A High-Rate, Nanocomposite LiFePO$_4$/Carbon Cathode

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We describe here a new type of template-prepared nanostructured LiFePO$_4$ electrode, a nanocomposite consisting of monodispersed nanofibers of the LiFePO$_4$ electrode material mixed with an electronically conductive carbon matrix. This unique nanocomposite morphology allows these electrodes to deliver high capacity, even when discharged at the extreme rates necessary for many pulse-power applications. For example, this nanocomposite electrode delivers almost 100% of its theoretical discharge capacity at the high discharge rate of 3 C, and 36% of its theoretical capacity at the enormous discharge rate of 65 C. This new nanocomposite electrode shows such excellent rate capabilities because the nanofiber morphology mitigates the problem of slow Li$^+$-transport in the solid state, and the conductive carbon matrix overcomes the inherently poor electronic conductivity of LiFePO$_4$.
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Lithium-ion batteries are the power source of choice for portable electronics, a multibillion dollar market.[1] This outstanding commercial success has spawned great international interest in applying this technology to systems that demand higher power, such as the electric component of hybrid vehicles.[2] This would require new electrode materials that are less expensive, more energetic, and more environmentally friendly than the present ones. Of particular interest is the olivine-structured LiFePO$_4$ cathode developed by Goodenough and co-workers,[3] which offers several appealing features, such as a high, flat voltage profile and relatively high theoretical specific capacity (168 mAh g^{-1}), combined with low cost and low toxicity. However, the current designs of cells based on LiFePO$_4$ technology have not shown the ability to deliver high specific capacity at high discharge rates. For this reason, LiFePO$_4$ is currently not a promising electrode material for high-rate and pulse-power applications.

The discharge reaction for LiFePO$_4$ (Eq. 1) entails intercalation of Li$^+$ (from the contacting electrolyte phase) along with an equivalent number of electrons into the electrode material

$$FePO_4 + Li^+ + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} LiFePO_4 \qquad [1]$$
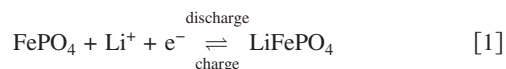
The rate capabilities of LiFePO$_4$ are limited primarily by its intrinsically poor electronic conductivity and by the low rate of Li$^+$ transport within the micrometer-sized particles used to prepare the battery electrode. A number of approaches have been proposed to improve this material's inherent poor electronic conductivity, including carbon coating[4] nanofibril textures,[5] optimized synthesis procedures,[6] and foreign metal doping.[7]

We describe here a new approach for preparing high rate-capability LiFePO$_4$ electrodes. This approach builds on the application of the template synthesis method for preparing nanofiber Li-ion battery electrodes.[8-12] However, the method was modified such that the template-prepared LiFePO$_4$ nanofibers are mixed with carbon particles, and coated by thin carbon films, to yield a nanocomposite LiFePO$_4$/carbon matrix. As we have shown previously,[10-12] the nanofiber morphology mitigates the slow Li$^+$-transport problem, because the distance Li$^+$ must diffuse within the electrode material is minimized. The carbon matrix obtained with this new template-based method obviates the poor electronic conductivity problem. These nanocomposite LiFePO$_4$/carbon electrodes can deliver a capacity of 150 mAh g^{-1} at a rate of 5 C (C = h^{-1})[7] and maintains a substantial fraction of the theoretical capacity even at rates exceeding 50 C. To our knowledge, performance at this level has never been achieved by other types of LiFePO$_4$.

Experimental

Materials and synthesis.— The sol-gel method developed by Croce et al.[13] was employed for the synthesis of the electrode precursor solution. Accordingly, LiOH monohydrate (Aldrich), ferric nitrate nonahydrate (Fisher), ascorbic acid (Fisher), phosphoric acid, and ammonium hydroxide were used to create the LiFePO$_4$ precursor solution. The template membranes were commercially available polycarbonate filters (Poretics). Pt foil (2.5 × 1.5 × 0.025 cm, 99.99% purity, Aldrich) was used as the current collector. LiClO$_4$ (Aldrich), ethylene carbonate (Aldrich), diethyl carbonate (Aldrich) were used as received for preparing the electrolyte.

