Li Reaction Behavior of GaP Nanoparticles Prepared by a Sodium Naphthalenide Reduction Method

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Li reaction phenomena of GaP nanoparticles (<30 nm) prepared by a sodium naphthalenide reduction method at 390 °C in an autoclave were investigated using electrochemical, in (ex) situ X-ray diffraction (XRD), and X-ray absorption spectra (XAS) measurements between 1.5 and 0 V. During the first discharge reactions, lithium intercalated Li₂GaP and irreversible Li_nP₇ phases were formed. Li₂GaP was only stable above 0.36 V after which it decomposed to Li_xGa and electrochemically inactive Li_nP phases. Overall, the reversible capacity contribution (~800 mAh/g) was from the reversible phase transformation between the Li_xGa and Ga phases.

Introduction

Current directions in the field of metal phosphides research include investigating new appropriate preparation techniques and the modifications of quantum dots by means of surface chemistry.¹⁻²¹ Cheon et al. recently synthesized wurtzite and zinc blende structured GaP nanorods.1 They used different stabilizers to influence the crystallographic phase transformation from the zinc blende to the wurtzite structure. They proposed that the formation of a zinc blende structure was favored with highly steric ligands, such as trioctylamine, while wurtzite was dominant when a less bulky alkyl amine was used (e.g., hexadecylamine). Davidson et al. synthesized GaP nanowires in hexane at 500 °C and 37 MPa by reacting P(SiMe₃)₃ and (tBu)₃Ga in the presence of 7.5-nm-diameter dodecanethioalstabilized gold nanoparticles (seed material) on a Si/SiO deposition substrate.² However, these surfactants are not favorable for use in anode materials in Li secondary batteries due to decomposition of the surfactants during electrochemical reactions.

On the other hand, some surfactant-free GaP preparations have been reported, and Treece et al. used solid-state reactions as a general synthetic route to binary III–V compounds.³ The generic reaction scheme of $MX_3 + Na_3Pn \rightarrow MPn + 3NaX$ (M = Al, Ga, In; X = F, Cl, I; Pn = P, As, Sb) has been used to prepare crystalline powders of crystalline semiconductors. Aubuchon et al. obtained nanocrysatlline GaP from thermal decomposition of two analogues of [Br₂GaP(SiMe₃)₂]₂ or [I₂-GaP(SiMe₃)₂]₂ at 300 °C.⁴ Gao et al. prepared GaP from a mild benzene and thermal route at 240 and 300 °C, respectively, using Na, P, and GaCl₃ for 6 h as the starting materials according to the following reaction:

$$3Na + GaCl_3 \rightarrow 3NaCl + Ga$$
 (1)

$$Ga + P \rightarrow GaP$$
 (2)

However, this reaction requires a high pressure to obtain nanocrystalline GaP.⁵

Recently, transition metal phosphides, such as CoP_{3} ,²² MnP_{4} ,²³ FeP_{2} ,²⁴ $Sn_{3}P_{4}$,²⁵ VP_{4} ,²⁶ and $Cu_{3}P^{27}$, have been investigated as possible candidates for anode materials in Li-ion batteries and can be categorized into two groups depending on the transition metal and phosphors bonding stability upon lithium reaction. MnP_{4} , $Cu_{3}P$, and VP_{4} resulted in topotactic lithium insertion without breaking bonds between transition metal and phosphor, and the overall reaction can be written as follows

$$M_x P_y \rightarrow Li_t M_x P_y \rightarrow Li_t P + M_x P_y \leftrightarrow Li_z M_x P_y$$
 (3)

For instance, Kim et al. reported that VP₄ reacted with lithium through a topotactic reaction, phase transformation occurred from monoclinic Li_3VP_4 into the cubic Li_6VP_4 phase, and decomposition resulted to form Li_3P and VP followed by lithium insertion into the VP phase.²⁶

On the other hand, Sn_3P_4 , FeP_2 , CoP_3 , and $Cu_3P^{27,28}$ resulted in the direct decomposition of metal phosphide into metal or lithum phosphide. For instance, Li reaction in CoP_3 can be written as

$$CoP_3 \rightarrow Li_3P + Co \leftrightarrow 3LiP + Co$$
 (4)

In the case of CoP₃, the initial uptake of Li forms highly dispersed cobalt clusters embedded in a matrix of Li₃P; extraction of Li from this ion-conductive matrix on charging yields nanoparticles of LiP without oxidation of Co.²² However, when an active transition metal is formed from the decomposition reaction, lithium can reversibly react with the active metal. Sn_3P_4 was formed in a final reaction²⁵

$$\operatorname{Sn} + \operatorname{LiP} \operatorname{and} \operatorname{Sn} \to \operatorname{Li}_4 \operatorname{Sn}, \operatorname{LiP} \to \operatorname{Li}_3 \operatorname{P}$$
 (5)

