

Short communication

Optimization of carbon coatings on LiFePO₄

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Abstract

The electrochemical performance of LiFePO₄ in lithium cells is strongly dependent on the structure (disordered/graphene or D/G ratio) of the in situ carbon produced during synthesis from carbon-containing precursors. Addition of pyromellitic acid (PA) prior to final calcination results in lower D/G ratios, yielding a higher-rate material. Further, improvements in electrochemical performance are realized when graphitization catalysts such as ferrocene are also added during LiFePO₄ preparation, although overall carbon content is still less than 2 wt.%. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

LiFePO₄ is of interest as a cathode material for Li-ion batteries intended for large-scale applications such as hybrid electric vehicles (HEVs) because of its potential for low cost and improved safety. To fulfill this promise, however, the power capability of this material needs to be improved. A factor limiting the performance of LiFePO₄ is its low electronic conductivity, calculated to be about 10⁻⁹ S cm⁻¹ at room-temperature [1]. Although an attempt to improve the intrinsic conductivity by doping with multivalent cations has been reported recently [2], it is not clear that substitution on the Li sites actually occurs under the conditions described [3,4]. In contrast, it has been shown that carbon-coating the LiFePO₄ particles [5] results in greatly improved room-temperature electrochemical performance. This may be accomplished by adding organic or polymeric precursors during synthesis [6], although the total amount of carbon should be kept low to avoid adversely affecting the tap density [7]. To maximize power capability without incurring an energy density penalty, it is therefore necessary to optimize the conductivity of the coating.

Higher electronic conductivity scales with lower D/G (disordered/graphene) and increased sp²/sp³ ratios in carbon [8]. We have previously noted a correlation between the structure

of carbon in LiFePO₄ samples and the utilization upon discharge in lithium cells at room-temperature [9]. Significantly, some materials with low amounts of carbon and low D/G ratios outperformed those with more carbon having a more disordered structure. While optimizing the carbon structure is key to obtaining good performance, it is difficult to produce highly graphitic coatings at the relatively low temperatures (600–800 °C) used for synthesis of LiFePO₄ [8]. Herein, we show how, with the proper choice of additives and graphitization catalysts [10], better coatings may be produced, which result in greatly enhanced electrochemical behavior.

2. Experimental

LiFePO₄ was synthesized by a sol-gel procedure described in our previous publications [9,11]. Pyromellitic acid (PA) and ferrocene were dissolved in acetone or ethanol and added to the sample after an initial firing at 500 °C under flowing N₂. This mixture was then planetary milled for 1 h, dried, and subjected to a final firing at 600 °C under flowing nitrogen for 10 h.

The phase purity of samples was verified by X-ray powder diffraction (XRD) using a Philips X'Pert diffractometer with monochromatized Cu K_α radiation. The carbon and hydrogen contents of selected samples were measured by Luvak, Inc. (Boylston, MA).

An integrated Raman microscope system “Labram” made by ISA Groupe Horiba was used to observe individual particles of

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LiFePO₄. The excitation wavelength was supplied by an internal He–Ne (632 nm) 10 mW laser. The power of the laser beam was adjusted to 0.1 mW with neutral filters of various optical densities. The size of the laser beam at the sample was $\sim 1.2 \mu\text{m}$.

Laminated electrodes containing 80 wt.% active material, 8 wt.% Kynar poly(vinylidene fluoride) (PVdF binder grade 2801-00, lot 97C8118, Elf Atochem North America, Inc., Technical Polymers Department), 6 wt.% SFG-6 synthetic flake graphite (Timcal Ltd., Graphites and Technologies), and 6 wt.% compressed acetylene black were prepared as previously described in [9]. Electrodes were punched out to 1.8 cm² size, with loadings of about 5–10 mg cm⁻² active material. For some experiments, carbon-coated aluminum current collectors were used as backings for the positive electrodes. The thickness of the carbon coating was approximately 5 μm .

Two thousand and thirty-two size coin cells were assembled in a helium-filled glove box, using lithium metal as a counter electrode and 1 M LiPF₆ in 1:2 ethylene carbonate/dimethyl carbonate (EC/DMC) as the electrolytic solution (Merck). Cells were cycled galvanostatically between 2.0 and 3.9 V at various rates using a MacPile II (Bio-Logic, SA, Claix, France) potentiostat/galvanostat.

3. Results and discussion

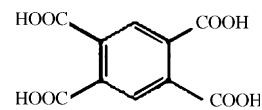
LiFePO₄ may be prepared by a number of different routes, including hydrothermal synthesis [12,13], carbothermal reduction [14], sol–gel [9,15–17] or aqueous precipitation routes [18], microwave processing [19], and solid-state synthesis under an inert or reducing atmosphere [20,21]. Samples made from precursors with organic moieties (oxalates, acetates, etc.) [9] or processed in plastic containers [3] typically contain small amounts of residual (in situ) carbon from pyrolysis of the organics or polymers. Even small amounts of in situ carbon may turn samples deep gray or black (Fig. 1) so that color is not a reliable indicator of successful doping with aliovalent ions, unless contact with carbonaceous materials was strictly avoided during preparation.