An approximately 1 cm^2 piece of the polycarbonate filter was immersed in a precursor solution of 1 M LiFePO$_4$ in water for 24 h. This solution was synthesized with ferric nitrate, lithium hydroxide, and phosphoric acid in proportions for a 1:1:1 molar ratio. Ascorbic acid, in equimolar ratio to the total metal (Li$^+$ plus Fe^{2+}) content, aided the synthesis by forming a complex with the iron, and ammonium hydroxide was used to raise the pH to ∼2. The impregnated template was then attached to a Pt current collector and dried in air at 80°C for 10 min. A 10 μL drop of precursor solution was placed on top of the dried filter to increase the amount of active material in the sample. It was dried again under the same conditions. This assembly, template intact, was heated in a reducing atmosphere of flowing Ar/H$_2$ gas (95/5 %). The temperature was slowly taken over the course of 4 h from 250 to 650°C and held there for 12 h. This procedure yields the Fe(II) oxidation state necessary for LiFePO$_4$ and decomposes the template into the carbon necessary for improved conductivity.

Instrumental methods.— A field-emission gun-scanning electron microscope (FEG-SEM) JEOL JSM 6335F instrument was used to obtain SEM images of the electrode. The nanostructured electrodes on Pt foil were prepared for imaging by attaching them to a SEM stub by conductive copper tape. No conductive metal sputtering was required for the composite electrodes, but a thin Au/Pd sputtering was applied to the LiFePO$_4$ (Fig. 1c) prior to imaging. The XPS studies were performed on a Kratos XSAM 800 spectrometer with Al-Kα exitation (180 W). The sample, mounted onto a stainless steel sample stub, was inserted into the sample analyzer chamber by means of a quick insertion probe, and spectral acquisition commenced after the pressure decreased to 5 × 10^{-9} Torr. High resolution C 1s spectra were recorded at a take-off angle of 75° relative to the sample surface. Data analysis was done by using the DS 800

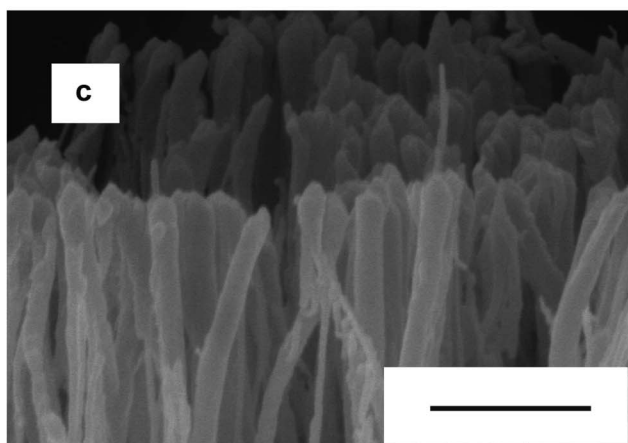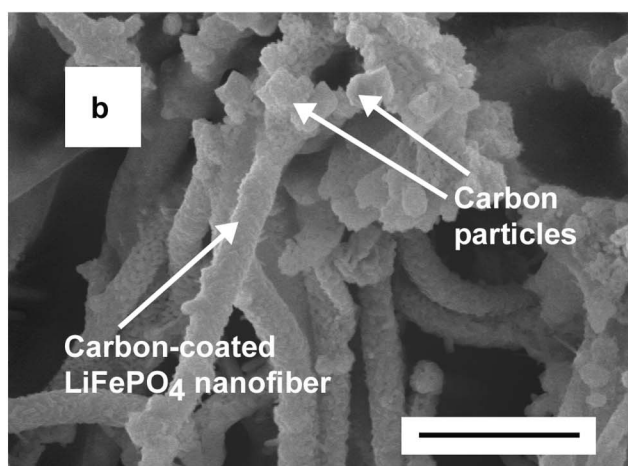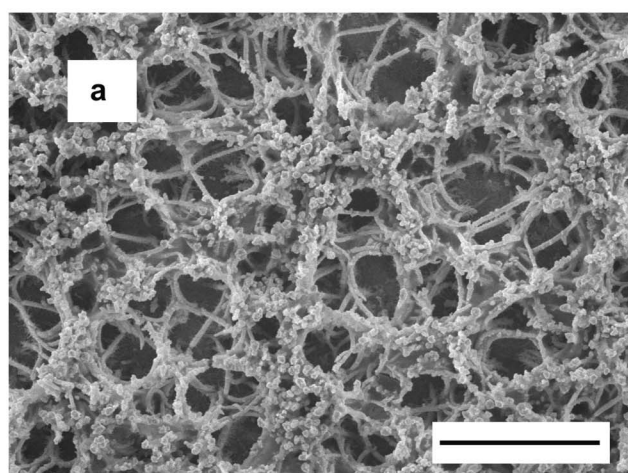**Figure 1.** Scanning electron micrographs: (a) Lower magnification image of the nanocomposite LiFePO$_4$/carbon electrode. Scale bar = 12 μm. (b) Higher magnification image of the nanocomposite LiFePO$_4$/carbon electrode. Composite fiber diameter is 350 nm. Scale bar = 1.5 μm. (c) Image of LiFePO$_4$ electrode synthesized by template dissolution method (absence of carbon). LiFePO$_4$ fiber diameter is 170 nm. Scale bar = 1 μm.

