved by adapting our reaction scheme to the U-tube apparatus. In our setup, the precursor solutions are poured into the two half-cells of the U-tube, which are separated by a nanoporous polycarbonate membrane. As the precursors diffuse into the pores of the template, the pore walls spatially confine the precipitation of amorphous FePO_4 material. If the interaction between the two precursors is stronger than the corresponding interaction between the precursors and the pore wall, then the nucleation process will begin at random sites within the pores themselves and the solid material will grow to fill the

porous network. In the event that the interaction between the precursor materials and the pore walls is stronger, then nucleation is expected to follow a heterogeneous process whereby the solid material begins to precipitate on the surface of the pore wall.

Under these conditions, either nanotubes or nanowires may be obtained by controlling reaction conditions, such as time and precursor concentration.⁵⁹ Therefore, we first examined the effect of the reaction time on product morphology. In order to optimize this reaction parameter, we allowed the precipitation of FePO_4 to proceed in a 200 nm pore size polycarbonate template for 1, 6, 12, and 24 hours, respectively. Within the first hour, solid material began to protrude from the pores of the template into the Na_3PO_4 reaction solution, forming a solid backing layer on the outer surface of the template. This phenomenon has been previously observed for the U-tube synthesis of metals and metal oxides.^{53, 60} This excess material can be removed by physically abrading the outer surfaces of the template prior to nanowire isolation. This step is important for preserving the morphological integrity of the nanowire samples.

The morphology of the amorphous nanowires is shown in the representative SEM images, presented in Figure S2. Allowing the reaction to proceed for just one hour produced fractured nanowires with an average length of about $1.4 \pm 0.5 \mu\text{m}$ seen in Figure S2A. The truncated length of the nanowires, with respect to the $\sim 7 \mu\text{m}$ thickness of the template, and the presence of uneven, jagged surfaces indicate that the reaction did not proceed long enough for the material to fully expand within the pores of the template. Analysis of the products obtained after 6 and 12 hours (Figures S2B and C) revealed nanowire lengths of 1.8 ± 0.5 and $4.9 \pm 1.0 \mu\text{m}$, respectively. Again, these reduced lengths, by comparison with the approximate thickness of the template, suggest that longer reaction times are needed to maximize nanowire aspect ratios. Meanwhile, the observation of truncated nanowires, as opposed to nanotubes, at shorter reaction

times suggests that the reaction undergoes homogeneous nucleation, whereby the interaction between the Fe^{3+} and PO_4^{3-} ions is more favored than the corresponding heterogeneous interaction between these precursor molecules and the adjacent pore walls. After allowing the precipitation to occur for 24 hours (Figure S2D), the fully formed nanowires exhibited smooth, straight surfaces with lengths of $7.4 \pm 1.1 \mu\text{m}$ and diameters of $200 \pm 31 \text{ nm}$.

With suitable precursor concentrations and reaction times, we then investigated the purity of the as-obtained product. In precipitating amorphous FePO_4 nanowires from aqueous solutions of simply FeCl_3 and Na_3PO_4 , with no added HCl , we noticed that the color of the template altered from a translucent white to an opaque orange hue. After isolating the nanowires from the polycarbonate template, they were annealed at 550°C for 10 hours, thereby crystallizing the product for further XRD investigation. The diffraction pattern shown in Figure 1 reveals not only the presence of crystalline FePO_4 but also multiple diffraction peaks consistent with iron oxide impurities. As the Na_3PO_4 precursor dissolves into water and equilibrates, hydroxide ions are formed. The reaction between Fe^{3+} and OH^- produces insoluble $\text{Fe}(\text{OH})_3$, which is thermally converted into iron oxide upon annealing. Although the addition of HCl to the ferric chloride precursor significantly reduces the formation of visible iron oxide impurities in the template, unwanted residues can be further removed by excising portions of the template containing the characteristic orange/brown coloration of iron oxide.⁵³ The two portions of the template were isolated and annealed separately. Diffraction patterns in Figure 1 show that phase-pure FePO_4 was obtained from the “purified” portion of the template (region I), whereas the small fraction of the template with an orange coloration contained many iron oxide impurities (region II).

3.2. Size Controlled Synthesis of Amorphous FePO_4 Nanowires

The ability to selectively control the diameter of our as-obtained nanowires is a significant advantage to utilizing template-assisted techniques. In our case, utilizing commercially available templates with distinctive pore sizes offers a facile route towards synthesizing nanowires possessing various diameters. Specifically, we have exchanged the 200 nm pore size PC template, previously used in the synthetic setup, with a 50 nm pore size PC template to produce nanowires that have a significantly smaller diameter. Although the reduction in pore size may impact the diffusion of the precursors into the pores with adverse effects upon the resulting length and crystallinity of the nanowires,^{31, 39} we found that our initial experimental parameters, such as reaction time and precursor concentration, also produced high-quality amorphous nanowires under the 50 nm pore size conditions.

We were able to determine that our 50 nm diameter nanowires maintain their smooth surfaces and high aspect ratios, an observation which indicates that the precursors were allowed to fully permeate and react within the pores of the template. The diameters of the amorphous FePO₄ nanowires were measured to be 101 ± 12 nm, with lengths of up to several microns (Figure S3A). Deviation between the measured diameters of our as-synthesized nanowires and the nominal reported pore sizes of the polycarbonate template has been observed previously under U-tube conditions.^{39, 42, 53} While the exact reason for the size deviation is not entirely clear, apart from inhomogeneities in the pore size distribution, it is conceivable that the continuous formation and growth of solid material within the pores of the template may exert enough strain on the pore walls, such that the pores themselves expand, resulting in nanowires possessing diameters that are larger than expected.

Elemental analysis of the 50 nm nanowires (Figure S3B) indicates that the sample is composed of iron, phosphorous, and oxygen, with additional peaks associated with carbonaceous

impurities within the SEM chamber as well as the Si support. While this result does not specifically confirm the chemical FePO_4 structure, the presence of only these specific elements suggests that our established reaction pathway limits the number of potential impurities in the finalized product. A representative SEM image of the amorphous FePO_4 nanowires produced from a 200 nm pore size template is shown in Figure S3C. The average diameter of the wires was measured to be 200 ± 31 nm, with lengths of about 7.43 ± 1.10 μm . The EDAX spectrum (Figure S3D) displays similar peaks to the 50 nm nanowire and bulk samples. Consistent with the XRD data seen in Figure 1, our as-synthesized materials are expected to be reasonably pure in terms of both chemical composition and morphology. Overall, these results demonstrate that our synthetic method is fully capable of producing morphologically pure nanowires with a reasonably simple means of experimental control over diameter.

3.3. Conversion of Amorphous FePO_4 to Crystalline LiFePO_4

There are several methods reported in the literature for the chemical conversion of amorphous FePO_4 to the more attractive LiFePO_4 material.^{39, 42, 53, 61} These methods must effectively achieve two specific chemical goals: the reduction of Fe^{3+} to Fe^{2+} and the incorporation of Li^+ ions into the chemical structure. Thus far, the most popular reducing agent has been LiI , since it is cheaper and easier to handle than more powerful lithium-based reducing agents, such as *n*-butyl lithium.⁵⁸ Although LiI may not completely reduce Fe^{3+} to Fe^{2+} under simple wet chemistry conditions, likely due to hindered kinetics, materials synthesized through this technique have shown promising electrochemical performance.^{53, 55, 56, 62} As such, we have adapted the previously reported chemical lithiation of amorphous FePO_4 by LiI in acetonitrile to produce crystalline LiFePO_4 nanomaterials.