The amount of residual carbon present in samples varies in complex ways with the furnace conditions; some is lost as CO or CO₂ during carbothermal reduction, particularly if Fe(III) species are present. Near or above 800 °C, these processes may result in the formation of iron carbide, iron phosphocarbides and/or iron phosphides from reaction with LiFePO₄ itself [3,4]. Nevertheless, the presence of carbon or carbonaceous materials during synthesis is beneficial as grain growth is inhibited

and oxidation of iron by adventitious oxygen is slowed or prevented.

The structure of the in situ carbon influences the electrochemical behavior of LiFePO₄ samples. Electrode utilization rises as D/G ratios and the amorphous carbon content decreases (i.e. the electronic conductivity increases) [9]. The observation that some samples with low carbon contents outperform those with larger amounts of poor-quality carbon is significant, and suggests that the amount of coating necessary to ensure good high-rate performance can be minimized provided that the structure is optimized. A considerable challenge is the temperature limitation (<750–800 °C) imposed by LiFePO₄ synthesis conditions. For example, the graphene content and electronic conductivity are low for carbons prepared from polymeric precursors at temperatures below about 700 °C [22,23] but increase dramatically above this temperature. However, the considerable variations found in the in situ carbon of LiFePO₄ samples suggest that much can be done to manipulate the structure, even considering the temperature constraints.

It is a common practice to use polymeric or organic additives as carbon sources during synthesis of LiFePO₄ (see, e.g. Ref. [24]). The Raman spectra and C, H, and N elemental analyses of LiFePO₄ powders processed with poly(acrylonitrile), perylenetetracarboxylicdianhydride or other well-known graphite precursors, show that these additives do not decompose sufficiently at the relatively low synthesis temperatures to form an ideal coating [11]. In some cases, the addition of the precursors actually resulted in electrode materials with electrochemical performance inferior to that of samples processed without additives. In contrast, pyromellitic acid (PA, I) decomposes readily, as evidenced by lower H/C ratios in the resulting products when compared to those processed with the above-mentioned additives. The quality of the carbon for samples processed with PA also improves over that for those synthesized with no additives, as can be seen by the increased sharpness and intensity of the G-band in the Raman spectrum of the former (compare middle and bottom spectra in Fig. 2).



(I)

The overall carbon content in the final products generally increases somewhat as more PA is used, although this is very

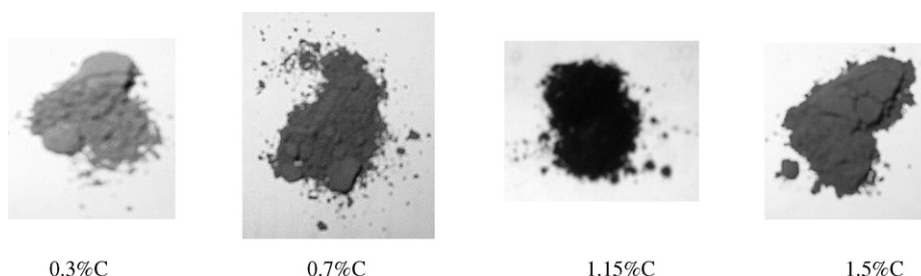


Fig. 1. Photographs of LiFePO₄ powders containing varying amounts of in situ carbon. The first three samples were prepared by sol–gel synthesis following procedures outlined in Ref. [11], and the rightmost sample was prepared by the solid-state reaction described by Yamada et al. [21].

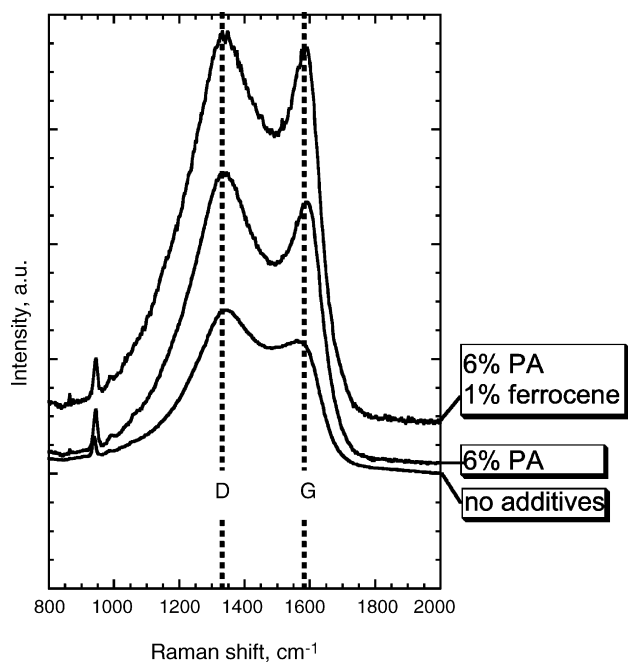


Fig. 2. Raman spectra of LiFePO₄ samples processed with and without additives as indicated. The D and G bands of in situ carbon are marked. The band at 942 cm⁻¹ corresponds to the symmetric vibration of the PO₄ group in LiFePO₄.