Figure 2. A schematic of the synthesis of the LiFePO$_4$ nanocomposite electrode. The last panel represents the carbon coating (shaded) encasing the LiFePO$_4$ nanowires (striped.)

software package. Peak positions were all referenced to 70.9 eV for the Pt 4f$_{7/2}$ peak (literature value for metallic platinum used as sample support).

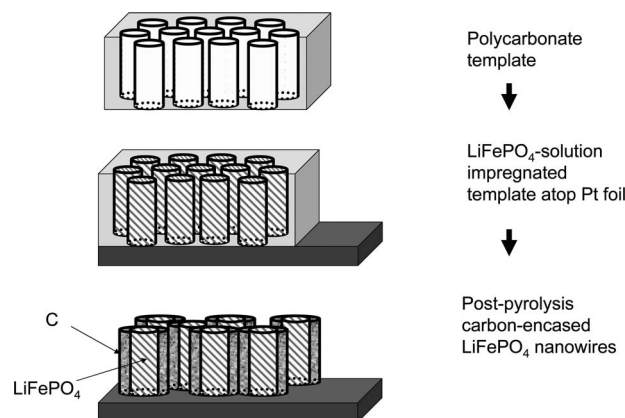*Electrochemistry.*— Cyclic voltammetric and constant current charge/discharge experiments were performed in a three-electrode cell using a Solartron 1287 potentiostat, driven by the CorrWare software package. The electrolyte for these experiments was 1 M LiClO$_4$ in ethylene carbonate:diethyl carbonate (3:7 v/v). The nanostructured LiFePO$_4$/carbon was the working electrode and lithium ribbon was the reference electrode and counter electrode. Potentials are reported *vs.* the Li/Li$^+$ reference. The experiments were performed in the inert atmosphere of a glove box filled with argon gas.

Results

Commercially available (Poretics) polycarbonate filters were used as the templates. Two different templates were used. For the electrochemical studies we wanted a template with small diameter pores so that correspondingly small diameter nanofibers of LiFePO$_4$ would be obtained. For this reason we used a template with nominally 50 nm diam pores for the electrochemical studies. This template was 6 μm thick and had a pore density of 6×10^8 pores per cm^2 of surface area. To obtained detailed images of the morphology of the nanocomposite structure we found it prudent to use a template with nominally 100 nm diam pores. The larger LiFePO$_4$ nanofibers obtained from this template are more easily imaged with scanning electron microscopy. This template was also 6 μm thick and had a pore density of 4×10^8 pores per cm^2.