In the first step, the amorphous FePO_4 material is chemically converted into amorphous LiFePO_4 .^{55, 58} In particular, as the Fe^{3+} is reduced to Fe^{2+} by the dissolved iodide, lithium ions are simultaneously incorporated into the chemical structure of the material. After isolating the amorphous product, the morphology of the products was investigated by SEM. As shown in Figure S4A, the size and shape of the originating FePO_4 material are essentially maintained and conserved. Specifically, the spherical particles possess diameters of 29 ± 10 nm, while the nanowires produced from 50 nm and 200 nm pore size templates exhibit average diameters of 91 ± 9 and 202 ± 33 nm, respectively. We observed a decrease in the length of the nanowires, with average measurements of 3.5 ± 1 μm and 4.6 ± 1.5 μm for the products obtained from 50 nm and 200 nm pore size templates, respectively. The decrease in nanowire length may be attributed to mechanical fracturing and fragmentation of the more fragile 1-D structure, during the extended period of rigorous stirring. Indeed, a number of small particles and other apparent nanowire fragments can be observed in associated SEM images (Figures S4B and S4C).

Upon crystallization, the size of the spherical particles is significantly increased, due to sintering during the thermal treatment. The uncontrolled growth of the crystallites allows for the formation of asymmetric structures, and the spherical morphology is now less uniform. As shown in Figure 2A, the surfaces of the particles are smooth, with an average diameter of 220 ± 57 nm. For the case of the nanowires produced from 50 nm pore size templates, the change in structure was also quite dramatic, as can be seen in Figure 2B. Although the diameters of the nanowires were conserved at an average of 98 ± 18 nm, the morphologies of the crystalline nanowires were not pristine. They maintained their overall 1-D structure, but the wires exhibit roughened surfaces. On the other hand, the nanowires produced from the 200 nm-sized pores (Figure 2C) possessed an average diameter of 185 ± 35 nm and an average length of 3.0 ± 0.9

μm . However, it is apparent from the SEM image that some particles are also present in the sample. Mechanical strain on the nanowires, induced by the sonication step required to remove the sample from the annealing vessel, may have caused fracturing of the material. As the nanowires break into smaller pieces, a decrease in the average wire length and the observation of particulate debris can be expected. Nonetheless, while this result is not ideal, the vast majority of the sample maintained the desired 1-D morphology.

The composition and crystallinity of the as-obtained products were evaluated by X-ray diffraction (XRD), high-resolution synchrotron XRD, and high resolution TEM. The XRD patterns for all three lithiated samples are displayed in Figure 2D-F, respectively, with all present peaks corresponding to the standard pattern for olivine LiFePO_4 (JCPDS #83-2092). This result initially confirmed to a first approximation that the lithiation and crystallization steps successfully converted the as-synthesized amorphous materials into phase-pure LiFePO_4 , with no additional crystalline impurities.

However, to obtain a clearer idea about the purity of our as-prepared samples, additional high-resolution synchrotron XRD data processed in the context of Rietveld refinements were gathered with the intent of more rigorously accounting for the presence of any remnant impurities and possible anti-site disorder for Fe and Li ions in the structure. The data are summarized in Figure 3. Our as-prepared bulk-like particles were determined to be $a = 10.326(0)$ Å, $b = 6.004(6)$ Å, and $c = 4.690(0)$ Å with a cell volume of $290.800(6)$ Å³. Moreover, the bulk-like sample appeared to co-exist with an approximately 30% Li_3PO_4 impurity, as indicated by the green asterisks in Figure 3. The reliability factor for this fit was noted to be an acceptable value of $R_{\text{wp}} = 3.3\%$.

The collective crystallographic information obtained, including the cell parameters, volumes, and anti-site defect concentrations, as determined from Rietveld refinement analysis, is shown in Table 1. The formation of this impurity likely can be attributed to the presence of an excess quantity of Li ions in the material. However, we should note that the as-prepared Li_3PO_4 was effectively phase segregated from LiFePO_4 itself, which exists as the predominant, majority phase and is essentially stoichiometric in nature.^{56, 62} The implications of the formation of Li_3PO_4 on the resulting electrochemical behavior of the bulk material will be discussed later.

By contrast, we noted that the LiFePO_4 nanowires prepared using the 200 nm template sample do not evince any such impurity, as determined by the absence of any Li_3PO_4 peaks in the high resolution XRD as well as the lack of any other crystalline impurities associated with LiFePO_4 . The as-obtained lattice constants were not significantly different as compared with those of bulk-like powders. These were computed to $a = 10.327(9) \text{ \AA}$, $b = 6.005(8) \text{ \AA}$, and $c = 4.692(6) \text{ \AA}$ with a corresponding cell volume of $291.069(3) \text{ \AA}^3$. The reliability factor for this fit was determined to be an acceptable value of $R_{\text{wp}} = 3.3\%$. Moreover, our nanowires possessed negligible (within the limits of error of the measurement) anti-site disorder for both Li and Fe ions, thereby suggesting that as-obtained LiFePO_4 nanowires were high quality in terms of chemical purity. Detailed structural parameters associated with both LiFePO_4 bulk-like particles and the corresponding nanowires are shown in Table 1.

The HRTEM images presented in Figures 4, 5, and 6 validate the XRD results. Specifically, a low magnification TEM image of a typical bulk-like particle is shown in Figure 4A. Further analysis of the high-resolution TEM (HRTEM) image in Figure 4B reveals the perfect long-range crystal ordering with lattice fringes observed for the $[-12-1]$ zone ascribed to the particle. Moreover, direct measurement of the expected lattice spacings, i.e. $d(111) = 0.348$

nm and $d(-101) = 0.425$ nm, along with the optical Fourier Transform pattern shown in the inset also is consistent with the appropriate (hkl) reflections expected for the $[-12-1]$ zone associated with the bulk-like LiFePO_4 particles. The Fourier diffraction pattern (DP) shown in the inset of Figure 4B is in good numerical agreement with the calibrated DP in Figure 4C, recorded from a larger area of the nanoparticle, as shown in Figure 4A. The diffraction spots can be assigned to the (111), (101), as well as (210) planes.

Representative nanowires produced from a 50 nm pore size template are highlighted in the dark field TEM image (Figure 5C). The surface of the wire appears to be roughened and fractured, as it exhibits low angle grain boundaries, which is consistent with our observations from SEM. The high magnification image in Figure 5A indicates that the wire is highly crystalline. Its corresponding SAED pattern is shown in Figure 5B. The SAED pattern in 5B exhibits a $[01-1]$ zone pattern, which can be attributed to LiFePO_4 . Diffraction spots have been indexed to the (200) and (011) planes in this specific zone. It can be seen from these data that the 50 nm NWs grow anisotropically along the a -axis, although low angle grain boundaries can be seen due to the small diameter of the NWs.

In Figure S5, additional HRTEM characterization was used to further corroborate the assertion that we had synthesized single crystalline 50 nm NWs with the appropriate growth directions. Specifically, in Figure S5A, a dark field image of 2 LFP NWs can be seen. This result demonstrates internal consistency in the crystallinity within the NW sample, as the individual crystals lying in the correct Bragg condition are highlighted. In the bottom righthand part of Figure S5A, a high magnification image of the boxed area can be observed, further demonstrating the presence of low angle grain boundaries within our 50 nm NWs. In Figure S5B, a SAED pattern is included for the area, delineated in Figure S5A. This SAED pattern

suggests that some of our 50 nm NWs are actually polycrystalline. In the bottom righthand portion of the image, there is a special calibrated ring pattern obtained by the rotational averaging of all diffraction spots observed for that localized region. The diffraction rings obtained by this procedure match well with the expected reference fringes (shown with bright bars in the inset) for appropriate (*hkl*) reflection positions of crystalline LiFePO₄. Herein, even though there are a lot of data within this pattern, for the sake of clarity, only seven strong rings are marked with the corresponding referencing bars.