LiP is an insulator, and once Li_3P changed into LiP in reactions 3, 4, and 5, it had a detrimental effect on the reversibility of the phosphorus electrode. As long as the electrochemical window is limited to below 0.72 V, the Li_3P matrix is believed to be relatively stable. However, above 0.75 V, capacity fading was severe and showed ~0 mAh/g after 30 cycles. The preparation method for metal phosphides described above primarily used ball-milling or high temperature solid-state reactions.

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Li Reaction Behavior of GaP Nanoparticles

In the case of Cu₃P, some contradicting Li reaction mechanisms have been reported. Nazar's group proposed that the electrochemical reaction of Cu₃P with lithium led to the formation of metallic copper Li₂CuP and Li₃P using ex situ X-ray diffraction (XRD) results.²⁷ On the other hand, Mauvernay et al. reported that in situ XRD and first-principles electronic structure calculations combined with electrochemical cycling results showed a different reaction mechanism compared with that reported by Nazar's group.²⁸ They proposed that complete insertion of 3Li^+ in the Cu₃P electrode proceeded with the formation of three intermediate phases with lithium composition Li_xCu_{3-x}P (x = 1, 2, 3), according to the reactions

$$Cu_{3}P + xLi \rightarrow xLiCu_{3-x}P + xCu$$
(6)

$$\mathrm{Li}_{x}\mathrm{Cu}_{3-x}\mathrm{P} + (2-x)\mathrm{Li} \rightarrow \mathrm{Li}_{2}\mathrm{Cu}\mathrm{P} + (2-x)\mathrm{Cu}$$
(7)

Compared with these transition metal phosphides that use electrons in d orbitals, semiconducting intermetallic compounds (e.g., InSb) that use electrons in sp orbitals have also been investigated. Vaughey et al. reported that the InSb with a zincblende-type (diamond) structure could accommodate 2 mol of lithiums (Li₂InSb) with 5.6% volume expansion.²⁹ The new phase Li2InSb was proposed to form according to the reaction $2Li + InSb \rightarrow Li_2InSb$, while further lithiation of Li_2InSb resulted in a displacement of reaction during which the In atoms are replaced by Li, according to the reaction $xLi + Li_2InSb \rightarrow$ $Li_{2+x}In_{1-x}Sb + xIn (x_{max} = 1)$. Later, however, Hewitt et al. reported contradicting results to those above using in situ XRD, and Li3Sb and In are formed above 0.65 V, according to the reaction $3Li + InSb + In.^{30}$ The indium product subsequently reacts with Li, forming the InLix phases InLi and In₄In₇ in sequence. In addition, they proposed that only 0.27 mol of Li per InSb might be intercalated, according to the reaction xLi + InSb \rightarrow Li_{0.27}InSb. The capacity of Li_{0.27}InSb corresponds to 30 mAh/g.

In this study, we report on the lithium reaction behavior of GaP nanoparticles with different particle sizes produced by sodium naphthalenide reduction of GaCl₃ in ethylene glycol dimethyl ether (glyme) and concurrent reaction with P at 390 °C without pressurized conditions.

Experimental Section

Synthesis. Dissolved sodium chunks with naphthalene in a glyme solution were rapidly added with stirring at room temperature via a cannula to a 500 mL Schenk flask containing 100 mL of glyme, 1.76 g of GaCl₄, and 0.31 g of phosphor. The mixed solution was refluxed at 390 °C for 1 and 4 h and cooled to room temperature. The solution was rinsed with water six times to remove NaCl and was centrifuged at 5000 rpm to remove the precipitates. Finally, the precipitates were vacuum-dried at 80 °C for 5 h.

