Nanoparticle iron-phosphate anode material for Li-ion battery

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Nanoparticle crystalline iron phosphates (FePO₄·2H₂O and FePO₄) were synthesized using a (CTAB) surfactant as an anode material for Li rechargeable batteries. The electrochemical properties of the nanoparticle iron phosphates were characterized with a voltage window of 2.4–0 V. A variscite orthorhombic FePO₄·2H₂O showed a large initial charge capacity of 609 mAh/g. On the other hand, a tridymite triclinic FePO₄ exhibited excellent cyclability: the capacity retention up to 30 cycles was ~80%, from 485 to 375 mAh/g. The iron phosphate anodes exhibited the highest reported capacity, while the cathode LiFePO₄ has an ideal capacity of 170 mAh/g. © 2004 American Institute of Physics. [DOI: 10.1063/1.1835995]

Since the introduction of commercial lithium-ion batteries for portable devices in the 1990s, the development of new anode materials is essential for improving the energy density. The graphite generally used in lithium rechargeable batteries has a capacity of 372 mAh/g. These capacity limitations have inspired researchers to find alternative anode materials. Li–Sn alloy has been studied due to its high capacity, while the cathode LiFePO₄ has an ideal capacity of 170 mAh/g. © 2004 American Institute of Physics. [DOI: 10.1063/1.1835995]

The FePO₄·2H₂O was fabricated by using a cationic surfactant, cetyl-trimethyl-ammonium bromide (CTAB). The CTAB surfactant (1.4 g) was added to distilled water (20 ml) and stirred for 30 min. Then, FeCl₃·6H₂O (3 g) and H₃PO₄ (6.5 g) were gradually added to the solution, and stirred until they were completely dissolved. Subsequently, the suspensions were aged at 90 °C for a week in an oven. The resultant was then washed with de-ionized water, filtered off, and dried at 100 °C for 4 h. The tridymite FePO₄ was obtained from dehydration of FePO₄·2H₂O at 400 °C annealing for 8 h in a furnace.

The electrode composition was iron-phosphate anode: binder: carbon black in a weight ratio of 3:1:1. A slurry was then prepared by mixing them with a N-methyl-2-pyrrolidone (NMP) solution. The coin-type half cells (2016 size) prepared in an argon-filled glove box contained an iron-phosphate anode, a Li metal counter electrode, and a microporous polyethylene separator. The electrolyte used was 1 M LiPF₆ with ethylene carbonate/diethylene carbonate/ethylmethyl carbonate (EC/DEC/EMC). The cycle life of the cells was performed at a rate of 61 mA/g for FePO₄·2H₂O, and 49 mA/g for FePO₄ between a voltage window of 2.4 and 0 V. Note that open circuit voltages of our samples were around 2 V. For the XRD measurements, the cells were dis-
assembled in a glove box (H_2O level <50 ppm), and the cycled iron-phosphate powders were rinsed thoroughly with a DMC solution to remove any LiPF_6 salts.

As shown in Fig. 1, transmission electron microscopy (TEM) was used to identify the microstructures of the iron phosphates. The average nanoparticle size confirmed by TEM is approximately 100 nm for FePO_4·2H_2O, and 50 nm for FePO_4. These are in good agreement with the x-ray diffraction patterns shown in Fig. 2. The size estimated from the Scherrer formula of D_k versus k (the scattering vector) was a few hundred nanometers for FePO_4·2H_2O, and 40 nm for FePO_4. Interestingly, a high-resolution TEM shows that both orthorhombic FePO_4·2H_2O and triclinic FePO_4 have a nanostructured periodicity (~0.3 nm). This curling-shaped nano-periodicity was also observed in carbon, WS_2, Ga_2O_3, V_2O_5, etc. More detailed studies of the role of nanostructures on the electrochemical properties are currently underway. Amorphous iron-phosphate anodes showed a rapid capacity decay, thus showing less than 100 mAh/g after 10 cycles, even with a similar initial-charge capacity.  

The crystal structure of the as-synthesized iron phosphate was very similar to the one reported in the literature for the variscite AlPO_4·2H_2O or GaPO_4·2H_2O. Using the simulation technique (ATOMS) after replacing Al with Fe, the crystal structure of the as-prepared iron phosphate was identified as an orthorhombic FePO_4·2H_2O, which is a variscite structure with the space group Pbca [Fig. 2(a)], with lattice parameters of a=0.9926 nm, b=0.8619 nm, and c=0.9976 nm. After annealing at 400 °C for 8 h, the water molecules in FePO_4·2H_2O were successfully removed, and the XRD data of Fig. 2(b) confirmed a triclinic FePO_4 phase, which has a space group P1 with a=1.0163 nm, b=1.7624 nm, c=8.3733 nm, and α=90.01°, β=90.03°, γ=89.98°. The schematic figures of the variscite FePO_4·2H_2O and tridymite FePO_4 are shown in Fig. 3.

To investigate the superior electrochemical properties of iron phosphates, coin-type half cells were cycled in extreme conditions, between 2.4 and 0 V. Analogous tin-phosphate anode showed severe capacity fading even between 1.5 and 0 V, and getting much worse with higher cut-off voltages. Figure 4 shows the voltage profiles and capacity retention of the variscite FePO_4·2H_2O and the
tridyline FePO₄. The initial charge capacity of the FePO₄·2H₂O is high (609 mAh/g), but the capacity faded noticeably during cycling. In contrast, the tridyline FePO₄ had an initial charge capacity of 485 mAh/g, which is approximately three times higher than the ideal capacity of cathode LiFePO₄. In addition, the capacity retention [Fig. 4(b)] at a rate of 49 mA/g up to 30 cycles was ~80% (from 485 to 375 mAh/g). It should be noted that the irreversible capacity of the variscite FePO₄·2H₂O anode (~897 mAh/g) is larger than the tridyline FePO₄ (~344 mAh/g), which is probably due to the side reactions with both the H₂O molecules and residual surfactants.

The electrochemical reactions of cathode LiFePO₄ involved the Fe⁴⁺/Fe²⁺ redox coupling. Therefore, the theoretical capacity of the LiFePO₄ cathode is only 170 mAh/g. However, iron-phosphate anodes can have a high capacity, probably due to the Fe³⁺/Fe²⁺/Fe⁰ redox reactions. Poizot et al. reported that the 3d transition-metal oxides could be reversibly reduced and oxidized, coupled with the formation/destruction of Li₂O, with the formation of a nanoparticle 3d transition metal. Analogous reactions may apply to iron phosphates, and more detailed experiments (Mössbauer, XANES, etc.) are currently underway to identify the reaction mechanisms. To confirm the phases during discharging/charging, the XRD patterns of both FePO₄·2H₂O and FePO₄ were investigated (Fig. 5). As the anode was discharged (lithiated) to 0 V, the crystalline peaks of the FePO₄·2H₂O and FePO₄ disappeared, indicating an amorphous or nanocrystalline state.

In conclusion, nanoparticle iron phosphates (FePO₄·2H₂O and FePO₄) were achieved using a CTAB surfactant as a new anode material for Li rechargeable batteries. The synthesized triclinic iron phosphate exhibited excellent cyclability: the capacity retention up to 30 cycles was ~80%, from 485 to 375 mAh/g. Also, the capacity is approximately three times higher than the ideal value of cathode LiFePO₄. This original nanoparticle iron phosphate demonstrates a potential for use as Li battery anode materials.

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