HRTEM images corresponding to the 200 nm LFP NWs can be observed in Figure 6. Figure 6C focuses on a single crystalline 200 nm NW. A higher magnification image can be noted in Figure 6B, corresponding to the Fourier transform in Figure 6A, identified as the [011] zone of LiFePO₄. The NW edge (Figure 6C) follows the *a*-axis direction, associated with the (200) spot direction in the FT pattern. Figure 6E is a SAED pattern that can be assigned to the [011] zone for LiFePO₄, thereby further corroborating the FT shown in Figure 6A. The appropriate selected area image of the 200 nm NWs for which the SAED pattern was obtained is described in Figure 6D, which provides for additional evidence, supporting the idea of NW growth parallel to the *a*-axis. Figure 6F reveals the defocused diffraction pattern for the region shown in Figure 6D, which implies a direct relationship between the NW orientation (in the central BF image spot) and the *a*-lattice direction, as defined by the (200) reflection.

Additional HRTEM images are shown in Figure S6. Specifically, Figure S6A represents a low magnification TEM image of a typical 200 nm nanowire. The nanowire appears to possess a highly textured surface with regions, featuring uneven color contrast and brightness, thereby implying that the electron diffraction signal fluctuates to some extent throughout the material, likely because of slight spatial variations in thickness and surface roughness within its length.

This observation may be indicative of a slightly porous structure. The measured d -spacing (Figure S6B) of 0.369 nm corresponds to the (0-11) plane aligned parallel with the [100] vector, i.e. the a -axis, associated with the LiFePO_4 crystal. Such an observation agrees well with the localized diffraction pattern (DP) orientation, seen in Figure S6C.

By comparing the DP with a theoretically calculated pattern (as shown by the overlaid dark square), we have been able to conclude that the 200 nm nanowire, as shown in Figure S6A, likely has a preferred growth direction associated with the a -axis of the crystalline LiFePO_4 structure. Specifically, all of the sharp and uniform diffraction spots in Figure S6C can be attributed to the [011] zone pattern for a LiFePO_4 crystal, implying that the nanowire possesses a long range crystalline ordering with a preferred anisotropic growth direction along the a -axis. Moreover, the measured spacings of $d(011) = 0.373$ nm and $d(200) = 0.514$ nm in Figure S6C can be ascribed to the reference (hkl) reflections of LiFePO_4 single crystals (JCPDS #83-2092) and, in particular, for a large a -lattice parameter of $2*d(200) = 1.3$ nm. Figure S6D represents an additional SAED pattern taken from the low-index [010] zone of LiFePO_4 . These spots have been indexed to the (200), (010), and (002) reflections, respectively, of LiFePO_4 , thereby further supporting the idea of a -axis growth.

Moreover, we note that both of the preferred growth directions for the 50 nm and 200 nm nanowires, along the a -axis, result in an interesting structural consequence. That is, in both cases, one of the lattice normal vectors, i.e. (a , b) for the nanowire surfaces, possesses a b direction for the (010) lattice planes, corresponding to the preferred Li ion transport pathway.^{63, 64} Overall, our observations from HRTEM and XRD data suggest that our as-obtained LiFePO_4 nanowires are likely to be both single-crystalline and phase-pure.

3.4. Electrochemical Performance of 200 nm LiFePO_4 Nanowires

Crystalline 200 nm diameter LiFePO_4 nanowires were prepared as an electrode for a coin cell battery setup. The incorporation of carbon particles in the electrode has been shown to vastly reduce resistance by assisting in the transport of electrons produced by the LiFePO_4 cathode material to the current collector.^{63, 65-67} This step is critical to overcoming the low conductivity inherent to LiFePO_4 , which would typically result in a dramatically reduced specific capacity at high rates, relative to the theoretical value, under practical coin cell conditions.

Constant current charge/discharge experiments were run at room temperature from 2 to 3.6 V at a rate of C/10, and the corresponding data can be observed in Figure 7A. The associated charge and discharge profiles of the 200 nm diameter nanowires are presented in Figure S7.

These experiments were run in order to demonstrate that our 200 nm-diameter NWs were electrochemically active as compared with bulk as a comparative standard. The bulk material showed average electrochemical properties, exhibiting a decrease in specific capacity over the course of 10 cycles, which is indicative of average rate performance and reversibility.

While it is reasonable to conclude from these data that our chemical lithiation procedure appears not to be as efficient as the corresponding electrochemical lithiation protocol, more experiments must be conducted to confirm this result. The value of the specific capacity after 10 cycles was measured to be 111.5 mAh/g, revealing that the bulk-like particles likely achieved 66% of the theoretical value (i.e. 170 mAh/g). By comparison, the average specific capacity (i.e. 26.4 mAh/g) of our as-synthesized 200 nm NWs, as determined by the relatively small amount of LiFePO_4 active material present in the electrode, is significantly below that of the theoretical value (i.e. 170 mAh/g), which may be due to poor electronic conductivity and sheer lack of active material. Moreover, our electrode preparation will need to be optimized, but the main goal

of this report was to successfully demonstrate our ability to synthesize chemically pure, crystalline LiFePO_4 nanomaterials that are electrochemically active.

To put our results into context, we should note that as compared with alternative lithium ion battery cathode materials, our NWs are not as high performing. Other groups have generated alternatives to conventional LFP materials including but not limited to Cr-V-O nanoparticles⁶⁸ and V_2O_5 hierarchical octahedrons.⁶⁹ Specifically, Sheng et al. were able to synthesize Cr-V-O nanoparticles that achieved a capacity of 260 mAh/g at 100 mA/g with greater than an 80% capacity retention capability measured after 200 cycles, whereas An et al. demonstrated that 3D porous V_2O_5 octahedron cathodes could exhibit a capacity of 96 mAh/g retained with little capacity loss after 500 cycles. Moreover, Li-based cathode materials represent particularly promising classes of structures.^{70, 71} In particular, a novel spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$ material was found to give rise to a capacity of as much as 115 mAh/g measured in the 300th cycle at 5 C with a 91.3% capacity retention capability observed over 300 cycles. A related structure, namely a unique layered $\text{Li}_{1.2}\text{Ni}_{0.16}\text{Co}_{0.08}\text{Mn}_{0.56}\text{O}_2$ cathode material possessing a hollow spherical motif synthesized using a molten salt method in a NaCl flux, was tested electrochemically at varying temperatures; a high reversible capacity of 250 mAh/g for example was measured at a temperature of 60°C at 2 C with no significant capacity fade. Although all of these groups have moved beyond conventional LFP in order to synthesize innovative and electrochemically active materials, the goal of our paper is explicitly different. That is, we aim herein to gain unique and valuable insights into the exact correlation between the overall structure and the resulting electrochemical properties of lithium iron phosphate.

Hence, the charge and discharge curves in Figure S7 are promising in that they show that our nanowires are at least responsive electrochemically. The plateau seen in this Figure suggests

that the potential of 200 nm-diameter nanowires, during the charging process for the oxidation of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, is 3.4 V vs. Li/Li^+ . In fact, the higher than anticipated voltage observed for the 200 nm nanowires (i.e. 3.5 V) can be ascribed to the impedance present within the cell. This increased resistance can be attributed to a number of reasons, including the nature of the electrolyte as well as morphological differences in the samples analyzed (i.e. particles versus wires). In our case, we can potentially attribute the observed increase in impedance to both morphology and poor contact between the active material and the current collector, as the other parameters during coin cell assembly were effectively maintained constant throughout for all of the cells analyzed including those for bulk.

