

ADVANCED MATERIALS

DOI: 10.1002/adma.200600644

Reversible Lithium Intercalation in Teardrop-Shaped Ultrafine SnP_{0.94} Particles: An Anode Material for Lithium-Ion Batteries**

By Youngsik Kim, Haesuk Hwang, Chong S. Yoon, Min G. Kim,* and Jaephil Cho*

The discovery, in 1997, of an amorphous tin-based composite oxide with a theoretical gravimetric capacity more than twice that of carbon (372 mA h g⁻¹) was an important development in the field of high-capacity Li-ion cells.^[1] Following this discovery, much research was devoted to lithium-reactive metals and metal oxides, such as Sn, Si, SnO₂, and Sn₂P₂O₇, because of their high capacities and relatively low average working potentials (<1.5 V).^[2-12] However, these materials have significant disadvantages for practical use in rechargeable lithium batteries. One problem is their very poor reversible capacity, with over 40 % loss due to the formation of an inactive matrix phase within the lithium phase (i.e, Li₂O) and severe side reactions with the electrolytes after the first cycle. Another obstacle for their practical application is their high volume change (over 300%) due to the formation of the Li_xM and M phases, which eventually leads to particle pulverization and, in turn, electrical isolation from the current collectors.

Recently, metal phosphides (MPs) have been suggested as a promising anode material. MPs can react reversibly with Li at an average voltage of 1 V, even though their average working voltages are higher than those of Sn, Si, and SnO₂.^[13-15] Depending on the nature of the metal, reactions involving MPs and lithium can be categorized into two categories:

$$MP_n \leftrightarrow Li_x MP_n$$
 (Li intercalation) (1)

$MP_n \leftrightarrow M(Li_xM) + Li_xP$ (metallization or metal alloying) (2)

An example of the first case is MnP_4 ,^[13] in which lithium intercalation takes place by an electrochemical redox process:

[*] Dr. M. G. Kim Beamline Research Division, Pohang Accelerator Laboratory Pohang University of Science and Technology Pohang 790-784 (Korea) E-mail: mgkim@postech.ac.kr Prof. J. Cho, Y. Kim,^[+] H. Hwang Department of Applied Chemistry, Kumoh National Institute of Technology Gumi 730-701 (Korea) E-mail: jpcho@kumoh.ac.kr Prof. C. S. Yoon Division of Materials Science and Engineering, Hanyang University Seoul (Korea)

[+] On leave from the Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA.

[**] The authors wish to acknowledge the Pohang Light Source (PLS) for the XAS measurements. This work was supported by the Division of Advanced Batteries in the NGE Program (Project No. 10016439). Supporting Information is available online from Wiley InterScience or from the author.

 $MnP_4 \leftrightarrow Li_7MnP_4$. The P–P bonds in the MnP₄ are cleaved on Li insertion to produce crystalline Li₇MnP₄, and are, after reoxidation to MnP₄, only reformed between 0.57 and 1.7 V. The material decomposes to Mn and Li₃P below 0.5 V.^[16] Despite performing the reaction cycles in the limited voltage window, a rapid capacity loss from 700 to 350 mA h g^{-1} was observed in the MnP₄ electrode during the first few cycles, stabilizing after 50 cycles. A more recent study by Gillot et al.^[17] suggested that the poor capacity retention is the result of the irreversible decomposition of Li₇MnP₄ into Li₃P and Mn instead of recrystallization of MnP₄ from Li₇MnP₄. Similarly, MP_n compounds such as FeP₂, CoP₃, Cu₃P, VP₄, and Sn₃P₄ also exhibited decomposition reactions.^[14,15,18-21] These materials also showed rapid capacity fading resulting from i) particle pulverization due to the large volume change, and ii) formation of the poor conductor LiP from Li₃P above 0.65 V. Based on these results, the best candidates for anode materials should meet the following criteria: they should have a low average working potential (below 0.7 V), a low irreversible capacity (no capacity fading), a high reversible capacity (over 700 mA h g^{-1}), and a good life-cycle performance. More importantly, lithium-intercalating compounds with a volume change comparable to graphite (<15%) need to be investigated.

In this study, we report on the preparation and electrochemical structural transformation of a fully reversible new lithium intercalation compound, $SnP_{0.94}$, with a reversible capacity of 740 mA h g⁻¹ between 0 and 1.2 V. This material shows an excellent life-cycle performance. The synthesis of uniformly dispersed teardrop-shaped tin phosphide particles was based on the reaction of tin acetate in a mixed solution of trioctyl phosphine (TOP) and trioctylphosphine oxide (TOPO).