A sol-gel method developed by Croce et al.[13] (see Experimental section) was used to deposit the LiFePO$_4$ nanofibers within the pores of this template. In all of our previous examples of template-synthesized nanofiber electrodes[10-12] after synthesis of the nanofibers the template would be totally removed to yield the nanofibers protruding from an underlying current collector surface like the bristles of a brush. For the LiFePO$_4$ nanofibers prepared here we instead pyrolyzed the polycarbonate in a reducing Ar/H$_2$ environment at a temperature of 650°C (see Experimental section). This yields graphitic carbon particles intimately mixed with the LiFePO$_4$ nanofibers, and thin carbon films that coat these fibers. A schematic of this process is shown in Fig. 2.

A lower magnification scanning electron microscopic (SEM) image of the resulting LiFePO$_4$/carbon nanocomposite electrode is shown in Fig. 1a. Because of the relatively low porosity of the template, there is substantial void volume, but in analogy to our prior nanofiber electrodes of this type,[10-12] the LiFePO$_4$ nanofibers can be seen crossing through this void space. Higher magnification images (Fig. 1b) show that there are carbon particles dispersed through this matrix and that the LiFePO$_4$ nanofibers are coated with thin carbon films. To prove that these fibers are coated with carbon films, we prepared fibers in the same template, but instead of then pyrolyzing the template, we simply removed it quantitatively by burning it away in O$_2$ plasma. Hence, in this sample the fibers are not coated with carbon films.[10-12] An image of these fibers is shown
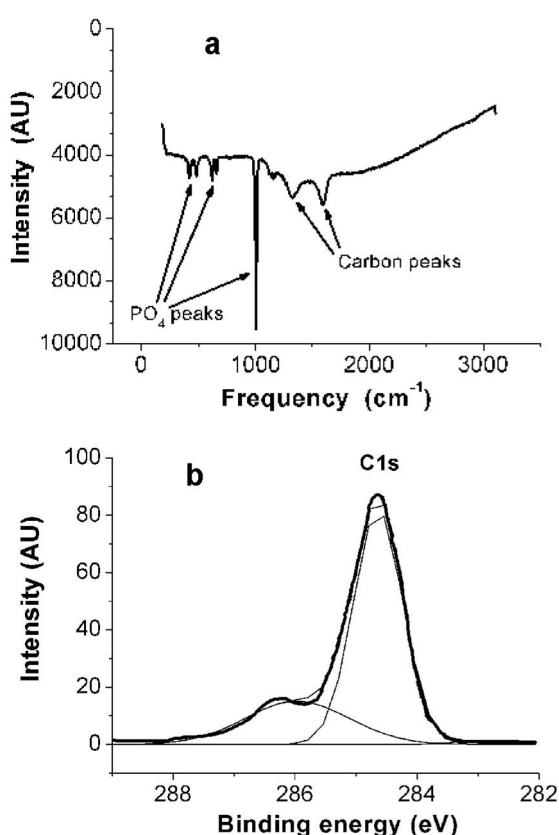
Figure 3. (a) Raman spectrum for the nanocomposite LiFePO$_4$/carbon electrode. The peaks are assigned to PO$_4^{3-}$ (from LiFePO$_4$) and carbon (from pyrolysis of the template membrane). (b) XPS C 1s peak for the carbon in the nanocomposite electrode. Relative peak areas show that the amphorous form is dominant ($\sim$80%), but graphitic carbon is also present ($\sim$20%).

Figure 4. Electrochemistry: (a) Cyclic voltammogram for the nanocomposite LiFePO$_4$/carbon electrode prepared using a template with 50 nm diam pores. Scan rate = 0.1 mV s^{-1}. (b) Constant-current discharge curve for the nanocomposite electrode at a discharge rate of 3 C.

in Fig. 1c. The fibers from the pyrolyzed membrane (Fig. 1a and b) have a textured surface morphology and have a larger diameter than the fibers from the plasma-removed membrane (Fig. 1c). Both the larger diameter and the textured surface are due to the carbon coating surrounding the fibers from the pyrolyzed membrane.

