LiFePO$_4$ Nanoparticles Embedded in a Nanoporous Carbon Matrix: Superior Cathode Material for Electrochemical Energy-Storage Devices

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Considerable attention has been focused on electric vehicles (EVs) and hybrid electric vehicles (HEVs) in an attempt to relieve the pressure from increased oil prices and environmental issues. High-performance energy-storage devices with both high energy and high power densities are essential to such vehicles. Amongst all the commercially available devices, lithium-ion batteries (LIBs) currently represent the state-of-the-art technology in high-energy batteries, and they have occupied a prime position in the marketplace to power portable electronic devices, such as laptops, personal digital assistants, and cellular phones.[1–3,6,7] However, the mass and charge transport, as confirmed by recent work on single crystals,[18] which is a good electronically conducting anode material, the nanostructure design of electrode materials for high-power and high-energy lithium batteries by combining the advantages of nanometer-sized particles of active materials into a nanoporous carbon matrix, [30] needs to be mentioned. However, the lithium sites,[10] ii) Surface coating or admixing with electronically conductive materials (carbon,[21–26] Ag,[21] and conducting polymers) has also been studied. This technology has been widely used for improving the electronic conductivities of poor electronically conductive electrode materials. However, perfect surface coatings and desired mixtures are often very difficult to achieve, hence the power-performance enhancement of such electrode materials is still limited. iii) Decreasing the particle size may also improve the transport issues. According to the diffusion formula $t = L^2/2D$ (where $t$ is the diffusion time, $L$ is the diffusion distance, and $D$ is the diffusion coefficient), reducing the particle size can significantly shorten the diffusion time of Li in LiFePO$_4$, resulting in a much enhanced power performance. However, nanometer-sized LiFePO$_4$ usually exhibits a poor cycling performance,[17] is difficult to mass produce, and there are also handling problems in terms of separation, admixing with carbon black, and electrode preparation.[18]

Recently, Maier and coworkers[8,9] reported an optimized procedure intended for both high-power and high-energy performance of electrode materials using mixed conducting 3D networks. These materials constitute a nanometer-sized network composed of mesopores filled with electrolyte and electronically conductive coating agents (RuO$_2$, C–RuO$_2$), together with a microscopic network superimposed on the nanoscopic network and carbon black. In the case of carbon, which is a good electronically conducting anode material, the above concept of transforming it into a nanoporous material can be easily realized, as it is already a mixed conducting 3D network. This has been corroborated by recent work on porous carbon monoliths showing a superior high-rate performance.[29] In this communication, we propose and realize an alternative optimized nanostructure design of electrode materials for high-power and high-energy lithium batteries by combining the advantages of nanoporous carbon and nanometer-sized active particles. Superior electrode materials are obtained by dispersing nanometer-sized particles of active materials into a nanoporous carbon matrix (hereafter abbreviated as NP@NPCM). In view of its facility in terms of synthesis and porous structure, the design is superior to either directly coating nanoparticles with thin carbon layers or inserting nanoparticles into a nonporous carbon matrix. In the latter case, the relevant work of Derrien et al., who reported on a Sn–C nanocomposite anode, that is, Sn nanoparticles dispersed in a carbon matrix,[30] needs to be mentioned. However, their design was not meant for achieving high power because of...
the nonporous carbon matrix used. Furthermore, their design has thus far not been extended to cathode materials. The power of our concept is demonstrated by the synthesis of a nanocomposite of LiFePO₄ nanoparticles embedded in a nanoporous carbon matrix (hereafter abbreviated as LFP-NP@NPCM), which can be fully charged or discharged within a period of less than 30 s, similar to a supercapacitor, but with more energy density. This nanocomposite combines the advantages of high power, resulting from nanometer-sized LiFePO₄ particles because of the decreased Li diffusion time in the crystal lattice, and manageability of the microscale composites. In this nanocomposite, the electronically conducting nanoporous carbon matrix with mesopores filled by electrolyte can be considered not only as a mixed conducting 3D network that allows both Li⁺ and e⁻ to migrate and reach each LiFePO₄ nanoparticle, but also as an electrolyte container for high-rate charging/discharging. It is because of this dual functional nanoporous carbon network and the nanometer-sized LiFePO₄ particles that the LFP-NP@NPCM nanocomposite shows a superior high power/energy capability when used as cathode material both in LIBs and supercapacitors.

The LFP-NP@NPCM nanocomposite was synthesized by a facile method combining both a sol–gel synthesis procedure and a solid-state reaction synthesis route. Pluronic F127, a block copolymer, was employed as a nanopore-forming agent for obtaining the nanoporous carbon matrix. Figure 1a shows the X-ray diffraction (XRD) pattern of the as-obtained LFP-NP@NPCM nanocomposite. All intense peaks in the spectrum can be well indexed to orthorhombic LiFePO₄ (JCPDS Card No. 40-1499, space group Pmnb(62)), except for a small diffraction peak at about 30.3°, corresponding to Fe₂P₂O₇. The mean crystallite size of LiFePO₄ is 8 nm, estimated from the widths of the major diffraction peaks of (020), (011), and (004) by Scherrer’s formula. No obvious peaks corresponding to graphite are found in the XRD pattern, indicating the carbon matrix has mesopores of about 3.8 nm and 10 nm in diameter, which is consistent with the high-magnification TEM observations (Fig. 2b).