XRD and X-ray Absorption Spectra (XAS) Measurement. Ex situ XRD measurements were performed using the composite electrode separated from the cell at a designated cell potential. XRD patterns were obtained using a Cu K α X-source on a Rigaku instrument operated at 11 kW. Electrochemical in situ cell preparation for X-ray absorption fine structure (XAFS) measurement has been carried out in an inert-gas-filled glovebox to prevent any oxidation and contaminations. After being assembled with Li foil, a separator, and a 30 μ m thick GaP electrode, the cell is vacuum sealed with an aluminum pouch. X-ray photon flux is enough to transmit through the electrochemical cell without any interaction. Ga K-edge X-ray absorp-



Figure 1. XRD patterns of the GaP nanoparticles prepared at 390 °C for 1 and 4 h.

tion spectra were recorded on the BL7C1 beam line of Pohang light source (PLS) with a ring current of 130-185 mA at 2.5 GeV. A Si(111) double crystal monochromator has been employed to monochromatize the X-ray photon energy. The data were collected in transmission mode with N2-gas-filled ionization chambers as detectors. Higher order harmonic contaminations were eliminated by detuning to reduce the incident X-ray intensity by \sim 30%. Energy calibration has been simultaneously carried out for each measurement with (Ga₂O₃) powder placed in front of the third ion chamber. The data reduction of the experimental spectra was performed by the standard procedure reported previously. Total in situ XAFS spectra have been divided into four groups along with electrochemical reactions, as denoted by the 1D scan of the first discharge, 1C scan of the first charge, 2D scan of the second discharge, and 2C scan of the second charge, respectively.

Electrochemical Characterization. Coin-type half-cell tests were conducted, using samples at a 0.1 C rate between 1 and 1.5 V, using the same C rate for charging and discharging. Cathodes for battery test cells were made of the active material (~25 mg), super P carbon black (MMM, Belgium), and polyvinylidene fluoride (PVdF) binder (Solef) in a weight ratio of 80:10:10. A cathode slurry was prepared by thoroughly mixing a N-methyl-2-pyrrolidene (NMP) solution with the PVdF, the carbon black, and the powdery GaP material. Electrodes were prepared by coating the cathode slurry onto an Al foil, followed by drying at 130 °C for 20 min. Coin-type battery test cells (size 2016R), containing a cathode, a Li metal anode, and a microporous polyethylene separator, were prepared in a helium-filled glovebox. The electrolyte used was 1.03 M LiPF₆ with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (3/3/4 vol %) (Cheil Ind. Korea).

Results and Discussion

Figure 1 exhibits the XRD patterns of as-prepared GaP particles refluxed for 1 and 4 h at 390 °C. All of the peaks were indexed to a zinc blende structure. A broad peak between 30 and 40° in Figure 1 was originated from the residual P that existed as an amorphous phase. We observed that lower hydrothermal temperatures led to a higher peak intensity of the phosphor. However, this peak completely disappeared after a prolonged reflux time. Particle size was estimated to be 19 and 27 nm for 1 and 4 h of reflux time, respectively. Figure 2 shows transmission electron microscopy (TEM) images of the identical samples (1 and 4 h) used for XRD analysis. These TEM images also confirmed the presence of the aggregated nanosized



Figure 2. Plots of (a) voltage profiles of GaP nanoparticles prepared at 390 °C for 1 and 4 h in coin-type half cells and (b) cycle life vs charge capacity of part a (0.1 C = 60 mA/g).



Figure 3. TEM images of the GaP nanoparticles prepared at 390 $^{\circ}$ C for (a) 1 and (b) 4 h.

particles and agree well with the crystal size estimate from the XRD measurement.

Figure 3 shows voltage profiles of as-prepared GaP particles with 19 and 27 nm particle sizes between 0 and 1.5 V at a rate of 0.1 C (=60 mA/g). For the 19-nm-sized particles, the first discharge and charge capacity were 1200 and 400 mAh/g, respectively, showing an irreversible capacity ratio of 70%. After 30 cycles, the capacity retention was 50%. The difference in electrochemical properties between the samples may be related to the amorphous phase on the particle surface. If this amorphous phase on the 19-nm-sized particles is a poor lithium conductor, a larger initial IR drop is expected in 19-nm-sized particles than in 27-nm-sized particles. As can be seen in Figure 3a, 19-nm-sized particles (1 h) show a larger initial IR drop during the discharge.

For the 27-nm-sized particles, the first discharge and charge capacity were 1690 and 790 mAh/g, respectively, showing an irreversible capacity ratio of 48%. The capacity retention after 30 cycles was 40%. The 27-nm-sized particles showed better



Figure 4. Ex situ XRD patterns of the cells containing GaP nanoparticles prepared at 390 °C for 4 h. All of the GaP electrodes were separated after charging or discharging at certain voltages, followed by applying a constant voltage for 1 h.

electrochemical performance but exhibited a larger irreversible capacity than Sn_3P_4 or VP_4 with a value of 85%.^{25,26} Further, compared with Sn_3P_4 and VP_4 , which showed a capacity retention of ~0 mAh/g after 30 cycles between 1.4 and 0 V, our samples showed much improved capacity retention between 0 and 1.5 V. Previous studies showed that this rapid capacity fade was related to the conversion of the Li₃P phase to an insulator LiP phase above 0.75 V. In these regards, lithium reaction behavior and the fading mechanism of GaP may be different from Sn_3P_4 and VP_4 .