The presence of carbon in this matrix was confirmed by X-ray diffraction analysis, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The X-ray diffraction data (not shown) exhibit the major peaks of LiFePO$_4$ at 2θ of 20.775°, 25.562°, and 29.706°, as well as the d$_{002}$ peak of carbon thin film[14] at 2θ = 26.381°. Figure 3a shows the Raman spectra of the nanocomposite LiFePO$_4$/carbon electrode. The most intense peak (centered around 1000 cm^{-1}) and others at the lowest frequencies correspond to the PO$_4$ stretching modes of LiFePO$_4$. The bands at 1350 and 1580 cm^{-1} are assigned to carbon.[15]

The presence of carbon was also confirmed by XPS analysis (Fig. 3b). The high resolution C 1s spectrum may be fitted to three peaks with binding energies of 283.2 ± 0.5, 284.7 ± 0.3, and 286.0 ± 0.3 eV. According to Miller et al.,[16] the lowest binding-energy peaks may be assigned to graphitic (283.2 eV) and amorphous (284.7 eV) carbon. The predominance of the 284.7 eV peak indicates that most of the carbon present is amorphous; this is confirmed by the X-ray diffraction data. The peak at the highest binding-energy (286.0 eV) is due to oxygen-containing surface functional groups. Oxygen functional groups are nearly always observed on carbon surfaces that have been exposed to air.[16]

We estimated the weight percent of carbon in the composite electrode gravimetrically using an Ultra-Micro-Balance SC2 (Satorius). LiFePO$_4$ nanofibers were synthesized within the pores of the polycarbonate template on a 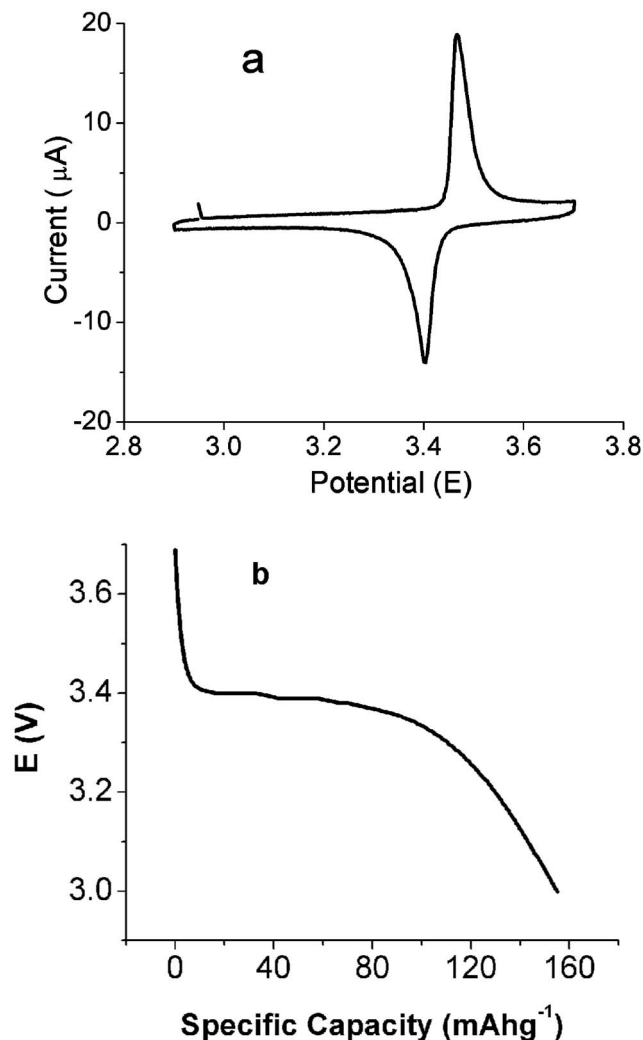Pt current collector, and the polymer was pyrolzyed as described previously. The mass of this composite, corresponding to the masses of the Pt current collector, the nanofibers, and the carbon, was obtained. This composite was then heated in air at 600°C for 30 min to burn off the carbon, and the mass was measured again. The difference between these two masses is the mass of carbon in the composite. Replicate analyses on four identically prepared samples gave a carbon content of 7 ± 4% in the nanofiber/carbon composite.

This unique LiFePO$_4$/carbon nanocomposite electrode should be ideally suited for high rate applications because the distance that Li$^+$ must diffuse in the electrode material is limited to the radius of the nanofibers[10-12] and because the carbon matrix should provide for good electronic conductivity through the composite. This was confirmed experimentally via electrochemical characterization of these electrodes. The electrochemical studies were done on electrodes prepared in templates with 50 nm diam pores.