In order to test the potential application of the LFP-NP@NPCM nanocomposite in high-power LIBs, we investigated its electrochemical performance with respect to Li insertion/extraction. Since the capacity contribution from the carbon matrix is negligible between the voltage limits of 2.2 and 4.2 V (vs. Li⁺/Li) used in our experiments, we only include the mass of active LiFePO₄ when calculating the specific capacity of the LFP-NP@NPCM composite. Figure 3a shows the charge–discharge profiles of the initial 15 cycles for the nanocomposite at a current rate of C/9 (completing the discharge or charge process in 9 h). It can be seen that the polarization between the charge and the discharge plateaus is greatly reduced to 60 mV from 180 mV. The results are consistent with the gradually increasing anodic/cathodic current and the gradually reduced overpotential between the two peak potentials in the initial cyclic voltammograms (see Supporting Information, Fig. S3). These phenomena have been discussed in detail in the literature and can be attributed mainly to a progressively increased active surface area of LiFePO₄ for the electrochemical reaction resulting from the gradual penetration of electrolyte into the particles’ interior. The more remarkable exhibition of this phenomenon in the LFP-NP@NPCM nanocomposite is probably due to the very
allowing for effective contact between embedded LiFePO₄ carbon matrix, which finally serves as an electrolyte container for novel and superior electrochemical energy-storage devices with both high-power and high-energy densities (inset of Fig. 3c).

Another excellent property of the LFP-NP@NPCM nanocomposite is the superior cycling performance. The discharge capacity loss is less than 3% over 700 cycles at a rate of 1.5 C (Fig. 3d). The Coulombic efficiency (calculated from the discharge capacity/charge capacity) always approaches 100%, as shown in the inset of Figure 3d. In addition, the stable cycling properties imply that the nanoporous carbon matrix provides not only sufficient Li⁺ and e⁻ transport but also an elastic buffer for releasing the strain on/from LiFePO₄ during the lithium insertion/extraction process. It is worth noting that the LFP-NP@NPCM nanocomposite shows quite good contact with the carbon black additive to form a mixed conducting 3D network on the microscale level⁸ (see Supporting Information, Fig. S5). Furthermore, the nanocomposite has also been shown to work without the addition of carbon black (see Supporting Information, Fig. S6). These electrochemical results demonstrate that the LFP-NP@NPCM nanocomposite is a superior cathode material for LIBs, with high power/energy capabilities and long cycle life.

In order to understand the superior electrochemical performance of the LFP-NP@NPCM nanocomposite, we need to closely study the charge–discharge curves. Taking the discharge curve at a current rate of C/9 (inset of Fig. 4a) as an example, there are two main parts contributing to the total discharge capacity. One is the plateau capacity (region I), at a voltage of about 3.4 V versus Li⁺/Li; the other is the sluggish slope capacity (region II) between 3.4 V and 2.2 V. This type of discharge profile has already been observed in many systems with LiFePO₄/carbon composites and (or) nanometer-sized LiFePO₄, but the sluggish slope is different from the abrupt slope reported in the typical discharge curves of micrometer-sized LiFePO₄.⁹,28 For region I, the discharge plateau at about 3.4 V obviously represents the biphasic reduction reaction from FePO₄ to LiFePO₄ (the lithium intercalation process into the crystal lattice), as has generally been accepted.¹³ For region II, the origin of the sluggish slope below the voltage plateau is still not clear. As shown in Figure 4a, the capacity of region I (C₁) decreases almost linearly with increasing discharge rates, demonstrating that this lithium intercalation process may be a dynamics-controlled process, while the capacity of region II (C₁i) first decreases with a slope similar to that of the capacity of region I at lower discharge rates (smaller than 20 C), and then is almost constant (about 10 mA h g⁻¹) at higher discharge rates (larger than 20 C). This indicates that an energetically favored lithium-storage process (not a kinetic phenomenon) might be involved in region II.¹⁰ Therefore, we speculate that the sluggish slope might also partly correspond to an interfacial Li storage process similar to that reported for sluggish penetration process of electrolyte into the nanoporous carbon matrix, which finally serves as an electrolyte container allowing for effective contact between embedded LiFePO₄ particles and the electrolyte during charge/discharge operations.²⁸ Note that all the electrochemical results discussed refer to the stable performance obtained after several initial cycles. Figure 3b and 3c shows the outstanding high-power and high-energy performance of the LFP-NP@NPCM nanocomposite (also see Supporting Information, Fig. S4). The results clearly show that the LFP-NP@NPCM nanocomposite can be fully charged or discharged within a very short period of a few tens of seconds, delivering both a high power density and a high energy density. While the power density increases by about 50 times (from 38 W kg⁻¹ to 1875 W kg⁻¹), its capacity retains about 60% (from 145 mA h g⁻¹ to 85 mA h g⁻¹). At a very high power density of up to 20 kW kg⁻¹ (completing the discharge or charge process in about 16 s, corresponding to a rate of 230 C) the discharge energy density was still 87 Wh kg⁻¹. Comparable results have been reported in the literature.¹³ However, the reported results were never carried out at rates as high as those obtained in our work. Compared to supercapacitors, which are addressing the extremes of power-density needs (~1–20 kW kg⁻¹) of commercially available devices, their energy density is only about 1–20 Wh kg⁻¹, whereas the LFP-NP@NPCM nanocomposite may be used for novel and superior electrochemical energy-storage devices with both high-power and high-energy densities.
According to this model, Li$^+$ ions are stored on the ionic conducting side of the interface, while electrons (e$^-$) are localized on the electronic conducting side, resulting in charge separation. In the case of the LFP-NP@NPCM nanocomposite, the ionic conducting and the electronic conducting parts could be the LiFePO$_4$ nanoparticles and the nanoporous carbon matrix, respectively (Fig. 4b). From this hypothesis, we calculate the interfacial Li content to be $3.1 \times 10^{-5}$ mol m$^{-2}$, resulting from the interface area of about 12 m$^2$ g$^{-1}$ (calculated from the surface area of LiFePO$_4$ sphere-like particles with diameter of 70 nm) of LiFePO$_4$ nanoparticles/carbon matrix, and the constant capacity ($\sim$10 mA h g$^{-1}$) at higher discharge rates (larger than 20 C). The interfacial Li-content value is very close to $3.2 \times 10^{-5}$ mol m$^{-2}$, which corresponds to the Li content of a monolayer.