dependent upon the furnace conditions. H/C ratios also rise, particularly above 8 wt.%, indicating that complete decomposition becomes more difficult for large amounts of PA. Interestingly, it is possible to observe a broad reflection attributable to elemental carbon with graphitic character in the XRD pattern of LiFePO₄ processed with 50 wt.% PA (Fig. 3), clearly illustrating how dramatically PA affects the C structure. (This sample, although not realistic because of the large amount of carbon coating, was generated to allow observation of the graphite peak in the XRD, which is normally rather insensitive to detection of small amounts of a minor phase.)

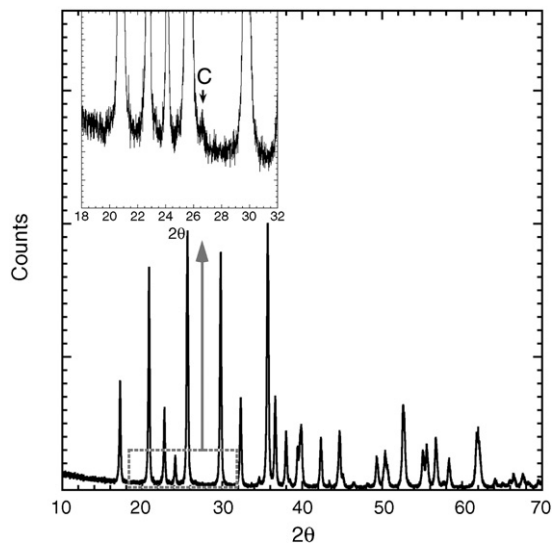


Fig. 3. XRD pattern of a LiFePO₄ sample processed with 50 wt.% PA. The 002 reflection of elemental carbon with some graphene character is marked in the inset.

The best rate behavior is obtained when LiFePO₄ is processed with 4–8 wt.% PA, which yields materials with in situ carbon content below 1 wt.% [25]. There is a correlation between pressed pellet conductivities measured by AC impedance and the rate performance [25], but not necessarily with the amount of carbon. Secondary particles in these samples have a lava rock-like appearance, and size distributions are wide [11]. Processing with PA does not appear to change the primary particle size (~200 nm) significantly, indicating that the observed rate effects are indeed due to the improved C structure.

It is well known that some iron compounds [26–28] can catalyze the formation of graphite at relatively low temperatures. Graphite may precipitate upon decomposition of Fe₃C (cementite) near 650 °C during the production of cast iron, in a process known as “dusting”. Furthermore, carbon nanotubes, which consist of curled graphene sheets, can be made at temperatures as low as 600–700 °C using organic or polymeric carbon sources and iron compounds as promoters [29,30]. An investigation into the mechanism of nanotube formation at 650 °C using iron nitrate and acetylene [30] indicates that iron oxides form from the decomposition of iron nitrate, which then catalyze decomposition of the feeder gas to hydrogen and carbon. Iron oxide reacts with the carbon to form iron carbide, which then serves as nucleation sites for the nanotubes. Oxidation of C to CO or CO₂, however, may compete with the nanotube formation.

These observations explain the variability in the in situ carbon structure found in LiFePO₄ samples processed similarly, since iron oxides are common surface impurities. Anything more than trace oxidation of LiFePO₄ samples during synthesis is clearly undesirable, severely limiting the options for producing graphitic carbon this way. Instead, addition of small amounts of graphitization catalysts such as iron nitrate, ferrocene, or ferrocene derivatives along with PA during LiFePO₄ synthesis can be used to improve the carbon structure (Fig. 2). When iron nitrate is added, there is no increase in the amount of in situ carbon but H/C ratios are lowered and the rate behavior is improved to a limited degree. Addition of ferrocene results in both an overall increase in carbon content and a much lower H/C ratio, pressed pellet conductivities, as measured by AC impedance, increase [25], and rate capability is improved dramatically (Fig. 4). Again these effects can be attributed to carbon structure, as particle size and morphology is not significantly changed by the addition of the iron-containing species.

Modeling work by Srinivasan and Newman [31] shows that contact resistance between the porous electrode and the current collector is partly responsible for power limitations in LiFePO₄ cells. Coating the current collector on the cathode side with a thin conductive carbon coating can decrease the contact resistance and results in much better high-rate performance (Fig. 5).

