Nanoparticle iron-phosphate anode material for Li-ion battery

Dongyeon Son
School of Materials Science and Engineering, and Research Center for Energy Conversion and Storage, Seoul National University, Seoul, Korea

Eunjin Kim
Department of Applied Chemistry, Kumoh National Institute of Technology, Gumi, Korea

Tae-Gon Kim
School of Materials Science and Engineering, and Research Center for Energy Conversion and Storage, Seoul National University, Seoul, Korea

Min Gyu Kim
Beamline Research Division, Pohang Accelerator Laboratory, Pohang University of Science and Technology, Pohang, Korea

Jaephil Cho
Department of Applied Chemistry, Kumoh National Institute of Technology, Gumi, Korea

Byungwoo Park[a)]
School of Materials Science and Engineering, and Research Center for Energy Conversion and Storage, Seoul National University, Seoul, Korea

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Nanoparticle crystalline iron phosphates ($FePO_4 \cdot 2H_2O$ and $FePO_4$) 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 $FePO_4 \cdot 2H_2O$ showed a large initial charge capacity of 609 mAh/g. On the other hand, a tridymite triclinic $FePO_4$ 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 $LiFePO_4$ 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.[1] 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 compared to commercial graphite.[2–4] However, Sn–metal anode has a problem with severe capacity fading due to structural instability related to large volume changes.

Iron phosphates have been explored as cathode materials only.[5,6] Padhi *et al.* reported an olivine-type $LiFePO_4$ cathode, which has a theoretical capacity of 170 mAh/g. As lithium is intercalated/deintercalated from the octahedral sites, olivine-type $LiFePO_4$ has a flat voltage plateau at 3.4 V versus Li. In addition, iron phosphates exhibited different types of structures depending on the synthesis conditions. For instance, $FePO_4$ showed a trigonal structure at normal pressure, but converted to orthorhombic structure at high pressure.[7] More recently, Song *et al.*[8] and Reale *et al.*[9] reported monoclinic (with a space group $P2_1/n$), orthorhombic (with *Pbca*), or hexagonal (with $P6_3mc$) $FePO_4$. These iron phosphates exhibited an open circuit voltage of approximately 4 V, and showed a voltage plateau at ~3 V (working as cathodes) with discharge capacities below 100 mAh/g.

We report here a possibility of iron phosphates as anode materials for Li rechargeable batteries. Despite iron phosphates being briskly investigated as a positive electrode, the anode materials of $FePO_4$ have not been reported. The capacity of synthesized nanoparticle iron phosphates is approximately three times higher than the ideal capacity of the $LiFePO_4$ cathode.

The $FePO_4 \cdot 2H_2O$ 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, $FeCl_3 \cdot 6H_2O$ (3 g) and H_3PO_4 (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 $FePO_4$ was obtained from dehydration of $FePO_4 \cdot 2H_2O$ 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 $LiPF_6$ with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC). The cycle life of the cells was performed at a rate of 61 mA/g for $FePO_4 \cdot 2H_2O$, and 49 mA/g for $FePO_4$ 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-

a)Electronic mail: byungwoo@snu.ac.kr

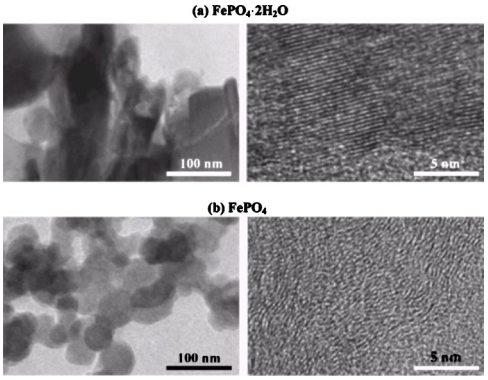

FIG. 1. High-resolution TEM images of the iron phosphates: (a) as-synthesized $FePO_4 \cdot 2H_2O$, and (b) $FePO_4$ (annealed at 400 °C for 8 h).

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 $FePO_4 \cdot 2H_2O$, 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 Δk versus k (the scattering vector) was a few hundred nanometers for $FePO_4 \cdot 2H_2O$, and ~ 40 nm for $FePO_4$. Interestingly, a high-resolution TEM shows that both orthorhombic $FePO_4 \cdot 2H_2O$ 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.[10–15] 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