Figure 4 shows ex situ XRD patterns of the 27-nm-sized GaP electrode between 1.5 and 0 V. The patterns showed that the GaP phase was observed up to when the electrode discharged to 0.5 V, indicating that Li can be inserted in GaP topotactically, that is, Li_{0.4}GaP. The amount of lithium inserted based upon the discharge capacity was approximately 100 mAh/g, from which 0.4 lithiums can be topotactically inserted into GaP. Upon discharging to 0.32 V, the GaP peaks disappeared completely, indicating the decomposition of the Li_xGaP phase into other phases. During the initial discharging region, an effective change of XRD pattern was not observed in the present study, in spite of the Li-ion insertion. It can be considered that Li-ion is simply adsorbed on the molecular pore surface with a proper free volume in the initial discharge state and the Li-ion insertion is disordered into the mlolecular channel. The process deserves to lead to local structural distortion and short range disorder, which can be supported by extended X-ray absorption fine structure (EXAFS) result variation of peak B in the Fourier transform (FT) of EXAFS in Figure 6. However, a three-



Figure 5. Differential capacity plot vs cell potential after the first, second, and third cycles.



Figure 6. Plots of voltage as a function of reaction time under independently applied current densities for the first and second cycles where the electrochemical reaction time was consistent with the XAFS correction time.

dimensional long range polymeric network of GaP effectively remains. Therefore, initial Li-ion insertion results in the change of relative XRD peak intensity ratio rather than XRD peak shift. Furthermore, the crystal size of GaP in the present study is several tens of nanometers. The XRD peak width is very broad. Thus, the peak shift commented on by a reviewer is very difficult to observe in this case. More Li-ion insertion is not allowed to maintain the polymeric network. The excess Li-ion leads to cleavage of long range ordering and then phase transition to the Ga metallic phase.

Previous MP studies reported that the formation of the Li₃P phase was dominant in this voltage region, but in our case, the diffraction peaks did not match with Li₃P. Since the diffraction peaks of other types of Li_nP phases are superimposed onto each other between 30 and 40°, it is not possible to distinguish between them. In addition, a differential capacity plot supports the lack of existence of a Li₃P phase. In Figure 5, a differential capacity plot of the GaP showed a strong peak at 0.25 V during the discharge which completely disappeared upon charging. This implies that the phase transition at 0.3 V is irreversible. Previous studies on Sn₃P₄ and VP₄ revealed no peak at 0.25 V, and the phase transformation from LiP to Li₃P appeared as a large peak around 0.75 V, which showed reversible phase transition.^{25,26} In our case, a small peak around 0.75 V disappeared upon subsequent cycling, indicating that this phase was not LiP. In accordance, the peak at 0.25 V is believed to be due to irreversible Li_nP phases. Instead, a reversible reaction that occurs between 0.4 and 0.8 V is a main source for Li reaction, that is, Li_xGa. Ga is in the liquid state at room temperature, but it turned

into the solid-state Li_2Ga after full lithiation (Li_2Ga peaks around 21° were superimposed with Li_nP).

In order to confirm the structural evolution of GaP during Li reactions, in situ Ga K-edge XAFS experiments were carried out. Figure 6 shows plots of voltage as a function of reaction time under independently applied current densities for the first and second cycles where the electrochemical reaction time was consistent with the XAFS correction time. As an example, a low current density of 0.05 mA/cm² was used in the initial discharge region (D1) in order to observe correct structural evolution for the fast electrochemical reaction, as shown in the figure inset.

For the first discharge (1D scan), the spectral variation of the Fourier transform magnitudes (FT) for cutoff voltageresolved Ga K-edge EXAFS spectra can be classified into four regions (D1, D2, D3, and D4) depending on the electrochemical reaction, as shown in Figure 7. The pristine GaP presents two distinct FT peaks, A and B at \sim 2.0 and \sim 3.6 Å, respectively, corresponding to Ga-P bonding and Ga-Ga scattering, respectively, by way of phosphorus atoms. The GaP consists of a honeycomb structure through a GaP4 tetrahedral polymeric network which leads to a molecular channel with a proper free volume (Figure 8). In the D1 region (3.3-0.5 V) of the first electrochemical Li-ion uptake region, there is no effective spectral change for the electrochemical reaction, as shown in Figure 7a. This means that Li-ion uptake has no effect on the molecular structure of GaP. The molecular pores with free volume can allow Li-ion uptake corresponding to a discharge capacity of ~90 mAh/g without local structural variation around the Ga atoms.