Figure 1a and b shows transmission electron microscopy (TEM) images of tin phosphide nanoparticles, prepared from a mixed solution of TOP and TOPO by a thermal decomposition method. Tin phosphides such as SnP, SnP₃, and Sn₄P₃ have been reported in literature,^[22–25] and these were prepared by the traditional stoichiometric solid-state reaction of tin and red phosphorus at high temperatures. Recently, nanometer-sized Sn₄P₃ was also prepared from tin and red phosphorus powders using a mechanical-milling method.^[19,26] TOP and TOPO are known as capping reagents that direct the selective growth of anisotropic nanocrystals by changing the crystallographic surface energies.^[27] Several different shapes of nanoscale metal phosphide particles, such as nanospheres, nanorods, and nanowires, have been formed by controlling the amount and ratio of TOP/TOPO.^[27,28] In our case, the





Figure 1. a,b) TEM images of teardrop-shaped $SnP_{0.94}$ particles. c) SAED pattern of the tail portion of a $SnP_{0.94}$ particle. d) SAED pattern of the head portion of a $SnP_{0.94}$ particle. e) HRTEM image of the tail section of $SnP_{0.94}$ particle. Stacking faults appear as the streaky extra spots (indicated by arrows) in the SAED patterns and thin platelets (indicated by arrows) in the HRTEM images.

TOP–Sn complex could not be prepared due to the low solubility of tin acetate in TOP. Instead, tin acetate, TOP, and TOPO were mixed and heated at 390 °C for 1 h. The solutionphase thermal decomposition method led to the formation of uniform teardrop-shaped tin phosphide particles (Fig. 1a).

Figure 1c and d show selected-area electron diffraction (SAED) patterns taken from the head and tail portions of the teardrop-shaped particles, respectively. The bright diffraction spots are clearly visible, which is indicative of the well-developed crystallinity of the particles. The patterns are essentially identical over the entire teardrop-shaped particle, suggesting that each particle is a single crystal of SnP_{0.94}. The SAED patterns were indexed to the [001] zone of a hexagonal lattice, in agreement with the X-ray diffraction (XRD) results (see below). The SAED patterns also indicate that the *c*-axis of the hexagonal lattice is aligned in the longitudinal direction of the particle, suggesting that the preferential growth direction is along the *c*-axis. Similar observations were made for all the examined particles. Moreover, the diffraction patterns contain

forbidden streaked peaks (indicated by arrows), which are probably due to the presence of thin platelets of stacking faults in the *c*-direction. In a high-resolution TEM (HRTEM) image of the tail section of the particles), thin platelets of stacking faults were indeed observed (Fig. 1e, indicated by white arrows).

Figure 2 shows voltage profiles of the 1st, 10th, 20th, 30th, and 40th cycle of tin phosphide between 1.2 and 0 V at a current rate of 120 mA g⁻¹. The first discharge and charge capacities were 850 and 740 mA h g⁻¹, respectively, showing a Coulombic efficiency of 87 %. However, the Coulombic efficiency after 2 cycles was 98 %, and fully recovered to 100 % after 20 cycles, as shown in the inset of Figure 2. The capacity retention after 40 cycles was 92 % of the first-charge capacity. This value is far superior to that previously reported for the MnP₄ anode,^[13] which showed a capacity that rapidly decreased to 350 mA h g⁻¹ after only a few cycles.



Figure 2. Voltage profiles of the samples after the 1st, 10th, 20th, 30th, and 40th cycle at a rate of 120 mA g⁻¹ between 0 and 1.2 V. The inset is a plot of the charge capacities and Coulombic efficiencies of the SnP_{0.94} electrode up to the 40th cycle.

Figure 3 shows XRD patterns of SnP_{0.94} particles for the pristine particle (indicated as (1) in Fig. 3a and b), after the first discharging (0 V, (4)), the first charging (1.2 V, (8)), and after 10 and 20 cycles. From the XRD pattern of the pristine particle, it is found that the crystal structure of tin phosphide has a 2D layered structure (see Supporting Information, Table S1). The tin atoms are hexagonally packed in the unit cell and closely linked with two kinds of diphosphorus atomic pairs, P(1)-P(1) and P(2)-P(2). The layered $SnP_{0.94}$ slab consists of a polymeric network of -[Sn-P-P-Sn]- that exhibits zigzag bonding (see Supporting Information, Figs. S2 and S3).^[22] The XRD patterns recorded after the first dischargecharge process closely resemble that of the pristine particle. These results show that SnP_{0.94} maintains constant lattice parameters when undergoing the electrochemical reactions, indicating no significant phase transition from the layered structure to other crystal structures or other phases. It is also seen that no overall variation of the XRD pattern is observed

