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Short communication

High power Nb-doped LiFePO₄ Li-ion battery cathodes; pilot-scale synthesis and electrochemical properties

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Abstract

High power, phase-pure Nb-doped LiFePO₄ (LFP) nanoparticles are synthesised using a pilot-scale continuous hydrothermal flow synthesis process (production rate of 6 kg per day) in the range 0.01 to 2.00 at% Nb with respect to total transition metal content. EDS analysis suggests that Nb is homogeneously distributed throughout the structure. The addition of fructose as a reagent in the hydrothermal flow process, followed by a post synthesis heat-treatment, affords a continuous graphitic carbon coating on the particle surfaces. Electrochemical testing reveals that cycling performance improves with increasing dopant concentration, up to a maximum of 1.0 at% Nb, for which point a specific capacity of 110 mA h g⁻¹ is obtained at 10 C (6 min for the charge or discharge). This is an excellent result for a high power cathode LFP based material, particularly when considering the synthesis was performed on a large pilot-scale apparatus.

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1. Introduction

Lithium iron phosphate (LFP, LiFePO₄) based cathodes for Li-ion batteries were initially developed by Goodenough and coworkers [1], and have generated interest as safer, more sustainable alternatives to current commercial Li-ion battery cathodes based on LiCoO₂ [2]. However, bulk LFP does not possess high electronic conductivity and high ionic diffusivity required for outstanding performance (in the ranges of 10⁻⁹ to 10⁻¹⁸ S cm⁻¹ and 10⁻¹⁷ to 10⁻¹₂ cm² s⁻¹, respectively) [3].

A number of approaches have been employed to improve the power and energy performance of pure LFP, which include coating LFP particles with conducting carbon or nano-sizing [4,5]. Furthermore, doping of metal ions (such as ions of Nb, V, or Mg) can also distort the olivine lattice, resulting in increased Li-ion transport, and furthermore generate Li⁺ vacancies to boost Li-ion conductivity and improve high power performance [6–11]. Du and co-workers reported that an optimal dopant level of 1 at% Nb in LFP (carbon coated), gave a specific capacity of 82 mA h g⁻¹ at 10 C (6 min for a charge/discharge) [12]. In contrast, Zhuang and co-workers achieved a specific capacity of 143 mA h g⁻¹ at 2 C for 1 at% Nb-doped LFP [13]. The improved discharge capacity achieved by Nb-doped LFP materials could justify the incorporation of the more expensive Nb metal ion in the LFP lattice in commercial cells.

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Continuous hydrothermal flow synthesis (CHFS) and similar flow methods represent a relatively under-explored approach for the synthesis of Li-ion battery anodes [14–16] and cathodes [17–22]. In CHFS, a flow of supercritical water is mixed with an aqueous metal salt, which results in rapid conversion of the aqueous metal salt to form nanoparticles of metal oxide [23–25] or phosphate [22,26,27]. Furthermore, CHFS is highly scalable, allowing synthesis of nanomaterials at multi-kg per day rate [28], including vanadium-doped LFP synthesised previously by the authors [22]. Herein, the authors report the first continuous synthesis and optimisation of carbon-coated Nb-doped LFP nanoparticle cathodes using a pilot-scale CHFS process.

2. Experimental

2.1. Materials and precursors

Iron(II) sulfate, FeSO₄·7H₂O (99.5%), and lithium hydroxide, LiOH·H₂O (99+%), were supplied by Fisher Scientific UK Ltd. (Loughborough, UK). Ammonium niobate(V) oxalate pentahydrate, C₂H₄NbO₆·5H₂O (99.99%), D(-)-fructose (≥99%), and phosphoric acid (85 wt%) were supplied by Sigma-Aldrich Ltd. (Dorset, UK). Deionised water was used throughout (>10 MΩ cm⁻¹). All starting solutions, precursors and deionised water were degassed with pure nitrogen gas prior to reaction.

2.2. Continuous hydrothermal flow synthesis

The synthesis was conducted using a pilot-scale CHFS reactor, a detailed description of which can be found elsewhere [28,29]. In the process, an aqueous precursor solution containing an appropriate mixture of ammonium niobate and iron(II) sulfate (total concentration 0.25 M, Table S1), fructose (≥99%), and phosphoric acid (85 wt%) were supplied by Sigma-Aldrich Ltd. (Dorset, UK). Deionised water was used throughout (>10 MΩ cm⁻¹). All starting solutions, precursors and deionised water were degassed with pure nitrogen gas prior to reaction.