The behavior at high rates of the LiFePO₄ used in the cells in Fig. 5 compares favorably to those of LiFePO₄ samples from several other sources [25] when cell design parameters are normalized [32]. However, further advances are still needed to achieve the high power required by HEV applications. The primary particle size of this material averages several hundred nanometers, and the particle size distribution is very wide. Interestingly, the high power performance is equivalent to, or

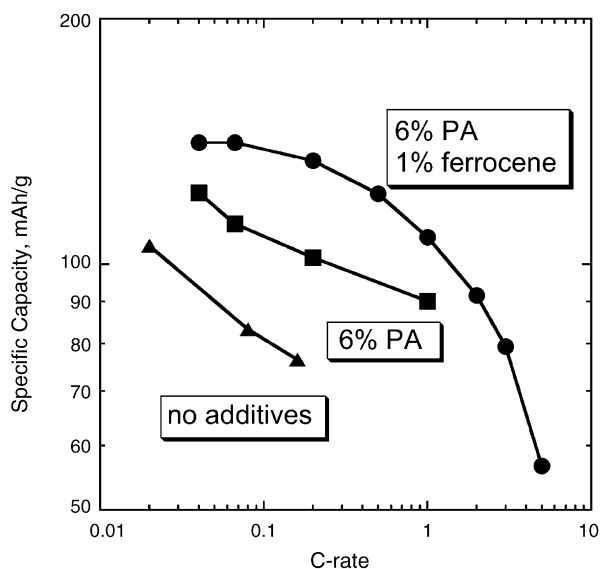


Fig. 4. Rate capabilities of electrodes containing LiFePO₄ samples processed with and without additives as indicated, in lithium cells at room-temperature. In situ carbon contents are 0.7% for the sample processed without additives, 0.76% for the sample processed with 6% PA, and 1.45% for that processed with 6% PA and 1% ferrocene.

somewhat better than that of samples from other sources with significantly smaller average primary particle sizes and narrower particle size distributions. This suggests that more progress can be realized just by narrowing the particle size distribution. It may not be absolutely necessary to engineer extremely small primary particles, which might have an adverse impact on tap density and exacerbate reactivity with electrolytic solutions. A narrower particle size distribution most likely can be achieved by better mixing; the presence of some large particles in current materials [25] suggests that carbon or carbon precursors, which inhibit grain growth, are not evenly distributed through-

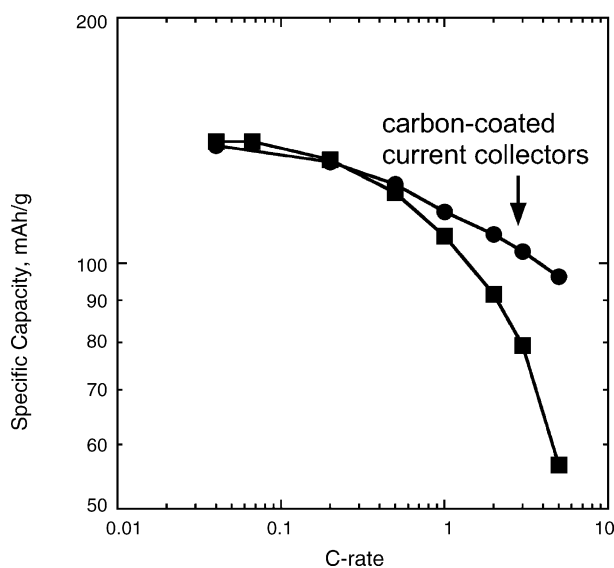


Fig. 5. Rate capabilities of electrodes containing LiFePO₄ processed with 6% PA and 1% ferrocene (1.45% C), with and without carbon-coated current collectors in lithium cells at room-temperature.

out the samples. At present, the optimum amount of carbon that allows maximal power capability without overly compromising energy density is unknown, but is certain to depend on particle morphology. A recent transmission electron microscopy/energy filtered imaging study of LiFePO₄ processed with ferrocene and PA shows that the carbon coating on primary particles is as thin as 2–5 nm [33]. It is not likely that carbon coats all the particles evenly in these samples, however. Better homogeneity of the carbon coating on LiFePO₄ particles may also lead to increased power capability. Future work in this laboratory will be directed towards these issues.

4. Conclusions

The electrochemical performance of LiFePO₄ is greatly enhanced when the structure of the in situ carbon covering the particles is improved. This may be achieved by adding small amounts of pyromellitic acid and graphitization catalysts such as iron nitrate or ferrocene during processing. The overall carbon content is still below 2 wt.% but the graphene content is higher and the H/C ratio is reduced compared to materials prepared without the additives. Further, advances may be realized when the particle size distribution of samples is narrowed and the coating coverage is made more homogeneous.

Acknowledgments

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