Of significance for the interpretation of our electrochemical data, we were unable to conclusively demonstrate the formation of Li-Fe anti-site pair defects in which a Li ion at the M1 site is exchanged with a Fe ion at the M2 site.^{67, 72, 73} This impurity is actually intrinsic⁵⁴ to LiFePO_4 and easily forms in olivine structures. Yet, this defect can potentially influence electrochemical performance, because it has been postulated that the presence of Fe ions on lithium sites can block the long-range 1D migration of the corresponding Li channel⁶⁵ (in particular, the (010) channel).⁶³ For instance, hydrothermally grown LiFePO_4 nanostructures synthesized by Yang and coworkers possessed about 3-5% of Fe ions, occupying Li sites, as determined by using Rietveld analysis.⁷² During the intercalation/de-intercalation process, these Fe ions localized in the M1 sites likely inhibited Li ion transport and concomitantly led to not only a noteworthy decrease in the Li ion diffusion coefficient but also a reduction in the availability of active volume, all of which would have diminished the overall potential capacity of this material. Hence, typically, these materials are heated above 450°C to remove this deleterious defect.^{54, 63} Interestingly, our material evinced no such impurities, as indicated by our

high resolution synchrotron XRD data, thereby supporting the notion that the presence of these impurities could not be the reason for our poor conductivity.

Furthermore, the observed variation in electrochemical behavior may be ascribed to the differences in size and morphology between the samples herein, which directly impact both electron and lithium ion transport.^{64, 74} To analyze and track the morphological evolution of the electrode before and after cycling, scanning electron microscopy was specifically utilized to document these changes. More specifically, the electrode was prepared and imaged prior to assembling the coin cell as well as after 1 cycle, in order to probe the effect of Li intercalation/de-intercalation on the electrode.

Images of individual electrodes containing bulk-like particles (Figure 7B and C) and the 200 nm diameter nanowires (Figure 7D and E) have been analyzed. Specifically, the electrode, containing 200 nm-diameter LiFePO_4 nanowires, shows reasonable surface uniformity, both pre- and post-cycling; it is not as if the Li intercalation/de-intercalation process caused the electrode to fracture and crack after electrochemical cycling. However, there are a few issues that are worth noting. *First*, there is a qualitative difference in physical appearance and packing between the 200 nm LiFePO_4 nanowires isolated immediately after synthesis (Figure 4B) and when physically incorporated into the electrode (Figure 7D). This observation may be as a result of the technique employed to synthesize the electrode, which tends to require a fair amount of mechanical, potentially destructive grinding in order to compact the mixture. *Second*, it is apparent that an inhomogeneous distribution and packing of the cathode material exists throughout the electrode, which may also be detrimental to the overall performance of the resulting cell. As stated previously, the conductivity of the material is directly related to both its size and shape. Hence, the slight but noticeable deterioration in morphology and packing, which

presumably affected electrode porosity and which is apparent from Figures 7D and 7E, before and after cycling, respectively, suggests that this factor had a negative effect upon the wires' overall electrochemical performance.

Moreover, without even considering the characteristics of the active material, the electrochemical measurement technique employed possesses a number of limitations of its own. That is, the specific methodology implemented to put together the coin cell assembly in these studies ultimately decreases the volume energy density of the LiFePO_4 used by 25% (i.e. 10% carbon black and 5% PTFE present in the cathode),¹⁴ thereby fundamentally affecting performance. From prior literature, it has been suggested that the electrode fabrication process needs to be specifically and carefully tailored to the type of LiFePO_4 material used (i.e. through optimization of the adhesion and miscibility characteristics of the LiFePO_4 relative to the other cell components, for instance),³ in order to inadvertently avoid lowering the volumetric and gravimetric energy density and hence the overall efficiency of the resulting coin cell configuration.^{6, 72} Herein our protocols did not necessarily lead to the formation of a homogeneous, uniform electrode, which would represent a minimum and necessary prerequisite for observing reasonable Li intercalation/de-intercalation. However, we reiterate that the reason for choosing this method of electrode synthesis was to use viable, reproducible, and relatively simple techniques, considering the relatively small amounts of LiFePO_4 nanowires that we had ambiently formed. Evidently, we learned that the quantity of active LiFePO_4 material matters. Hence, future work will rely on working with an optimized electrode set-up using larger quantities of electrochemically active single-crystalline LiFePO_4 nanostructures, tailored in terms of size, chemical composition, and morphology.

3.5. Electrochemical Lithiation of FePO_4 Nanowires

In order to assess the opportunity for electrochemical lithiation of the iron phosphate materials, commercial (bulk-like) and synthesized (nanowire) samples of FePO_4 were tested in electrochemical cells versus lithium metal electrodes. The first test of the FePO_4 was designed to be consistent with the test of the chemically lithiated material. Cells containing bulk-like FePO_4 material were cycled under a voltage range of 2.0 – 3.6 V at a 0.18 mA/cm^2 rate for ten cycles (Figure S8). After a lower capacity for the initial cycle, the discharge and charge capacities were measured to be $\sim 4 \text{ mAh/g}$ for cycles 2 - 10.

It was proposed that a lower cycling rate may improve the lithiation of the FePO_4 material, and that a nanowire structural motif would impact the delivered capacity of the FePO_4 material. Therefore, a second test was undertaken in terms of cycling both bulk-like and nanowire FePO_4 materials under a voltage range of 2.0 – 3.6 V at 0.018 mA/cm^2 rate for three cycles (Figure S9). For the bulk-like material, the discharge capacities were 16 and 18 mAh/g on cycles 1 and 2, respectively, with no discharge capacity observed on the third cycle (Figure S10A). Lithiation of the bulk-like material remained limited, even at this lower rate, with low charge capacities measured of 5 and 8 mAh/g on cycles 2 and 3. For the nanowire material, the discharge capacities were 0.17 and 0.17 mAh/g on cycles 1 and 2, with very little discharge capacity observed for the third cycle (Figure S10B). Lithiation of the bulk-like material was very limited even at this lower rate, with capacities $< 0.02 \text{ mAh/g}$ on all three cycles. The ten-fold lower capacity for the nanowire FePO_4 material relative to the bulk-like FePO_4 material under this test was similar to the six-fold lower capacity for the nanowire LiFePO_4 material, relative to that of the bulk-like LiFePO_4 material, as shown in Figure 7 above.

It was further hypothesized that a modification of the voltage window for the discharge-charge rate may improve the lithiation of the FePO_4 material. Therefore, a third test was

undertaken in terms of cycling both bulk-like and nanowire FePO_4 materials under a voltage range of 1.5 – 4.0 V at an 0.018 mA/cm^2 rate for ten cycles (Figure 8). For the bulk-like material, the cycle 1 discharge capacity was $\sim 70 \text{ mAh/g}$ for Cycle 1 and remained effectively constant at $\sim 30 \text{ mAh/g}$ for cycles 2- 10 (Figure 9A). The charge capacity remained at 30 – 40 mAh/g for all cycles, showing reasonable cycling efficiency but low capacity for the bulk-like material. For the nanowire material, the discharge capacities were $< 4 \text{ mAh/g}$ on all cycles, with very low charge capacities of $< 0.3 \text{ mAh/g}$ on all cycles (Figure 9B).

Under all electrochemical lithiation conditions tested, the nanowire FePO_4 material showed less capability for lithiation relative to the bulk-like FePO_4 material. A recent first-principles study of the chemical bonding and conduction behavior of LiFePO_4 using maximally-localized Wannier functions⁷⁵ lends additional insight into our empirical observations. Results of the calculations showed that the chemical bonding of Fe–O3 has an important impact upon the low-temperature conductivity of LiFePO_4 , as small polaron hopping is mainly mediated by Fe–O3 chemical bonds. Notably, our Rietveld analysis of the bulk-like and nanowire LiFePO_4 materials (Table 1) showed similar Fe1, O1, and O2 positions, but different O3 positions. Thus, we propose that the Fe-O3 geometry in our nanowire materials may be less favorable than that in the bulk-like materials, providing (to the best of our knowledge) the first empirical evidence with which to support this theory.

4. Conclusions

The strength of our contribution lies not only in our ability to generate lithium iron phosphate nanowires using mild reaction conditions with demonstrably high quality, crystallinity, and purity but also in our deliberate approach in including a set of results emanating

from the use of a sophisticated toolkit of complementary structural characterization (including synchrotron-based) techniques that have rarely been applied to this material. Specifically, in this study, we have described our success in the diameter and shape-controlled synthesis of 1-D LiFePO_4 nanostructures under sustainable conditions.