2.4. Preparation of printed electrodes and half cells and electrochemical testing

Cathode inks were prepared by thoroughly mixing the heat-treated samples, conductive agent (carbon black, Super P™, Alfa Aesar, Heysham, UK), and PVDF (polyvinylidene fluoride, PI-KEM, Staffordshire, UK) in an NMP solvent (N-methyl-2-pyrrolidone solvent, Sigma Aldrich, St Louis, USA). Two electrodes were prepared; set one had a wt% ratio of 80:10:10 S:C:B (sample: added carbon: binder), whilst set two contained a higher added carbon loading of 75:15:10 S:C:B. The preparation of the electrodes, coin cells and electrochemical tests are described in the Supporting Information.

2.5. Results and discussion

LFNP nanoparticles were synthesised using CHFS as described in the experimental section. For samples named LFNPN(x), x is the nominal Nb at% present in the precursor solution, relative to total transition metal content. The samples were heat-treated to further graphitize the surface carbon coatings, giving the corresponding ΔLFNPN(x) compounds.

Powder XRD patterns of heat-treated samples all displayed the pure LiFePO₄ olivine structure (Fig. 1), with no significant peak shift (within errors) between samples. This was in contrast to the report of Du and co-workers, where the addition of the Nb dopant was found to increase the (1 0 1) interplanar distance [12]. EDS analysis of sample ΔLFNPN(2.0) showed a uniform dispersion of Nb within

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**Fig. 1.** Normalised powder XRD patterns of the heat-treated (Δ) Nb-doped samples with the JCPDS reference pattern for LiFePO₄ (JCPDS 00-046-1499).
the particles (Fig. 2a–e). This implied Nb was homogeneously doped within the olivine structure, although techniques such as XAS could further confirm this in future work. FE-SEM analysis indicated the particle size and shape varied significantly within samples (Fig. S3), which formed agglomerated networks of <100 nm semi-spherical crystallites and larger networks of <100 nm semi-spherical crystallites and larger.

Fig. 2. EDS imaging of sample LFNP(2.0) showing a) the darkfield image, b) the Nb Kα signals, c) the Fe Kα signals, d) the O Kα signals and e) the P Kα signals; f) A TEM micrograph of sample ΔLFNP(1.0); g) Raman spectra of the heat-treated samples showing the graphitic D and G bands.

Fig. 3. a) Cyclic voltammograms at 0.05 mV s⁻¹ scan rate for all heat-treated samples, including a pure LFP sample from previous work; b) linear fits obtained from the cyclic voltammetry data of peak current (I_p) versus the square root of the scan rate (v¹/²) for samples ΔLFNP(1.0), ΔLFNP(1.5), and ΔLFNP(2.0) (active:carbon:binder wt% ratio 80:10:10).
Fig. 4. Variable C-rate tests (at C-rates shown) for all electrodes with S:C:B wt% ratios of a) 80:10:10 (including a pure LFP sample from previous work) and b) 75:15:10. c) Tests of $\Delta$LFNP(1.0), $\Delta$LFNP(1.5), and $\Delta$LFNP(2.0) at higher C-rates (solid active:carbon:binder {S:C:B} wt% ratio of 80:10:10). d) A voltage vs. capacity plot of $\Delta$LFNP(1.0) (80:10:10) at 0.5 C and 10 C. Capacity retention test data for all doped LFP samples with S:C:B wt% ratios of: e) 80:10:10; f) 75:15:10. The original capacity is the discharge capacity of each cell at 0.5 C. g) Capacity retention at a charge and discharge rate of 1 C of set 1 samples $\Delta$LFNP(0.01), $\Delta$LFNP(0.1), and $\Delta$LFNP(0.5) for 100 cycles and samples $\Delta$LFNP(1.0), $\Delta$LFNP(1.5), and $\Delta$LFNP(2.0) for 200 cycles. The capacity retention was relative to the highest capacity observed during these cycles.
rhombic-morphology particles, similar to LFP and doped LFP synthesised via CHFS previously [22]. Therefore, Nb-doping did not significantly alter crystallite size or morphology.

The carbon content of the heat-treated samples varied in the range 2.5–7.3 wt% (Table S1). TEM micrographs of the heat-treated compound ΔLFNP(1.0), showed the carbon formed a continuous coating approximately 3.5 nm thick (Fig. 2f). Raman spectroscopy analysis of the heat-treated samples, showed a D-band (1350 cm⁻¹) and G-band (1600 cm⁻¹, Fig. 2g), where the intensity ratio I_D/I_G was similar between samples (0.7–0.8, Table S2). No peak indicative of the PO₄ group could be observed, which in combination with the TEM, suggested the graphicitic carbon layer effectively covered the surface of the particles.