ADVANCED MATERIALS



Figure 3. a) Potential profiles of the SnP_{0.94} anodes between 1.2 and 0 V; numbers indicate where the X-ray absorption spectra and XRD measurements were taken. b) Powder XRD patterns of the as-prepared SnP_{0.94} particles, before discharging at point (1), after fully discharging to 0 V and 1.2 V, corresponding to points (4) and (8), and after 10 and 20 cycles (fully discharged to 0 V).

after 10 and 20 cycles. It should be noted that the original structure was maintained after continuous cycling. This result highlights the different electrochemical aspect of charge compensation for the Li-ion behavior compared with that of Sn_3P_4 and MP_n anodes (M = Mn, Co, Fe, Cu, and V), in which Li-ion insertion leads to reduction of the metal below 0.5 V. The XRD results demonstrate that the charge compensation by Li-ion insertion occurs in the short-range-ordered structure around Sn, and not through bulk lattice structural variation of layered $SnP_{0.94}$. For more detailed local structural analysis, a comparative X-ray absorption (XAS) spectroscopic study is introduced, because this technique is sensitive to structural changes at the molecular level.

Figure 4 shows normalized Sn L_{III}-edge X-ray absorption near edge structure (XANES) spectra and corresponding Fourier transform (FT) magnitudes of k^2 -weighted Sn L_{III}edge extended X-ray absorption fine structure (EXAFS) spectra. The XANES peak shape of SnP_{0.94} particles is quite similar to that of the Sn metallic state, as shown in Figure 4a, implying an overall lower valence state of the Sn ion rather than a divalent or tetravalent state. The abnormal lower valence of Sn is due to the very small electronegativity difference between tin and phosphor atoms (the Pauling constants of tin and phosphorous atoms are 1.96 and 2.19 Pauling units, respectively). Accordingly, the chemical bonding leads to a flexible polymeric network with a layered crystal structure. During discharging and charging ((1) to (8) in Fig. 3a), there is no distinct XANES spectral change for the SnP_{0.94} particles, as shown in Figure 4a. Compared to the Sn₄P₃ material reported earlier, the XANES spectra of the Sn₄P₃ exhibit peak feature variations during the discharge-charge process that are not reversible after one cycle, which means that the initial electronic state of Sn and the local structure of Sn₄P₃ have been changed effectively.^[19] Hence, the constant XANES feature on the Li-ion behavior in the present SnP_{0.94} suggests that there is no effective change in the Sn oxidation state, even in the electrochemical reaction for 4.5 mole Li-ion insertion/extraction (SnP_{0.94} + 4.5 Li \leftrightarrow Li_{4.5}SnP_{0.94}).

On the other hand, the FT peak feature of k^2 -weighted Sn L_{III}-edge EXAFS spectra shows an effective variation in Liion behavior (Fig. 4b). This means that the local structural variation around the Sn atom is part of the charge compensation process. Pristine SnP_{0.94} presents three distinct kinds of FT peaks: Sn–P bonding at 2.1 Å (peak A), direct Sn–Sn(1) metallic bonding at about 3.2 Å (peak B), and Sn-P-P-Sn(2) bonding 4.0 Å (peak C). Peak B corresponds to Sn-Sn bonding between the interlayers of SnP_{0.94} slabs, not between closely packed Sn atoms, whereas pure Sn metal gives an FT peak of Sn-Sn metallic bonding at about 2.9 Å (see Supporting Information, Fig. S3). Peak C is associated with the formation of a polymeric network by extended -[Sn-P-P-Sn]- bonding within a layer. On discharging, peak A starts to shift gradually to a lower r space, meaning a reduced Sn-P bond length. On discharging to 0.0 V, the average Sn-P bond distance (peak A) is shortened by about 0.15 Å with respect to that of the pristine particle. Peak B disappears abruptly, which indicates intercalation of the Li ion. The absence of peak B for the Li-ion insertion might be due to the fact that the Sn-Sn scattering between the SnP_{0.94} polymeric slabs is effectively shielded by the interference of the Li ion. The Li-ion positioning in the interlayer leads to local structural modification around the central Sn atom and prevents the scattering interaction between the central Sn atom and neighboring Sn(1)atom. Hence this spectral feature strongly suggests that the Li ion is located in the interstitial sites between the polymeric slabs. This fact is supported by an earlier report, in which the initial Li ion insertion begins by binding at the center of the P–P bond.^[13]

Conversely, peak C of Sn–P–Sn bonding shows no change, which means the polymeric –[Sn–P–Sn]– slabs are not broken, in spite of the Li-ion insertion. The peak feature variations are closely related to the effective local structural variation around the Sn atom. It is certain that at first the Li⁺ ion is intercalated in the intermolecular channel between the SnP_{0.94} slabs (Fig. 5). More Li-ion insertion gives rise to Li-ion binding at the diphosphorus (P–P) center. The Li ion located at the





Figure 4. a) Normalized Sn L_{III} -edge XANES spectra. b) Corresponding FT magnitudes of k^2 -weighted Sn L_{III} -edge EXAFS spectra for the first cycle.