Building upon our previous work, we have utilized an ambient, seedless, surfactantless, wet-solution-based U-tube method to generate 1-D amorphous FePO_4 precursors through the precipitation of FeCl_3 and Na_3PO_4 . The precursor chemistry and reaction time were optimized to yield chemically pure, high-quality amorphous FePO_4 nanowires, with spatial control over the diameters of the nanowires achieved through appropriately varying the pore size channel of the commercially available template. We have successfully converted our amorphous starting precursor material into the electrochemically active LiFePO_4 through chemical lithiation, while maintaining the specified size and 1-D morphology.

Structural characterization of the as-prepared 50 nm and 200 nm diameter crystalline LiFePO_4 material showed that the one-dimensional samples grew anisotropically along the a -axis direction, thereby exposing the b -direction. Specifically, a suite of high-resolution TEM techniques, including HAADF, SAED, and defocused diffraction methods, has confirmed the presence of enhanced crystallinity of both the 50 nm and 200 nm nanowires, taken from various regions. Moreover, our as-prepared 200 nm NWs were found to be not only phase pure but also single-crystalline by various additional structural characterization methods, including synchrotron X-ray diffraction.

The size and morphology of these as-synthesized nanowires have had an impact upon their electrochemical efficiency, when employed in a coin cell setup. However, our technique was not necessarily optimal because of low sample quantity considerations, and the mechanical

grinding may have fundamentally altered the morphology of our lithium iron phosphate materials when incorporated as a part of a functional electrode. Moreover, the relatively poor electronic conductivity, packing inhomogeneity, and poor contact with the current collector may also have affected the electrochemical performance of our 200 nm-diameter nanowires. Nevertheless, based on the collected charge/discharge curves, we were able to successfully demonstrate that, at a minimum, our LiFePO_4 material is electrochemically active. The electrochemical data for the chemically and electrochemically lithiated FePO_4 materials showed consistent trends for the bulk-like and nanowire material, where the bulk-like materials exhibited higher capacities in each case. The capacity trends may relate to the inherent Fe-O3 geometry for these materials, as recent calculations have shown that the chemical bonding of Fe-O3 has an important impact upon the low-temperature conductivity of LiFePO_4 .⁷⁵

Despite their advantageous structural and electrochemical properties, pure LiFePO_4 has not been directly applied as the cathode material in commercial batteries, because it exhibits poor electronic conductivity ($10^{-9} \text{ S cm}^{-1}$ at room temperature) and slow Li ion diffusion through the material, thereby preventing the realization of its full theoretical capacity at high charge and discharge rates.^{54, 76, 77} As a positive step towards understanding and potentially improving upon Li ion diffusion at a structural level, we have demonstrated that our nanowires can be synthetically grown along the a axis in terms of a viable growth direction.

Regarding possibilities for future work, apart from electrode optimization, in terms of additional ways for improving the conductivity of LiFePO_4 , one strategy will be to coat the surface of the material with a conductive carbon layer. This method has been widely used, as it helps to improve the specific capacity, cycling life, and rate performance of LiFePO_4 cathode material. In one report, coating LiFePO_4 particles with just 1 weight % carbon achieved a high

discharge capacity of 160 mAh/g at the 1C rate.⁷⁸ The carbon coating may also protect the metal oxide surface, thereby resisting chemical corrosion.⁷ Therefore, coating these nanowires may be advantageous for correspondingly improving capacity. Lastly, doping the Li and Fe sites with other metal ions, such as Mg, Zr, or Nb for lithium and Cr, Mn, Co, or Ni for iron, respectively, can enhance the materials' intrinsic conductivity.^{33, 63} These ideas represent a few plausible options to further enhance the performance of our lithium iron phosphate nanowires.

Electronic Supplementary Material: Supplementary material (including SEM images, diffraction patterns, and electrochemical profiles) is available in the online version of this article.

Acknowledgements

We thank Professor M.S. Whittingham (SUNY Binghamton) for helpful discussions. A Stony Brook University-Brookhaven National Laboratory seed grant involving SW and JG was used to initiate initial experiments. Synthesis research of the various samples (including support for JMP, MES, CK, JH, LW, and SSW) and HRTEM characterization (including support for SV and YZ) were otherwise funded by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division at Brookhaven National Laboratory, which is supported by the U.S. Department of Energy under Contract No. DE-AC02-98CH10886. The studies involving electrochemical lithiation were supported as part of the Center for Mesoscale Transport Properties, an Energy Frontier Research Center supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under award #DE-SC0012673.

Figure Captions

Figure 1. XRD patterns of the as-crystallized FePO_4 material (red), as well as of samples isolated from specific regions I (no Fe_2O_3 impurities) and II (with Fe_2O_3 impurities) of the originating PC template (blue and green curves, respectively).

Figure 2. Representative SEM images of crystallized chemically lithiated particles (A), nanowires produced from 50 nm pore sized PC templates (B), and nanowires produced from 200 nm pore sized PC templates (C). Corresponding X-ray diffraction patterns of as-prepared bulk and nanomaterials (in red), along with their corresponding crystallographic database standards (in black), are displayed in (D), (E), and (F), respectively.

Figure 3. High-resolution synchrotron X-ray diffraction patterns (in black) and corresponding Rietveld refinement patterns (red) of (A) bulk-like LiFePO_4 particles (green asterisks highlight the presence of a Li_3PO_4 impurity) and of (B) 200 nm LiFePO_4 nanowires produced using the PC template with the corresponding database standards shown below (in pink) for each material. Differences between the observed and calculated intensities are plotted in blue.

Table 1. Structural parameters, determined from the high-resolution synchrotron X-ray data analysis for both the 200 nm LiFePO_4 nanowire (top) and bulk-like LiFePO_4 (bottom) samples.

Figure 4. A low magnification TEM image of (A) crystalline LiFePO_4 particles. (B) A magnified HRTEM image is recorded along the $[-12-1]$ zone direction from the optical Fourier pattern (inset) of LiFePO_4 ($Pnma$) taken from this image. (C) An experimental diffraction pattern (DP) (magnified 1.4x), representing the $[-12-1]$ zone pattern for the 200 nm LiFePO_4 nanoparticles, highlighted in the HRTEM image (B).

Figure 5. HRTEM characterization for the 50 nm LiFePO_4 NWs. (A) A magnified HRTEM image of a 50 nm NW tip taken from (C). (B) A single area electron diffraction pattern taken

from (A), corresponding to the [01-1] zone of LiFePO_4 . (C) A dark field image of two 50 nm LFP NWs.

Figure 6. HRTEM characterization for the 200 nm LiFePO_4 NWs. (A) Fourier transform of an magnified image insert (B), identified as the [011] zone of LiFePO_4 , (B) A high magnification image of the 200 nm LFP NW used for the FT. (C) The NW edge follows the a -axis direction presented by the (200) spot direction in the FT pattern. (D) A high magnification image used for acquiring (E) a selected area electron diffraction image, corresponding to the [011] zone of LiFePO_4 (200 nm), as well as (F) a defocused diffraction pattern, highlighting the NW orientation (in the central BF image spot), which is almost parallel to the a -lattice direction, as defined by the (200) reflection.

Figure 7. (A) Capacity vs. cycle number for both the bulk-like particles as well as 200 nm diameter lithium iron phosphate nanowires. SEM images have been taken both before (B, D) and after (C, E) electrochemical cycling. (B) and (C) are connected with the bulk-like LiFePO_4 particles, whereas (D) and (E) are associated with the 200 nm-diameter LiFePO_4 nanowire system, both coupled with carbon black and PTFE.