Cyclic voltammetry experiments confirmed the presence of the Fe²⁺/Fe³⁺ redox couple at 3.45 V, indicated by the dotted line (Fig. 3a) with no additional redox activity observed due to the Nb dopant. The peak current generally increased with Nb content up to 1.5 at%, and thereafter, it decreased for 2.0 at% Nb-doping. This shows an increase compared to pure LFP (1.0 at%), and thereby, it decreased for 2.0 at% Nb-doping. This behaviour clearly demonstrates the addition of Nb, generally improved lithiation and delithiation kinetics in the samples. A pure ΔLFP electrode from previous work by the authors, is included as reference; while the peak current achieved by this sample is higher than that of the Nb-doped ΔLFP sample was much higher (9.1 wt% vs. 2.5 wt%, Fig. 3a). To investigate this further, a qualitative Li-ion diffusion coefficient analysis was conducted using the Randles-Sevcik equation (Equation (1)).

The calculated diffusion coefficients were very similar, with values of 2.0 × 10⁻¹⁰, 2.2 × 10⁻¹⁰ and 1.9 × 10⁻¹⁰ cm² s⁻¹ for samples ΔLFNP(1.0), ΔLFNP(1.5) and ΔLFNP(2.0), respectively. This shows an increase compared to pure LFP (1.0 × 10⁻¹⁰ cm² s⁻¹) previously reported by the authors, and suggested that Nb doping beyond 1 at% added little benefit to performance [22].

Constant current tests on the same cells, showed that the rate capability of samples increased with increasing Nb content (Fig. 4a,c), especially compared to the undoped ΔLFP sample, proving that incorporation of even a small proportion of Nb has a much greater effect on performance than any dopants present from precursor impurities [22]. The best performing sample ΔLFNP(1.0) displayed a capacity of 110 mA h g⁻¹ at 10 C, which surpasses capacities obtained for pure LFP materials made via continuous hydrothermal methods. Aimeal et al. achieved 75 mA h g⁻¹ at 0.1 C [32] and Kim et al. reported a capacity of 88 mA h g⁻¹ at 10 C [19]. Thus, the Nb-doped LFP reported herein offers a clear high power performance advantage over the undoped material.

Electrodes with higher added carbon content (S:C:B wt% ratio 75:15:10) were also examined. Much smaller variation in cell performance was observed, regardless of Nb content (Fig. 4b,f). In this case, the ΔLFNP(0.01) cell performed best, which suggested that the Nb dopant enhanced the electrical conductivity of LFP, and the effect is reduced with a higher proportion of conductive carbon in the electrode. This is consistent with conductivity analysis performed previously by other researchers [13,33].

The three highest performing electrodes (80:10:10 wt% S:C:B ratio) were ΔLFNP(1.0), ΔLFNP(1.5), and ΔLFNP(2.0), which were subjected to further constant rate tests using high C-rates (Fig. 4c). Beyond 10 C, most electrodes tended not to provide any appreciable capacity as the overpotential required to charge the cells often moved beyond the operating voltage window (Fig. 4d). All three electrodes recovered full capacity after cycling at 20 C. Comparing the capacity retention of all samples as a function of C-rate also indicated the limiting conductivity benefit of the Nb dopant up to 1 at% Nb (Fig. 4e), where ΔLFNP(1.0), ΔLFNP(1.5), and ΔLFNP(2.0) displayed an equal capacity retention of ca. 70% (of the original value at C/2) at 10 C (Fig. 4e). Excellent capacity retention (range 96–98%) was also observed in long term stability testing at a 1 C charge/discharge rate (range of 100–200 cycles) for the same cells (Fig. 4g).

3. Conclusions

The synthesis of nano-sized, carbon-coated, Nb-doped LFP was achieved at a production rate of ca. 0.25 kg h⁻¹ using a pilot-scale CHFS process. Elemental mapping suggested that Nb was evenly distributed throughout the LFP particles. Electrochemical testing showed improved performance with increasing Nb content, where the 1 at% Nb-doped sample achieved a specific discharge capacity of 110 mA h g⁻¹ at 10 C, a substantial improvement on pure LFP. Increasing dopant levels above 1 at% Nb led to no additional performance gains. Experiments with higher levels of conductive carbon additive suggested that Nb-doping increased the electrical conductivity of the material. This high performance is especially significant given the high production rate herein, and therefore represents evidence that continuous hydrothermal flow reactors could produce high-quality battery electrodes at scale.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2016.06.128.

Conflict of interest

The authors declare no competing financial interests.

References