Figure 5. Possible intercalating path from $SnP_{0.94}$ crystal structures which consists of a) Sn-P1 (2c site) and b) Sn-P2 (6i site) atomic pairs under the space group of P-3m1 (Sn atom: dark gray and P atom: orange).

interstitial site leads to the formation of Li–P bonding, which is related to partial P–P bond cleavage. The local structural variation, along with the Li-ion behavior, makes edge-shared Sn–P bonding shrink along the *z*-axis, and also causes static disorder of the Sn–Sn(1) interlayer interaction. The FT intensity variation of peak A is associated with the effect of the Li-ion content on the relative short-range order of Sn–P bonding.

Many earlier reports for similar anodic systems show metallization of the metal part of compounds for the charge compensation during the Li-ion insertion. For example, the layered structure of the Sn_4P_3 anode was destroyed and the phase was converted into LiP and Li_xSn alloys with Li insertion, leading to a sharp decrease in capacity (ca. 0 mA h g⁻¹ after 40 cycles) in the high-voltage region above 0.9 V.^[19] In this study, no reduction of Sn to the metallic state and -[Sn-P-P-Sn]- polymeric network was observed, even in the fully discharged state. Although Li-ion insertion leads to Li-P bonding, there always exists a phosphorus atom directly bonded to Sn. Therefore, it is certain that the existence of a diphosphorus pair prevents metallization of tin phosphide in the intercalation mechanism. On charging to 1.2 V, the FT peak features return reversibly to those of the pristine particle through schematic variation of the discharging process. Therefore, it was found that the excess positive charge by the 4.5 mole Li-ion intercalation can be compensated for by local structural variation around the tin ion within Sn-P-P-Sn slabs, rather than a change in the oxidation state of Sn.

In conclusion, good electrochemical cycling properties resulted from structural reversibility by a lithium intercalation/deintercalation mechanism through molecular channels, without a phase transition from $SnP_{0.94}$ to the metallic alloy Li_nSn. The reversible capacity, which was twice as large as that of a graphite anode, along with the low irreversible capacity and low working voltage suggest that this material could be employed as an anode material for next-generation high-capacity Li secondary batteries.

Experimental

 $SnP_{0.94}$ Synthesis: The SnP_{0.94} synthesis is based on the reaction of Sn acetate, Sn(C₂H₃O₂)₂, in a high-temperature solution of trioctyl phosphine (TOP), [CH₃(CH₂)₇]₃P, and trioctylphosphine oxide (TOPO), [CH₃-(CH₂)₇]₃PO. The preparative procedure is modified from the method for generation of FeP

nanorods previously reported by Park et al. [29]. Instead of injecting the TOP–Sn complex into a TOPO solution, 0.36 g of Sn acetate, 10 mL of TOP, and 5 g of TOPO were mixed, and heated at 390 °C for 1 h. For the resultant SnP_{0.94} without TOPO, 0.36 g of Sn acetate and 10 mL of TOP were mixed and heated at 390 °C for 1 h. Smoke evolution and a change in color to black appeared in the flask during heat treatments. The resulting black mixture was cooled to room temperature, and 50 mL of ethanol was added to produce a black precipitate. The black powderlike product was collected by centrifugation at 5000 rpm for 15 min, and washed twice with 50 mL of ethanol to remove excess TOP and TOPO. The final precipitate was vacuum-dried to powder. All reactions were carried out in a dry argon atmosphere with <10 ppm O₂ and H₂O.

Assembly of a Coin-Type Half-Cell with Li as the Anode: The electrode consisted of 80 wt % active materials, 10 wt % Super P carbon black, and 10 wt % poly(vinylidene fluoride). A mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) with 1 $\mbox{M LiPF}_6$ salts was used as the electrolyte. The cell was cycled at a rate of 120 mA g⁻¹



between 0 and 1.2 V. Sample preparation for EXAFS measurements was carried out in an inert-gas-filled glove-box to prevent any oxidation or contamination. The discharged and charged $\text{SnP}_{0.94}$ particles were disassembled and then sealed with polyimide tape (KAPTON-500H, 125 µm thickness). Sn L_{III}-edge XAS spectra were recorded on the BL7C1 beam line of the Pohang light source (PLS) with a ring current of 120–170 mA at 2.5 GeV. A Si(111) double-crystal monochromator was employed to monochromatize the X-ray photon energy. The data were collected in transmission mode with He (50%) and N₂ (50%) gas-filled ionization chambers as detectors. Higher-order harmonic contamination was eliminated by detuning to reduce the incident X-ray intensity by ca. 40%. Energy calibration was completed using standard Sn metal powder. The data reduction of the experimental spectra was performed by the standard procedure reported previously [11,12].