Figure 8. Electrochemical cycling of Li/FePO_4 cells under a $0.018 \text{ mA}/\text{cm}^2$ rate and in a 1.5 – 4.0 V potential window. Voltage versus specific capacity for (A) bulk-like (black) FePO_4 material and (B) nanowires (red) of FePO_4 material.

Figure 9. Electrochemical cycling of Li/FePO_4 cells under $0.018 \text{ mA}/\text{cm}^2$ rate and 1.5 – 4.0 V window. Specific capacity versus cycle number for (A) bulk-like (black) FePO_4 material and (B) nanowires (red) of FePO_4 material.

References

1. Padhi, A. K.; Nanjundaswamy, K. S.; Masquelier, C.; Okada, S.; Goodenough, J. B. Effect of Structure on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ Redox Couple in Iron Phosphates. *Journal of the Electrochemical Society* **1997**, 144, (5), 1609-1613.
2. Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. Phospho-olivines as Positive Electrode Materials for Rechargeable Lithium Batteries. *Journal of the Electrochemical Society* **1997**, 144, (4), 1188-1194.
3. Sides, C. R.; Croce, F.; Young, V. Y.; Martin, C. R.; Scrosati, B. A High-Rate, Nanocomposite LiFePO_4 /Carbon Cathode. *Electrochemical and Solid-State Letters* **2005**, 8, (9), A484-A487.
4. Huang, X.; Yan, S.; Zhao, H.; Zhang, L.; Guo, R.; Chang, C.; Kong, X.; Han, H. Electrochemical performance of LiFePO_4 nanorods obtained from hydrothermal process. *Materials Characterization* **2010**, 61, (7), 720-725.
5. Chung, S.-Y.; Bloking, J. T.; Chiang, Y.-M. Electronically conductive phospho-olivines as lithium storage electrodes. *Nature Materials* **2002**, 1, (2), 123-128.
6. Xu, B.; Qian, D.; Wang, Z.; Meng, Y. S. Recent progress in cathode materials research for advanced lithium ion batteries. *Materials Science and Engineering: R: Reports* **2012**, 73, (5-6), 51-65.
7. Ellis, B.; Kan, W. H.; Makahnouk, W. R. M.; Nazar, L. F. Synthesis of nanocrystals and morphology control of hydrothermally prepared LiFePO_4 . *Journal of Materials Chemistry* **2007**, 17, (30), 3248-3254.
8. Whittingham, M. S. Lithium Batteries and Cathode Materials. *Chemical Reviews* **2004**, 104, (10), 4271-4302.
9. Yi, T.-F.; Li, X.-Y.; Liu, H.; Shu, J.; Zhu, Y.-R.; Zhu, R.-S. Recent developments in the doping and surface modification of LiFePO_4 as cathode material for power lithium ion battery. *Ionics* **2012**, 18, (6), 529-539.
10. Lee, K. T.; Jeong, S.; Cho, J. Roles of Surface Chemistry on Safety and Electrochemistry in Lithium Ion Batteries. *Accounts of Chemical Research* **2013**, 46, (5), 1161-1170.
11. Lee, M.-H.; Kim, T.-H.; Kim, Y. S.; Song, H.-K. Precipitation Revisited: Shape Control of LiFePO_4 Nanoparticles by Combinatorial Precipitation. *The Journal of Physical Chemistry C* **2011**, 115, (25), 12255-12259.
12. Zheng, J.-c.; Li, X.-h.; Wang, Z.-x.; Guo, H.-j.; Zhou, S.-y. LiFePO_4 with enhanced performance synthesized by a novel synthetic route. *Journal of Power Sources* **2008**, 184, (2), 574-577.
13. Franger, S.; Le Cras, F.; Bourbon, C.; Rouault, H. Comparison between different LiFePO_4 synthesis routes and their influence on its physico-chemical properties. *Journal of Power Sources* **2003**, 119-121, (0), 252-257.
14. Arnold, G.; Garche, J.; Hemmer, R.; Ströbele, S.; Vogler, C.; Wohlfahrt-Mehrens, M. Fine-particle lithium iron phosphate LiFePO_4 synthesized by a new low-cost aqueous precipitation technique. *Journal of Power Sources* **2003**, 119-121, (0), 247-251.
15. Prosini, P. P.; Carewska, M.; Scaccia, S.; Wisniewski, P.; Passerini, S.; Pasquali, M. A New Synthetic Route for Preparing LiFePO_4 with Enhanced Electrochemical Performance. *Journal of the Electrochemical Society* **2002**, 149, (7), A886-A890.

16. Kim, J.-K.; Choi, J.-W.; Chauhan, G. S.; Ahn, J.-H.; Hwang, G.-C.; Choi, J.-B.; Ahn, H.-J. Enhancement of electrochemical performance of lithium iron phosphate by controlled sol-gel synthesis. *Electrochimica Acta* **2008**, 53, (28), 8258-8264.
17. Hwang, B.-J.; Hsu, K.-F.; Hu, S.-K.; Cheng, M.-Y.; Chou, T.-C.; Tsay, S.-Y.; Santhanam, R. Template-free reverse micelle process for the synthesis of a rod-like LiFePO_4/C composite cathode material for lithium batteries. *Journal of Power Sources* **2009**, 194, (1), 515-519.
18. Saravanan, K.; Balaya, P.; Reddy, M. V.; Chowdari, B. V. R.; Vittal, J. J. Morphology controlled synthesis of LiFePO_4/C nanoplates for Li-ion batteries. *Energy & Environmental Science* **2010**, 3, (4), 457-463.
19. Chen, Z.-y.; Zhu, W.; Zhu, H.-l.; Zhang, J.-l.; Li, Q.-f. Electrochemical performances of LiFePO_4/C composites prepared by molten salt method. *Transactions of Nonferrous Metals Society of China* **2010**, 20, (5), 809-813.
20. Liu, X.-h.; Wang, J.-q.; Zhang, J.-y.; Yang, S.-r. Fabrication and Characterization of LiFePO_4 Nanotubes by a Sol-gel-AAO Template Process. *Chinese Journal of Chemical Physics* **2006**, 19, (6), 530-534.
21. Wang, G.; Shen, X.; Yao, J. One-dimensional nanostructures as electrode materials for lithium-ion batteries with improved electrochemical performance. *Journal of Power Sources* **2009**, 189, (1), 543-546.
22. Teng, F.; Santhanagopalan, S.; Lemmens, R.; Geng, X.; Patel, P.; Meng, D. D. In situ growth of LiFePO_4 nanorod arrays under hydrothermal condition. *Solid State Sciences* **2010**, 12, (5), 952-955.
23. Zhu, C.; Yu, Y.; Gu, L.; Weichert, K.; Maier, J. Electrospinning of Highly Electroactive Carbon-Coated Single-Crystalline LiFePO_4 Nanowires. *Angewandte Chemie International Edition* **2011**, 50, (28), 6278-6282.
24. Koenigsmann, C.; Wong, S. S. One-Dimensional Noble Metal Electrocatalysts: A Promising Structural Paradigm for Direct Methanol Fuel Cells. *Energy & Environmental Science* **2011**, 4, (4), 1161 - 1176.
25. Mao, Y.; Zhang, F.; Wong, S. Ambient Template-Directed Synthesis of Single-Crystalline Alkaline-Earth Metal Fluoride Nanowires. *Advanced Materials* **2006**, 18, (14), 1895-1899.
26. Santulli, A. C.; Feygenson, M.; Camino, F. E.; Aronson, M. C.; Wong, S. S. Synthesis and Characterization of One-Dimensional Cr_2O_3 Nanostructures. *Chemistry of Materials* **2011**, 23, 1000-1008.
27. Tiano, A. L.; Koenigsmann, C.; Santulli, A. C.; Wong, S. S. Solution-based synthetic strategies for one-dimensional metal-containing nanostructures. *Chemical Communications* **2010**, 46, (43), 8093-8130.
28. Zhang, F.; Sfeir, M. Y.; Misewich, J. A.; Wong, S. S. Room-Temperature Preparation, Characterization, and Photoluminescence Measurements of Solid Solutions of Various Compositionally-Defined Single-Crystalline Alkaline-Earth-Metal Tungstate Nanorods. *Chemistry of Materials* **2008**, 20, (17), 5500-5512.
29. Zhang, F.; Wong, S. S. Controlled Synthesis of Semiconducting Metal Sulfide Nanowires. *Chemistry of Materials* **2009**, 21, (19), 4541-4554.
30. Zhou, H.; Park, T.-J.; Wong, S. S. Synthesis, Characterization, and Photocatalytic Properties of Pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$ Nanotubes. *Journal of Materials Research* **2006**, 21, (11), 2941-2947.