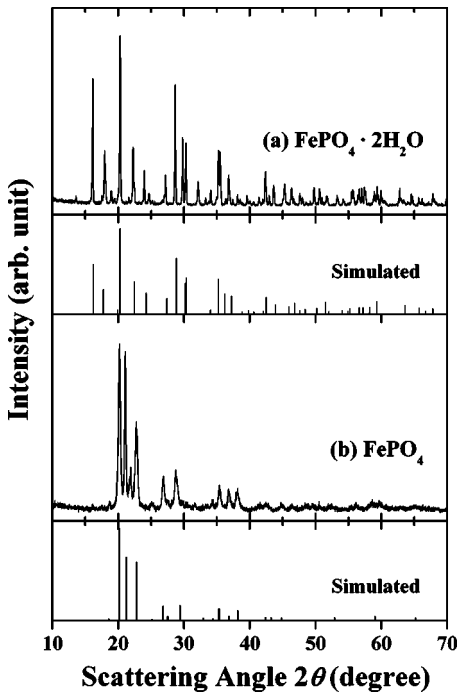

FIG. 2. Measured and simulated x-ray diffraction patterns of (a) as-synthesized $FePO_4 \cdot 2H_2O$, and (b) $FePO_4$ (annealed at 400 °C for 8 h).

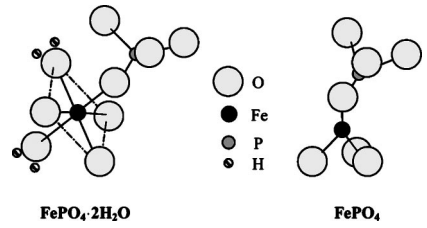

FIG. 3. Schematic representation of the basic crystal structures of iron phosphates: the variscite orthorhombic (*Pbca*) $FePO_4 \cdot 2H_2O$ and tridymite triclinic ($P1$) $FePO_4$.

100 mAh/g after 10 cycles, even with a similar initial-charge capacity.[16]

The crystal structure of the as-synthesized iron phosphate was very similar to the one reported in the literature for the variscite $AlPO_4 \cdot 2H_2O$ or $GaPO_4 \cdot 2H_2O$.[17,18] Using the simulation technique (ATOMS[19]) after replacing Al with Fe, the crystal structure of the as-prepared iron phosphate was identified as an orthorhombic $FePO_4 \cdot 2H_2O$, 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 $FePO_4 \cdot 2H_2O$ 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 $\alpha=90.01°$, $\beta=90.03°$, $\gamma=89.98°$. The schematic figures of the variscite $FePO_4 \cdot 2H_2O$ 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.[20–22] Analogous tin-phosphate anode showed severe capacity fading even between 1.5 and 0 V, and getting much worse with higher cut-off voltages.[1] Figure 4 shows the voltage profiles and capacity retention of the variscite $FePO_4 \cdot 2H_2O$ and the

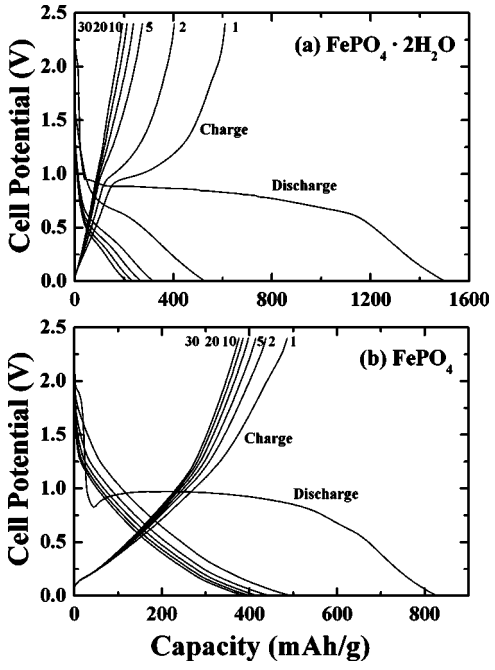

FIG. 4. Voltage profiles of the iron phosphates between 2.4 and 0 V. The cells were cycled at (a) 61 mA/g for variscite $FePO_4 \cdot 2H_2O$ (initial capacity of 609 mAh/g), and (b) 49 mA/g for tridymite $FePO_4$ (initial capacity of 485 mAh/g).

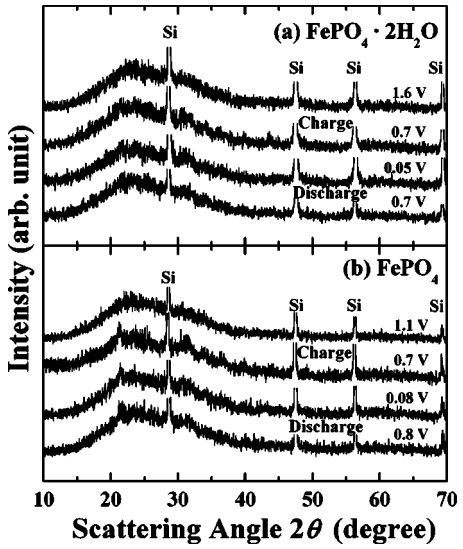

FIG. 5. XRD patterns of (a) the cycled $FePO_4 \cdot 2H_2O$ and (b) cycled $FePO_4$, during the first discharge and charge at a specific voltage.

tridymite $FePO_4$. The initial charge capacity of the $FePO_4 \cdot 2H_2O$ is high (609 mAh/g), but the capacity faded noticeably during cycling. In contrast, the tridymite $FePO_4$ had an initial charge capacity of 485 mAh/g, which is approximately three times higher than the ideal capacity of cathode $LiFePO_4$. 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 $FePO_4 \cdot 2H_2O$ anode (~897 mAh/g) is larger than the tridymite $FePO_4$ (~344 mAh/g), which is probably due to the side reactions with both the H_2O molecules and residual surfactants.

