Double Carbon Coating of LiFePO₄ as High Rate Electrode for Rechargeable Lithium Batteries

By Sung Woo Oh, Seung-Taek Myung, Seung-Min Oh, Kyu Hwan Oh, Khalil Amine, Bruno Scrosati,* and Yang-Kook Sun*+

Lithium iron phosphate, LiFePO₄, is one of the most promising positive electrode materials for next-generation lithium-ion batteries. It possesses several advantages, including low price, environmental compatibility, and intrinsic thermal safety.\[1,2\] Due to these favourable properties, many academic and industrial laboratories have devoted considerable effort to improve LiFePO₄ electrode performance, in terms of rate capability and lifetime, to a practical level.\[3–9\]

Past efforts have used various carbon sources to coat LiFePO₄ particles. These sources include sucrose,\[10–14\] poly(ethylene glycol),\[15,16\] citric acid,\[17\] poly(vinyl alcohol),\[18,19\] and ascorbic acid.\[20\] An important step ahead was marked by Xie et al.,\[21\] who showed that real success in terms of improving LiFePO₄ electrochemical performance can only be obtained by using π-bond sp³ character after carbonization.\[22\] We showed that material so prepared had a 6-μm spherical particle size, a tap density of 1.5 g cm⁻³, and promising electrochemical performance. This single-carbon-coating material was composed of micrometer-scale secondary particles containing nanoscale carbon-coated primary particles; this morphology provided interconnected open pores that favor electrolyte absorption and significantly reduce the diffusion path of the lithium ions. This feature, combined with the high tap density, resulted in electrodes having high volumetric energy density and rate capability. Here we report a double coating process that greatly improves the uniformity of the carbon coating on both the primary and secondary LiFePO₄ particles. In coin-type cell tests with electrodes composed of this material, the specific capacity, rate capability, and volumetric energy density reached levels rarely met by any previous materials of the same kind.

Figure 1 shows a schematic drawing of the philosophy behind, and the steps involved in, our refined process for the preparation of advanced double-coated LiFePO₄ electrodes (see also "Experimental"). First, secondary particles were formed by annealing a FePO₄⋅xH₂O-sucrose blend precursor at 500 °C. Carbon-coated nano-sized FePO₄ particles (200–300 nm) were obtained in this step. To produce high porosity and carbon networking, we mixed the particles with Li₂CO₃ for calcination under an argon/hydrogen (96/4 vol%) atmosphere, we obtained nanoporous microscale LiFePO₄ particles with high tap density. Figure 1 also illustrates the material formed during the synthesis step (see Figure 1, Supporting Information, for a comparison between the material formed during the single carbon coating process\[22\] and the new double carbon coating process described in this work). The precursor powders assumed a dark-grey colour during the second step, suggesting total carbonization of sucrose and a full coverage of the resulting carbon on the dehydrated FePO₄ surface.

Figure 2 shows the scanning electron microscopy (SEM) images obtained from a FePO₄ sample after the first synthesis step. The spherical morphology of the particles (Figure 2a) and their uniform distribution throughout the sample (Figure 2b) are readily evident. Figure 2b also indicates a particle size of about 8 μm. The specific surface area and the pore volume were estimated to be 6.71 m² g⁻¹ and 7.93 × 10⁻² cc g⁻¹, respectively. We used electron energy loss spectroscopy (EELS) to confirm the presence of carbon on the FePO₄ secondary particle surface. Figure 2c and 2d show a cross-sectional transmission electron microscopy (TEM) image and the corresponding EELS map, respectively, of the FePO₄ sample. These images reveal that the FePO₄ secondary particles are composed of small (about 200 nm) primary particles with pores, and that the carbon layer derived from the carbonization of sucrose indeed covers the primary particle surface with uniform thickness.

The EELS image also demonstrates an open network of interconnected nanosized pores evenly distributed throughout.
the interior of the particles. This network supports the validity of our synthesis approach that leads to carbon-coated FePO₄ particles with microscale spherical morphology. The amount of carbon was determined to be about 0.5 wt%, as confirmed by elemental analysis.