Cyclic voltammograms (CVs) for the nanocomposite electrode show reversible waves centered at 3.5 V associated with the reduction and reoxidation of the LiFePO$_4$ (Fig. 4a).[13,17] The difference in peak potentials (ΔE_p) for this nanostructured electrode is 60 mV (Fig. 4a). This may be in contrast to CVs for conventional, non-nanostructured, LiFePO$_4$ electrodes, which at comparable scan rates and in comparable electrolyte solutions show ΔE_p > 200 mV.[13,17]
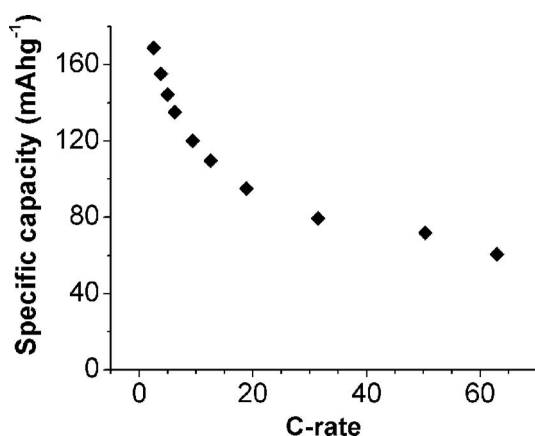
Figure 5. Specific capacity *vs* C rate for the nanocomposite LiFePO$_4$/carbon electrode prepared using a template with 50 nm diam pores.

This clearly shows that our nanostructured LiFePO$_4$ electrodes lack a resistive component that is present in the conventional electrodes. This verifies the major premise of this work, that the conductive carbon matrix overcomes the inherently poor electronic conductivity of LiFePO$_4$.

While the mass of the LiFePO$_4$ in the composite was determined gravimetrically (see above), we have found that not all of this LiFePO$_4$ is electroactive. This is because portions of the LiFePO$_4$ in the composite lose ohmic contact with the current collector during pyrolysis. For this reason we determined the electroactive mass from the area under voltammetric waves like those shown in Fig. 4a. This analysis requires that 100% of the electroactive material is oxidized during the forward scan and reduced again during the reverse scan, i.e., that diffusion in the fibers is finite rather than semi-infinite. Because of their small diameters, this is always the case for low scan rate voltammograms of our template-synthesized nanostructures.[10] The lack of diffusional tailing in the voltammogram in Fig. 4a shows that this is also the case for the nanostructured composite electrodes studied here. Also, we performed an independent experiment to determine the ratio of electroactive LiFePO$_4$ to total mass present. This was accomplished by dissolving the bare-LiFePO$_4$ nanowires in HNO$_3$ (postelectrochemistry) and analyzing the resulting solution for Fe-ion content. From this concentration, it was determined that 40% of the mass of LiFePO$_4$ is electroactive.

The constant-current discharge curve (lithium insertion, Eq. 1) for the nanocomposite electrode shows the flat voltage plateau centered at 3.5 V, characteristic of LiFePO$_4$ (Fig. 4b).[4,13,17] At the lowest discharge rate used (3 C), the specific capacity for the composite is 165 mAh g^{-1}, essentially identical to the maximum theoretical capacity, 168 mAh g^{-1}. While capacity falls off with increasing discharge rate (Fig. 5), the electrode retains 36% of its theoretical

capacity at discharge rates as high as 65 C. There are no other examples in the literature of LiFePO$_4$ being discharged at such large rates.

Conclusions

We have described here a new type of template-prepared nanostructured LiFePO$_4$ electrode. This electrode is a nanocomposite consisting of nanofibers of the LiFePO$_4$ electrode material mixed with an electronically conductive carbon matrix. This unique nanocomposite morphology allows these electrodes to deliver high capacity, even when discharged at extreme rates necessary for many pulse-power applications. We are currently working toward developing a commercially viable route for preparing such nanocomposite electrodes.

Acknowledgments

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