31. Zhou, H.; Wong, S. S. A Facile and Mild Synthesis of 1-D ZnO, CuO, and α -Fe₂O₃ Nanostructures and Nanostructured Arrays. *ACS Nano* **2008**, 2, (5), 944-958.
32. Zhou, H.; Zhou, W.-p.; Adzic, R. R.; Wong, S. S. Enhanced Electrocatalytic Performance of One-Dimensional Metal Nanowires and Arrays Generated via an Ambient, Surfactantless Synthesis. *Journal of Physical Chemistry C* **2009**, 113, (14), 5460-5466.
33. Fisher, C. A. J.; Hart Prieto, V. M.; Islam, M. S. Lithium Battery Materials LiMPO₄ (M = Mn, Fe, Co, and Ni): Insights into Defect Association, Transport Mechanisms, and Doping Behavior. *Chemistry of Materials* **2008**, 20, (18), 5907-5915.
34. Morgan, D.; Van der Ven, A.; Ceder, G. Li Conductivity in Li_xMPO₄ (M = Mn, Fe, Co, Ni) Olivine Materials. *Electrochemical and Solid-State Letters* **2004**, 7, (2), A30-A32.
35. Hong, Y.-S.; Ryu, K. S.; Park, Y. J.; Kim, M. G.; Lee, J. M.; Chang, S. H. Amorphous FePO₄ as 3 V cathode material for lithium secondary batteries. *Journal of Materials Chemistry* **2002**, 12, (6), 1870-1874.
36. Kim, S.-W.; Ryu, J.; Park, C. B.; Kang, K. Carbon nanotube-amorphous FePO₄ core-shell nanowires as cathode material for Li ion batteries. *Chemical Communications* **2010**, 46, (39), 7409-7411.
37. Liu, Y.; Xu, Y.; Han, X.; Pellegrinelli, C.; Zhu, Y.; Zhu, H.; Wan, J.; Chung, A. C.; Vaaland, O.; Wang, C.; Hu, L. Porous Amorphous FePO₄ Nanoparticles Connected by Single-Wall Carbon Nanotubes for Sodium Ion Battery Cathodes. *Nano Letters* **2012**, 12, (11), 5664-5668.
38. Patete, J. M.; Peng, X.; Koenigsmann, C.; Xu, Y.; Karn, B.; Wong, S. S. Viable methodologies for the synthesis of high-quality nanostructures. *Green Chemistry* **2011**, 13, (3), 482-519.
39. Koenigsmann, C.; Santulli, A. C.; Sutter, E.; Wong, S. S. Ambient, Surfactantless Synthesis, Growth Mechanism, and Size-Dependent Electrocatalytic Behavior of High-Quality, Single Crystalline Palladium Nanowires *ACS Nano* **2011**, 5, (9), 7471-7487.
40. Park, T. J.; Mao, Y. B.; Wong, S. S. Synthesis and characterization of multiferroic BiFeO₃ nanotubes. *Chemical Communications* **2004**, (23), 2708-2709.
41. Zhou, H.; Yiu, Y.; Aronson, M. C.; Wong, S. S. Ambient Template Synthesis of Multiferroic MnWO₄ Nanowires and Nanowire Arrays. *Journal of Solid State Chemistry* **2008**, 181, (7), 1539-1545.
42. Koenigsmann, C.; Sutter, E.; Chiesa, T. A.; Adzic, R. R.; Wong, S. S. Highly Enhanced Electrocatalytic Oxygen Reduction Performance Observed in Bimetallic Palladium-Based Nanowires Prepared under Ambient, Surfactantless Conditions. *Nano Letters* **2012**, 12, (4), 2013-2020.
43. Singh, S.; Krupanidhi, S. B. Synthesis, structural characterization and ferroelectric properties of Pb_{0.76}Ca_{0.24}TiO₃ nanotubes. *Materials Chemistry and Physics* **2011**, 131, (1-2), 443-448.
44. Hernandez-Sanchez, B. A.; Chang, K.-S.; Scancella, M. T.; Burris, J. L.; Kohli, S.; Fisher, E. R.; Dorhout, P. K. Examination of Size-Induced Ferroelectric Phase Transitions in Template Synthesized PbTiO₃ Nanotubes and Nanofibers. *Chemistry of Materials* **2005**, 17, (24), 5909-5919.
45. Yang, Z.; Huang, Y.; Dong, B.; Li, H. L.; Shi, S. Q. Sol-gel template synthesis and characterization of LaCoO₃ nanowires. *Appl. Phys. A* **2006**, 84, (1-2), 117-122.

46. Kuang, Q.; Lin, Z.-W.; Lian, W.; Jiang, Z.-Y.; Xie, Z.-X.; Huang, R.-B.; Zheng, L.-S. Syntheses of rare-earth metal oxide nanotubes by the sol-gel method assisted with porous anodic aluminum oxide templates. *Journal of Solid State Chemistry* **2007**, 180, (4), 1236-1242.
47. Zhang, F.; Wong, S. S. Ambient Large-Scale Template-Mediated Synthesis of High-Aspect Ratio Single-Crystalline, Chemically Doped Rare-Earth Phosphate Nanowires for Bioimaging. *ACS Nano* **2009**, 4, (1), 99-112.
48. Koenigsmann, C.; Wong, S. S. Tailoring Chemical Composition to Achieve Enhanced Methanol Oxidation Reaction and Methanol-Tolerant Oxygen Reduction Reaction Performance in Palladium-Based Nanowire Systems. *ACS Catalysis* **2013**, 3, (9), 2031-2040.
49. Park, T.-J.; Mao, Y.; Wong, S. S. Synthesis and Characterization of Multiferroic BiFeO₃ Nanotubes. *Chemical Communications* **2004**, 2708-2709.
50. Koenigsmann, C.; Santulli, A. C.; Gong, K.; Vukmirovic, M. B.; Zhou, W.-p.; Sutter, E.; Wong, S. S.; Adzic, R. R. Enhanced Electrocatalytic Performance of Processed, Ultrathin, Supported Pd-Pt Core-Shell Nanowire Catalysts for the Oxygen Reduction Reaction. *Journal of the American Chemical Society* **2011**, 133, (25), 9783-9795.
51. Koenigsmann, C.; Sutter, E.; Adzic, R. R.; Wong, S. S. Size- and Composition-Dependent Enhancement of Electrocatalytic Oxygen Reduction Performance in Ultrathin Palladium-Gold (Pd_{1-x}Au_x) Nanowires. *Journal of Physical Chemistry C* **2012**, 116, (29), 15297-15306.
52. Zhang, F.; Mao, Y.; Park, T.-J.; Wong, S. S. Green Synthesis and Property Characterization of Single-Crystalline Perovskite Fluoride Nanorods. *Advanced Functional Materials* **2008**, 18, (1), 103-112.
53. Song, Y.; Yang, S.; Zavalij, P. Y.; Whittingham, M. S. Temperature-dependent properties of FePO₄ cathode materials. *Materials Research Bulletin* **2002**, 37, (7), 1249-1257.
54. Yuan, L.-X.; Wang, Z.-H.; Zhang, W.-X.; Hu, X.-L.; Chen, J.-T.; Huang, Y.-H.; Goodenough, J. B. Development and challenges of LiFePO₄ cathode material for lithium-ion batteries. *Energy & Environmental Science* **2011**, 4, 269-284.
55. Shiratsuchi, T.; Okada, S.; Yamaki, J.-i.; Yamashita, S.; Nishida, T. Cathode performance of olivine-type LiFePO₄ synthesized by chemical lithiation. *Journal of Power Sources* **2007**, 173, (2), 979-984.
56. Galoustov, K.; Anthonisen, M.; Ryan, D. H.; MacNeil, D. D. Characterization of two lithiation reactions starting with an amorphous FePO₄ precursor. *Journal of Power Sources* **2011**, 196, (16), 6893-6897.
57. Liu, H. Synthesis of nanorods FePO₄ via a facile route. *J Nanopart Res* **2010**, 12, (6), 2003-2006.
58. Scaccia, S.; Carewska, M.; Wisniewski, P.; Prosini, P. P. Morphological investigation of sub-micron FePO₄ and LiFePO₄ particles for rechargeable lithium batteries. *Materials Research Bulletin* **2003**, 38, (7), 1155-1163.
59. Kandori, K.; Kuwae, T.; Ishikawa, T. Control on size and adsorptive properties of spherical ferric phosphate particles. *Journal of Colloid and Interface Science* **2006**, 300, (1), 225-231.
60. Dean, J. A., *Lange's Handbook of Chemistry*. McGraw-Hill Inc.: New York, 1992.
61. Koenigsmann, C.; Zhou, W.-p.; Adzic, R. R.; Sutter, E.; Wong, S. S. Size-Dependent Enhancement of Electrocatalytic Performance in Relatively Defect-Free, Processed Ultrathin Platinum Nanowires. *Nano Letters* **2010**, 10, (8), 2806-2811.