The electrochemical reactions of cathode $LiFePO_4$ involved the Fe^{3+}/Fe^{2+} redox coupling. Therefore, the theoretical capacity of the $LiFePO_4$ cathode is only 170 mAh/g. However, iron-phosphate anodes can have a high capacity, probably due to the $Fe^{3+}/Fe^{2+}/Fe^0$ redox reactions. Poizot *et al.*[23] reported that the 3*d* transition-metal oxides could be reversibly reduced and oxidized, coupled with the formation/destruction of Li_2O, with the formation of a nanoparticle 3*d* 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 $FePO_4 \cdot 2H_2O$ and $FePO_4$ were investigated (Fig. 5). As the anode was discharged (lithiated) to 0 V, the crystalline peaks of the $FePO_4 \cdot 2H_2O$ and $FePO_4$ disappeared, indicating an amorphous or nanocrystalline state.

In conclusion, nanoparticle iron phosphates ($FePO_4 \cdot 2H_2O$ and $FePO_4$) 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 $LiFePO_4$. This original nanoparticle iron phosphate demonstrates a potential for use as Li battery anode materials.

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[1] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, and T. Miyasaka, Science **276**, 1395 (1997).
[2] D. Aurbach, A. Nimberger, B. Markovsky, E. Levi, E. Sominski, and A. Gedanken, Chem. Mater. **14**, 4155 (2002).
[3] I. A. Courtney and J. R. Dahn, J. Electrochem. Soc. **144**, 2943 (1997).
[4] J.-M. Tarascon and M. Armand, Nature (London) **414**, 359 (2001).
[5] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, J. Electrochem. Soc. **144**, 1188 (1997).
[6] S.-Y. Chung, J. T. Blocking, and Y.-M. Chiang, Nat. Mater. **1**, 123 (2002).
[7] M. P. Pasternak, G. K. Rozenberg, A. P. Milner, M. Amanowicz, U. Schwaez, K. Syassen, R. D. Taylor, M. Hanfland, and K. Brister, Phys. Rev. Lett. **79**, 4409 (1997).
[8] Y. Song, P. Y. Zavalij, M. Suzuki, and M. S. Whittingham, Inorg. Chem. **41**, 5778 (2002).
[9] P. Reale, B. Scrosati, C. Delacourt, C. Wurm, M. Morcrette, and C. Masquelier, Chem. Mater. **15**, 5051 (2003).
[10] T. Hyeon, S. Han, Y.-E. Sung, K.-W. Park, and Y.-W. Kim, Angew. Chem., Int. Ed. **42**, 4352 (2003).
[11] T.-W. Kim, I.-S. Park, and R. Ryoo, Angew. Chem., Int. Ed. **42**, 4375 (2003).
[12] Y. D. Li, X. L. Li, R. R. He, J. Zhu, and Z. X. Deng, J. Am. Chem. Soc. **124**, 1411 (2002).
[13] U. M. Graham, S. Sharma, M. K. Sunkara, and B. H. Davis, Adv. Funct. Mater. **13**, 576 (2003).
[14] M. E. Sphar, P. Bitterli, R. Nesper, M. Muller, F. Krumeich, and H. U. Nissen, Angew. Chem., Int. Ed. **37**, 1263 (1998).
[15] G. R. Ratzke, F. Krumeich, and R. Nesper, Angew. Chem., Int. Ed. **41**, 2447 (2002).
[16] J. Cho, D. Son, and B. Park (unpublished).
[17] A. M. Beale and G. Sankar, J. Mater. Chem. **12**, 3064 (2002).
[18] H. Graetsch, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **56**, 401 (2000).
[19] E. Dowty, ATOMS. Shape software, 521 Hidden Valley Road, Kingsport, Tennessee, 2002.
[20] Y. J. Kim, H. Kim, B. Kim, D. Ahn, J.-G. Lee, T.-J. Kim, D. Son, J. Cho, Y.-W. Kim, and B. Park, Chem. Mater. **15**, 1505 (2003).
[21] J. Cho, Y. J. Kim, T.-J. Kim, and B. Park, Angew. Chem., Int. Ed. **40**, 3367 (2001).
[22] J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee, and B. Park, Angew. Chem., Int. Ed. **42**, 1618 (2003).
[23] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, and J.-M. Tarascon, Nature (London) **407**, 496 (2000).