The dehydrated carbon-coated (sucrose source) powder was calcinated with lithium carbonate and pitch to form the final double-coated LiFePO₄ material (see Figure 1). Figure 2S shows the x-ray diffraction (XRD) pattern for this material. All the peaks can be indexed as the olivine LiFePO₄ phase without any observable secondary peaks over the entire pattern. Table 1S reports the Rietveld refinement of the XRD data based on the orthorhombic (Pnma space group) crystal system, and Table 2S provides its lattice parameters. The observed and calculated XRD patterns agree well in Figure 2S, indicating that all elements are located in the sites listed in Table 1S.

Figure 3 shows the cross-sectional SEM images of the LiFePO₄ sample obtained from a focused ion beam cut. The particles have a spherical morphology with an average particle size of 8 μm (Figure 3a). Numerous surface pores are evident in the cross section of the magnified SEM image (Figure 3b). This finding confirms that the nanoporous internal structure of the carbon-coated LiFePO₄ was maintained during the calcination. The figure also shows that the pores are extended from the surface into the particle bulk, suggesting that the formed pores have wide open channels. The measured tap density is 1.5 g cm⁻³; this high tap density is of great importance to the transportation application in lithium batteries, since it guarantees low reactivity and a high volumetric energy density.

Because of the difficulty of detecting the carbon coating with SEM, the synthesized LiFePO₄ powders were examined by TEM-EELS. Figure 3c supports the SEM image of Figure 3a and 3b in concluding that our LiFePO₄ has a nanoporous internal structure, formed by nanosized primary particles having an average size of 200–300 nm, i.e., a value similar to that of the pore size. Smooth and thin carbon coating layers are evident near the edges of the primary particles (see Figure 3d).

The carbon content in the coated LiFePO₄ samples was estimated by elemental analysis to be 3.1 wt%. The sample electronic conductivity, measured by a four-probe method, was 8.8 × 10⁻² S cm⁻¹ at room temperature. This high conductivity, combined with the high tap density, indicated that these newly formed LiFePO₄ samples have almost perfect properties for achieving successful application as advanced electrodes in lithium cells.

Figure 4 reports the galvanostatic charge-discharge performance of a Li/C-LiFePO₄ cell, and the results confirm the promise of the above material characterization. The cell exhibits the typical voltage plateau along 3.5 V (vs. Li) associated with...
Fe ion dissolution. The control of iron dissolution is an important feature for LiFePO$_4$ electrodes. We have further checked this key parameter by storing two samples, i.e. a “standard”, carbon single-coated LiFePO$_4$ and the double-coated LiFePO$_4$ described in this work, in 20 cc of a solution of 1M LiPF$_6$ in an ethylene carbonate–diethyl carbonate, EC-DEC, mixture for one week at 60 °C. Inductively Coupled Plasma (ICP) tests showed that the amount of dissolved Fe passed from 55 ppm in the former case to 33 ppm in the case of the carbon double-coated sample. This result demonstrates that our material does indeed experience a minor iron dissolution even at 60 °C, as also confirmed by the excellent and stable response shown by lithium ion cells, formed by combining a MCMB anode with our double-coated cathode in the LiPF$_6$ EC-DEC electrolyte, when repeatedly cycled at 60 °C.

**Figure 5** shows the voltage profiles and the capacity delivery of the lithium cell using our double-coated LiFePO$_4$ cathode. The cell was charged at a constant current of 17 mA g$^{-1}$ (corresponding to 0.1 C rate) for each charging step and then discharged at progressively increasing rates. The cell performance was excellent: up to 10 C (1,700 mA g$^{-1}$), the delivered capacity was still 68% of the theoretical capacity, demonstrating exceptionally high conversion of the active material. In addition, the voltage profiles show a narrow gap between charge and discharge, indicating very low electrode resistance. This uniquely low electrode resistance was confirmed by impedance spectroscopy (data not reported). We believe that the particular morphology of our material, which confers upon the electrode high electronic conductivity and facile electrolyte absorption through the open pores, accounts for the observed high capacity. This unique morphology also assures high charge-discharge reversibility at temperatures from −20 °C to 60 °C (see Figure 4b and Figure 3, Supporting Information): no detectable decline in capacity was observed over 50 charge-discharge cycles at 25 °C, and it was possible to deliver high capacity at low temperature (0 °C and -20 °C) with good capacity retention. High capacity retention (94%) at 60 °C also implies that the material does not seriously suffer from
theoretical value, and even at 20 °C (3,400 mA g⁻¹), the cell was able to deliver substantial capacity, i.e., 47% of theoretical.