62. Wang, B.; Qiu, Y.; Ni, S. Ultrafine LiFePO_4 cathode materials synthesized by chemical reduction and lithiation method in alcohol solution. *Solid State Ionics* **2007**, 178, (11–12), 843–847.
63. Islam, M. S.; Driscoll, D. J.; Fisher, C. A. J.; Slater, P. R. Atomic-Scale Investigation of Defects, Dopants, and Lithium Transport in the LiFePO_4 Olivine-Type Battery Material. *Chemistry of Materials* **2005**, 17, (20), 5085–5092.
64. Nan, C.; Lu, J.; Li, L.; Li, L.; Peng, Q.; Li, Y. Size and shape control of LiFePO_4 nanocrystals for better lithium ion battery cathode materials. *Nano Res.* **2013**, 6, (7), 469–477.
65. Chung, S.-Y.; Choi, S.-Y.; Yamamoto, T.; Ikuhara, Y. Orientation-Dependent Arrangement of Antisite Defects in Lithium Iron(II) Phosphate Crystals. *Angewandte Chemie International Edition* **2009**, 48, (3), 543–546.
66. Yang, S.; Song, Y.; Zavalij, P. Y.; Stanley Whittingham, M. Reactivity, stability and electrochemical behavior of lithium iron phosphates. *Electrochemistry Communications* **2002**, 4, (3), 239–244.
67. Chen, J.; Graetz, J. Study of Antisite Defects in Hydrothermally Prepared LiFePO_4 by in Situ X-ray Diffraction. *ACS Applied Materials & Interfaces* **2011**, 3, (5), 1380–1384.
68. Sheng, J.; Li, Q.; Wei, Q.; Zhang, P.; Wang, Q.; Lv, F.; An, Q.; Chen, W.; Mai, L. Metastable amorphous chromium–vanadium oxide nanoparticles with superior performance as a new lithium battery cathode *Nano Research* **2014**, 7, (11), 1604–1612.
69. An, Q.; Zhang, P.; Xiong, F.; Wei, Q.; Sheng, J.; Wang, Q.; Mai, L. Three-dimensional porous V_2O_5 hierarchical octahedrons with adjustable pore architectures for long-life lithium batteries *Nano Research* **2015**, 8, (2), 481–490.
70. He, X.; Wang, J.; Kloepsch, R.; Krueger, S.; Jia, H.; Liu, H.; Vortmann, B.; Li, J. Enhanced electrochemical performance in lithium ion batteries of a hollow spherical lithium-rich cathode material synthesized by a molten salt method. *Nano Research* **2014**, 7, (1), 110–118.
71. Yang, J.; Han, X.; Zhang, X.; Cheng, F.; Chen, J. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode for rechargeable lithium ion batteries: Nano vs micro, ordered phase (P4332) vs disordered phase (Fd3m) *Nano Research* **2013**, 6, (9), 679–687.
72. Axmann, P.; Stinner, C.; Wohlfahrt-Mehrens, M.; Mauger, A.; Gendron, F.; Julien, C. M. Nonstoichiometric LiFePO_4 : Defects and Related Properties. *Chemistry of Materials* **2009**, 21, ((8)), 1636–1644.
73. Lee, M.-H.; Kim, T.-H.; Kim, Y. S.; Park, J.-S.; Song, H.-K. Optimized evolution of a secondary structure of LiFePO_4 : balancing between shape and impurities. *Journal of Materials Chemistry* **2012**, 22, 8228–8234.
74. Gaberscek, M.; Dominko, R.; Jamnik, J. Is small particle size more important than carbon coating? An example study on LiFePO_4 cathodes. *Electrochemistry Communications* **2007**, 9, 2778–2783.
75. Kou, X.-j.; Ke, H.; Zhu, C.-b.; Rolfe, P. First-principles study of the chemical bonding and conduction behavior of LiFePO_4 . *Chemical Physics* **2015**, 446, (0), 1–6.
76. Malik, R.; Zhou, F.; Ceder, G. Kinetics of non-equilibrium lithium incorporation in LiFePO_4 . *Nature Materials* **2011**, 10, (8), 587–590.
77. Meethong, N.; Huang, H.-Y. S.; Carter, W. C.; Chiang, Y.-M. Size-Dependent Lithium Miscibility Gap in Nanoscale $\text{Li}_{1-x}\text{FePO}_4$. *Electrochemical and Solid-State Letters* **2007**, 10, (5), A134–A138.

78. Chen, Z.; Dahn, J. R. Reducing Carbon in LiFePO_4/C Composite Electrodes to Maximize Specific Energy, Volumetric Energy, and Tap Density. . *Journal of the Electrochemical Society* **2002**, 149, (9), A1184-A1189.

Figure 1.

Figure 2.

Figure 3.

200 nm Nanowire				
Atom	x	y	z	Occupancy
Li	0.5	0.5	0	1
Fe	0.21853	0.25	0.0267	1
P	0.40479	0.25	0.58445	1
O1	0.40267	0.25	0.2689	1
O2	0.16286	0.54884	0.22128	1
O3	0.04822	0.25	-0.211	1
Space group: Pmna		Reliability Factor (Rwp): 3.29%		
Unit Cell Parameters: a = 10.32789 Å, b = 6.00579 Å, c = 4.69261 Å		Phase: 100% LiFePO ₄		
Cell Volume: 291.06917 Å ³				
Bulk-like Sample				
Atom	x	y	z	Occupancy
Li	0.5	0.5	0	1
Fe	0.21775	0.25	0.02557	1
P	0.40502	0.25	0.58446	1
O1	0.40029	0.25	0.25635	1
O2	0.16733	0.54493	0.21629	1
O3	0.04563	0.25	-0.20062	1
Space group: Pmna		Reliability Factor (Rwp): 3.29%		
Unit Cell Parameters: a = 10.32599 Å, b = 6.00463 Å, c = 4.69005 Å		Phase: 71% LiFePO ₄		
Cell Volume: 290.80068 Å ³		29% Li ₃ PO ₄		

Table 1.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.