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Pilot-scale continuous synthesis of a vanadium-doped LiFePO_4/C nanocomposite high-rate cathodes for lithium-ion batteries



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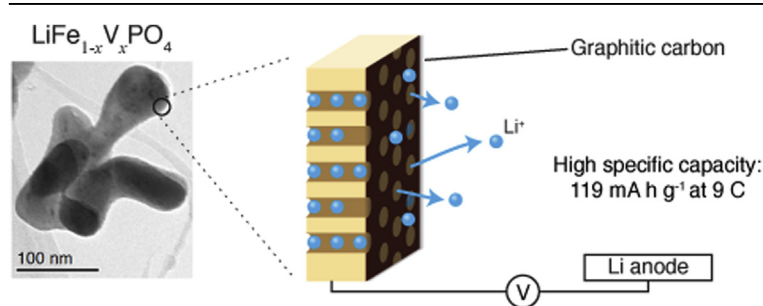
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HIGHLIGHTS

- Phase-pure and V-doped LiFePO_4 nanoparticles (<100 nm) are synthesized via CHFS.
- A continuous carbon coating is achieved, giving core/shell nanoparticles.
- The doped samples exhibit enhanced capacities at high discharge rates.
- Sample $\text{LiFe}_{0.95}\text{V}_{0.05}\text{PO}_4$ has high power performance at current rates up to 1.5 A g^{-1} .
- Theoretical and experimental techniques suggest vanadium occupies both the Fe and P sites.

GRAPHICAL ABSTRACT



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ABSTRACT

A high performance vanadium-doped LiFePO_4 (LFP) electrode is synthesized using a continuous hydrothermal method at a production rate of 6 kg per day. The supercritical water reagent rapidly generates core/shell nanoparticles with a thin, continuous carbon coating on the surface of LFP, which aids electron transport dynamics across the particle surface. Vanadium dopant concentration has a profound effect on the performance of LFP, where the composition $\text{LiFe}_{0.95}\text{V}_{0.05}\text{PO}_4$ achieves a specific discharge capacity which is among the highest in the comparable literature (119 mA h g^{-1} at a discharge rate of 1500 mA g^{-1}). Additionally, a combination of X-ray absorption spectroscopy analysis and hybrid-exchange density functional theory, suggest that vanadium ions replace both phosphorous and iron in the structure, thereby facilitating Li^+ diffusion due to Li^+ vacancy generation and changes in the crystal structure.

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1. Introduction

Olivine lithium iron phosphate (LFP) and its doped analogues have received significant attention for use as cathode materials in Li-ion batteries since their discovery by Goodenough et al. [1]. The

properties of LiFePO_4 make it a promising candidate to replace LiCoO_2 and other lithium transition metal oxides in many commercial secondary batteries. In theory, LiFePO_4 offers a moderate capacity of 170 mA h g^{-1} , relatively high thermal stability (compared to LiCoO_2) and contains abundant, inexpensive and non-toxic elements [2]. Unfortunately, pure bulk LiFePO_4 possesses low electronic conductivity and ionic diffusivity, reported to be in the range of 10^{-9} to $10^{-8} \text{ S cm}^{-1}$ and 10^{-17} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively [3–5], which results in low discharge capacity at high discharge rates. To some degree, these limitations have been addressed by reducing the crystallite size and incorporating dopants such as Nb, V, and Mg to modify the crystal structure and improve bulk electronic conductivity [6–8]. In addition, the use of conducting carbons or polymer coatings on the particle surface, has increased conductivity and discharge capacity [9,10].

Vanadium-doped LiFePO_4 is of particular interest as a high-rate cathode material in Li-ion batteries, as doping has been found to increase discharge capacity at high discharge rates. The literature, however, contains conflicting findings with respect to the synthesis, phase behavior and performance of these materials. Some researchers have found the best performance is observed when vanadium is found exclusively within the olivine structure [11]. This has been attributed to decreased Li^+ diffusion activation energy barriers and increased electronic conductivity within the material [12]. Structural refinement has indicated the V ions can either occupy Fe or Li sites within LFP, depending upon the stoichiometry of the precursors [13–17]. Vanadium has also been found to occupy the P site [8], although later attempts to repeat this substitution were unsuccessful [15]. However, optimal performance has also been found if vanadium-containing impurities such as $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ or VO_2 are present at the surface of the particles [15,18,19]. These are thought to improve electron and Li^+ transport dynamics between the particle surface and the surrounding cathode carbon matrix and electrolyte. These conclusions are supported by atomistic modelling research, which suggested aliovalent doping is impossible in LiFePO_4 on energetic grounds [20]. Therefore there is still some debate regarding the exact nature of V-doping in these materials, and how they benefit the electrochemical performance.

The synthesis of carbon-coated LiFePO_4 (hereafter referred to as LiFePO_4/C) has been achieved through a number of methods, including solid-state and hydrothermal syntheses [21–23]. Solid-state reactions currently account for most industrial-scale syntheses of LiFePO_4/C , although there is increasing interest in alternative methods, as the solid-state synthesis process usually involves high temperatures, multiple steps and lengthy heat-treatments. In contrast, batch hydrothermal reactions typically require lower synthesis temperatures. By incorporating surfactants, some degree of control over particle size and morphology can be achieved, although inevitably the use of surfactants adds additional cost and complexity [24,25].