In summary, we have developed a nanocomposite with highly dispersed nanoparticles of active materials in a nanoporous carbon matrix (NP@NPCM) for both high-power and high-energy electrode materials in electrochemical energy-storage devices, such as LIBs and supercapacitors. A key to its realization is, besides the preparation of nanometer-sized active particles, the use of a nanoporous carbon matrix, which serves as a mixed conducting 3D nano-network, enabling both Li$^+$ and e$^-$ to migrate and reach each active particle, hence realizing the full potential of nanoactive materials. The nanoporous carbon matrix can also serve as an electrolyte container for high-rate operation as well as an elastic buffer to relieve the strain during Li uptake/release. The success of this design was demonstrated in a superior cathode material consisting of the LFP-NP@NPCM nanocomposite. In view of its facility in terms of synthesis, it could also be extended to other cathode and anode materials, which will promote the development of next-generation electrochemical energy-storage devices (LIBs, supercapacitors, or hybrids) with both high-power and high-energy densities.

**Experimental**

**Synthesis:** The LFP-NP@NPCM nanocomposite was synthesized using a sol–gel procedure followed by a solid-state-reaction synthesis route. Typically, Pluronic F127 (0.9 g), NH$_4$H$_2$PO$_4 \cdot 2$H$_2$O (10 mmol, Aldrich), 1 mL of 0.5 mmol L$^{-1}$ HCl, LiCl (10 mmol, Aldrich), citric acid (2.5 g, Aldrich), and FeC$_2$O$_4 \cdot 2$H$_2$O (10 mmol, Aldrich) were dissolved in this order into a mixed solution of 5 mL water and 5 mL ethylene glycol (EG, nanometer-sized transition-metal oxides at low potential).
Aldrich) under stirring until a uniform sol was formed. After ageing at 80 °C for 7 days, porous gel precursors were obtained. To form the LFP-NP@NPCM nanocomposite, the gel precursors were first heated at 400 °C for 8 h under Ar, followed by milling and then heating at 700 °C for 12 h under Ar containing 5% H₂.

**Structural Characterization:** XRD measurements were carried out using a Philips PW3710 using filtered Cu Kα radiation (λ = 1.5406 Å). TEM (JEOL 4000EX, operating at 400 kV) and SEM (JEOL 6701F, operating at 10 kV) were used to investigate the morphology and size of the LFP-NP@NPCM nanocomposite. Raman measurements were performed using a Digilab FT33500 from Bio-Rad with a laser wavelength of 514.5 nm. The nitrogen adsorption and desorption isotherms at 77.3 K were obtained with a Nova 2000e surface area–pore size analyzer.

**Electrochemical Characterization:** Electrochemical measurements were performed using two-electrode Swagelok-type cells assembled in an argon-filled glove box. For preparing the working electrode of these lithium batteries, a mixture of LFP-NP@NPCM nanocomposite, carbon black (CB), and poly(vinyl difluoride) (PVDF, Aldrich) at a weight ratio of 70:20:10, was pasted on pure Al foil (99.6%, Goodfellow). Pure lithium foil was used as separator. The electrolyte consisted of a solution of 1 M LiPF₆ in 1:1:1 (in wt%) obtained from Ferro Corporation. Galvanostatic cycling of the assembled cells was carried out using an Arbin BT2000 system in the voltage range of 2.2–4.2 V (vs. Li⁺/Li⁻).

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