Received: March 25, 2006 Revised: June 13, 2006

- Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* 1997, 276, 1395.
- [2] I. A. Courtney, J. R. Dahn, J. Electrochem. Soc. 1997, 144, 2943.
- [3] J. O. Besenhard, J. Yang, M. Winter, J. Power Sources 1997, 68, 87.
- [4] K. D. Kepler, J. T. Vaughey, M. M. Thackeray, *Electrochem. Solid-State Lett.* 1999, 2, 307.
- [5] S. Panero, G. Savo, B. Scrosati, *Electrochem. Solid-State Lett.* 1999, 2, 365.
- [6] R. Retoux, T. Brousse, D. M. Schleich, J. Electrochem. Soc. 1999, 146, 2472.
- [7] Y. W. Xiao, J. Y. Lee, A. S. Yu, Z. L. Liu, J. Electrochem. Soc. 1999, 146, 3623.
- [8] J. Zhu, Z. Lu, S. T. Aruna, D. Aurbach, A. Gedanken, *Chem. Mater.* 2000, 12, 2557.

- [9] D. Aurbach, A. Nimberger, B. Markovsky, E. Levi, E. Sominski, A. Gedanken, *Chem. Mater.* 2002, 14, 4155.
- [10] E. Kim, D. Son, T. G. Kim, J. Cho, B. Park, K. S. Ryu, S. H. Chang, Angew. Chem. Int. Ed. 2004, 43, 5987.
- [11] M. Noh, Y. Kim, M. G. Kim, H. Lee, H. Kim, Y. Kwon, Y. Lee, J. Cho, *Chem. Mater.* 2005, 17, 3320.
- [12] Y. Kwon, M. G. Kim, Y. Kim, Y. Lee, J. Cho, *Electrochem. Solid-State Lett.* 2006, 9, A34.
- [13] D. C. S. Souza, V. Pralong, A. J. Jacobson, L. F. Nazar, *Science* 2002, 296, 2012.
- [14] V. Pralong, D. C. S. Souza, K. T. Leung, L. F. Nazar, *Electrochem. Commun.* 2002, 4, 516.
- [15] D. C. C. Silva, O. Crosnier, G. Ouvrard, J. Greedan, A. Safa-Sefat, L. F. Nazar, *Electrochem. Solid-State Lett.* 2003, 6, A162.
- [16] F. Gillot, L. Monconduit, M. Morcrette, M.-L. Doublet, L. Dupont, J.-M. Tarascon, *Chem. Mater.* 2005, 17, 3627.
- [17] F. Gillot, L. Monconduit, M.-L. Doublet, Chem. Mater. 2005, 17, 5817.
- [18] R. Alcantara, J. L. Tirado, J. C. Jumas, L. Monconduit, J. Olivier-Fourcade, J. Power Sources 2002, 109, 308.
- [19] Y. Kim, C. K. Lee, H. Sohn, T. Kang, J. Electrochem. Soc. 2004, 151, A933.
- [20] M. P. Bichat, T. Politova, J. L. Pascal, F. Favier, L. Monconduit, J. Electrochem. Soc, 2004, 151, A2074.
- [21] Y. Kim, B. W. Cho, H. Sohn, J. Electrochem. Soc. 2005, 152, A1475.
- [22] J. Gullman, J. Solid State Chem. 1990, 87, 202.
- [23] P. C. Donohue, Inorg. Chem. 1970, 9, 335.
- [24] O. Olofsson, Acta Chem. Scand. 1970, 24, 1153.
- [25] P. Eckerlin, W. Kischio, Z. Anorg. Allg. Chem. 1968, 363, 1.
- [26] Y. Kim, S. Lee, C. K. Lee, H. Sohn, J. Power Sources 2005, 141, 163.
- [27] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, Adv. Mater. 2003, 15, 353.
- [28] S. M. Lee, S. N. Cho, J. W. Cheon, Adv. Mater. 2003, 15, 441.
- [29] J. Park, B. Koo, K. Y. Yoon, Y. Hwang, M. Kang, J. Park, T. Hyeon, J. Am. Chem. Soc. 2005, 127, 8433.