Continuous synthesis processes are considered advantageous over batch type synthesis routes, as the former processes are often more flexible and can allow independent control over more reaction variables, and can rapidly convert ions in solution to the solid, often generating kinetic products. In continuous hydrothermal synthesis, a flow of supercritical water is mixed with aqueous metal salt(s) in a well-defined mixer arrangement, resulting in rapid reaction of the aqueous metal salt to form nanoparticles. Continuous hydrothermal reactors have already been used for the production of nanoparticle metal oxides, and more recently, have been extended to phosphates [26–29]. Continuous hydrothermal synthesis of LiFePO_4 was reported by Xu et al., where a precursor ratio of 1:1:3 for $\text{FeSO}_4\cdot\text{H}_3\text{PO}_4\cdot\text{LiOH}$ produced phase-pure LiFePO_4 for both subcritical and supercritical water feeds [30]. The use of

supercritical water gave an increase in particle size compared to the subcritical case (made at a scale of ca. 0.3 g h^{-1} assuming 100% yield). In contrast, Hong et al. found crystallite sizes were smaller when supercritical water was used as a feed (100 nm, with numerous morphologies) as opposed to subcritical water ($>1 \mu\text{m}$, with rhombic morphology), although in both cases there was significant variation in size and morphology with conditions (made at a scale of ca. 0.5 g h^{-1} assuming 100% yield) [31]. Furthermore, a residence time of around 40 s was required to give the pure olivine phase. In contrast, Aimable et al. were able to synthesize LiFePO_4 with a residence time of 12 s by using a Fe:P:Li ratio of 1:1:3.75 [32]. However, of the materials that were tested, the best high-rate performance of LiFePO_4 yielded a comparatively modest capacity (105 mA h g^{-1} at 1 C). To our knowledge, there are no reports of scaled-up continuous synthesis of doped LiFePO_4 or LiFePO_4/C nanomaterial in the academic literature, which provide high capacity and high-rate performance, although we are aware of commercial research in industry from Hanwha Corporation in Korea [33].

The purpose of this study is to generate a high performance LFP-based electrode using a continuous, low-temperature hydrothermal process. We attempted to generate nanoparticulate LFP with a uniform carbon coating by including a carbon source (fructose) in the precursors, and further improve the rate capability by incorporating varying levels of vanadium dopant in the structure. We utilize a combination of experimental and theoretical techniques to indicate the location and effect of vanadium, and aim to provide a new insight into the behaviour of these doped materials.

2. Experimental section

2.1. Synthesis

Carbon-coated vanadium-doped lithium iron phosphate samples (where the C is amorphous) were synthesized using a pilot-scale continuous hydrothermal flow synthesis (CHFS) reactor incorporating a confined jet mixer (CJM), the design of which has previously been described in detail [34], and schematics of both are shown in Fig. S1 and Fig. S2, respectively. Briefly, two aqueous solutions were prepared from the following precursors. The first solution consisted of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (99+%, Alfa Aesar, Heysham, UK), $\text{VOSO}_4\cdot 5\text{H}_2\text{O}$ (17–23% V, Acros Organics, Loughborough, UK), $0.375 \text{ M H}_3\text{PO}_4$ (85–88% wt%, Sigma Aldrich, Steinheim, Germany) and fructose (99%, Alfa Aesar, Heysham, UK) in deionized (D.I.) water. The composition of the first solution was varied in separate experiments as described in Table S1, where the sum of [Fe] and [V] was 0.25 M and the concentration of fructose was in the range 0.65 – 0.75 M . The second solution contained $0.8625 \text{ M LiOH}\cdot\text{H}_2\text{O}$ (99+%, Fischer Scientific, Loughborough, UK) in D.I. water. Each solution was pumped into a T-piece mixer ($0.25''$ internal diameter) with a flow rate of 200 mL min^{-1} each. The combined mixture of solutions 1 and 2 was pumped at 400 mL min^{-1} into the side arms of the CJM, where it rapidly combined with 400 mL min^{-1} of supercritical water at 450°C and 24.1 MPa , which emerged from the inner tube of the CJM as a turbulent jet (Fig. S2), resulting in extremely rapid mixing [34]. The nanoparticles of LiFePO_4/C (either pure or doped with V) rapidly formed in the mixture at a temperature of ca. 335°C [35]. The mixture was held at this temperature as it flowed through the outlet pipe with a residence time of ca. 6.5 s , before cooling to near ambient temperature by passing through a pipe-in-pipe countercurrent heat exchanger. The cooled slurry passed through a back-pressure regulator (BPR, Swagelok KHB series) which maintained the system pressure at 24.1 MPa , after which it was collected in a plastic container open to the atmosphere. The slurry was allowed to settle out and the supernatant

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