Another important feature of our carbon-double-coated LiFePO₄ electrode is its high tap density, 1.5 g cm⁻³. This value is much greater than those obtained for common (nano-sized) LiFePO₄ electrode morphologies, which are limited to a maximum of 1.0 g cm⁻³. As well known, a high tap density is a very welcome property for electrode materials in lithium batteries since it reflects high volumetric energy density. Indeed, on the basis of the cathode tap density and the charge-discharge response above discussed, we estimated for our Li/LiFePO₄ cell a volumetric energy density of 820 Wh m⁻³.

The results of this work clearly demonstrate that the double-carbon-coated LiFePO₄ electrode has highly desirable properties: a specific capacity approaching the theoretical limit, stable cycle life, exceptional rate capability, and a high tap density. This combination is not available in common LiFePO₄ cathode materials and leads us to believe that our double-carbon-coated LiFePO₄ electrode is a serious candidate for the development of high-performance, advanced lithium batteries directed to the hybrid vehicle and electric vehicle markets.

**Experimental Section**

**Synthesis of double-carbon-coated LiFePO₄**: Fe(NO₃)₃ 9H₂O and H₃PO₄ were first separately dissolved in distilled water with a molar ratio of 1:1. Then, sucrose was dissolved in an aqueous solution of Fe(NO₃)₃ 9H₂O at 0.2 to 1 molar ratio of Fe(NO₃)₃ 9H₂O. The three aqueous solutions were pumped into a continuously stirred tank reactor (capacity of 4 L). An aqueous NH₄OH solution was also pumped into the reactor to control the solution pH to 5. After proper nucleation and the particle growth of the precursor, the concentration (2 M), pH (2), temperature (50 °C), and stirring speed (1000 rpm) of the resulting mixture were precisely controlled throughout the synthesis process. The resulting carbon-coated FePO₄ hydrate powders were filtered, washed, and vacuum-dried at room temperature, then heat-treated at 500 °C for 10 h in an Ar/H₂ (96/4 in volume percent) atmosphere to obtain crystalline anhydrous FePO₄ powders. These powders were mixed with a stoichiometric amount of Li₂CO₃ and with pitch to provide the lithium source and the second carbon-coating source, respectively. The resulting material was calcined for 15 h at 750 °C in an Ar/H₂ (96/4 in volume%) mixture.

**Chemical physical characterization**: The synthesis products were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), the Brunauer–Emmett–Teller (BET) method, and elemental analysis for the control of their structure, morphology, surface area, and composition. Powder XRD analysis was performed with a Rint-2000 Rigaku instrument using Cu-Kα radiation. The FULLPROF Rietveld program was used for the powder diffraction pattern refinement. The SEM and TEM images were obtained with JSM 6400 and JEOL 2010 systems, respectively. The BET studies used an ASI-4 M system. The amount of carbon in the final products was determined by an EA110 system.

**Electrochemical characterization**: The electrochemical properties of the carbon-double-coated LiFePO₄ were measured in CR2032 coin-type cells. The cells were formed using a Li metal negative electrode, an electrolyte of 1M LiPF₆ in a 1:1 ethylene carbonate and diethyl carbonate mixture, and a LiFePO₄ positive electrode. The latter was prepared by casting, on an aluminum substrate, a slurry of LiFePO₄ powders (85 wt%), carbon black (electronic conductive additive, 7.5 wt%), and polyvinylidene fluoride (binder) in N-methylpyrrolidinone (7.5 wt%). The cells were tested in terms of galvanostatic charge-discharge cycles run at various rates and at room temperature. The cycling tests were controlled and monitored by automatic battery cyclers.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This research was supported by WCU (World Class University) program through the Korea Science and Engineering Foundation by Education, Science, and Technology (R31-2008-000-10092) and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2009-0092780).

Received: November 25, 2009
Revised: February 23, 2010
Published online: July 20, 2010