For the D2 region (0.5-0.32 V), on the other hand, further Li-ion insertion beyond the D1 region begins to affect the local structure around the Ga atoms (Figure 7b). Without effective spectral variation of peak A, the peak feature of peak B indicating the existence of a GaP₄ tetrahedral polymeric network changes randomly, although, overall, the FT peak pattern is constant until the 1D2_scan 27 corresponding to an additional discharge capacity of \sim 522 mAh/g. The maintaining of the FT peak feature for Ga-P and Ga-P-Ga scatterings means that the Li-ion uptake mechanism is still intercalation into molecular pores. Unlike in the D1 region, however, the random variation of peak B in the D2 region shows a local structural variation of the GaP₄ pores by higher Li-ion uptakes. Namely, the molecular pore channels initially saturated with a Li-ion uptake of ~ 100 mAh/g in the D1 region is forced to be local-distorted by the steric hindrance of excess Li-ion uptake into the molecular pores. The following positive charge excess in the free volumetric lattice can be compensated with crystal structural modification without oxidation state change of Ga, which allows a Li-ion amount of \sim 522 mAh/g to be effectively intercalated into the molecular channel. In summary, the amount of Li-ion for the \sim 612 mAh/g can be uptaken through the intercalation mechanism into molecular pores, $GaP \rightarrow Li_{1.8}GaP$, through the electrochemical regions D1 and D2.

The higher Li-ion uptakes beyond \sim 612 mAh/g lead to effective structural variation of the GaP pore structure (region D3 up to 0.3 V). As shown in Figure 7c, the intensity of peak A becomes weak and the peak position shifts toward a larger bonding distance region, while peak B gradually decreases and finally disappears at 1D3_scan 38 for an additional Li-ion uptake of \sim 184 mAh/g from scan 27, corresponding to a total discharge capacity of \sim 796 mAh/g. The new FT peak at 2.2 Å for 1D3_scan 38 corresponds to pure Ga–Ga metallic bonding. The disappearance of peak B is closely associated with an abrupt



Figure 7. Spectral variation of Fourier transform magnitudes (FT) for cutoff voltage-resolved Ga K-edge EXAFS spectra during the first discharging process.

cleavage of the GaP₄ tetrahedral polymeric network. This means that the intercalating mechanism into molecular pores is no longer effective in the higher Li-ion inserted region. The charge compensation mechanism is converted into a phase transition. The honeycomb-like pore structure stabilized with ~ 600 mAh/g cannot allow any more Li-ion uptake and begins to be broken. Figure 8 shows that the excess uptaken Li-ion can chemically bond with the phosphorus atoms of Ga-P bonds. The evolution of Li-P bonding gives rise to local structural distortion around the GaP₄ tetrahedral site and, then, formation of electrochemically inactive LinP clusters. Free Ga atoms can then be simultaneously aggregated through atomic rearrangement, and consecutive Li-ion uptakes lead to the formation of a Ga metallic phase. From the absence of FT peaks in the higher r space, it is found that there is no longer a GaP₄ polymeric network, which means the Ga metallic phase cannot grow into the close-packed bulk scale. The limitation to crystal growth of the Ga metallic clusters is due to the existence of neighboring Li_nP clusters. As

a result, the electrochemical Li-ion uptake mechanism in the D3 region has changed from Li-ion intercalation through molecular pores (\sim 612 mAh/g) to phase transition to a Ga metallic phase (\sim 184 mAh/g).

More Li-ion uptake is also possible in the later D4 region (below 0.3 V), following little distinct FT peak feature variation. As mentioned above, the structural phase transition from GaP to the Ga⁰ metallic phase can cover the discharge capacity of ~796 mAh/g, following the first Li-ion intercalation into the molecular channel. After the formation of a pure Ga⁰ metallic phase (1D3_scan 38), further Li-ion uptake of ~894 mAh/g proceeds until 0.0 V, which means the Ga⁰ phase can be considered as a new origin capable of Li-ion uptake. Since the Ga metallic phase exists in a liquidlike phase, it itself can uptake Li-ion like a sponge without systematic structural variation. As shown in Figure 7d, the FT peak of Ga–Ga metallic bonding at 2.2 Å shows a random change of the radial distribution function between 2.2 and 3.0 Å along with a gradual increase



Figure 8. Model for local structural variation by Li-ion uptake into molecular channels of GaP: (a) GaP; (b) lithium insertion into pores of GaP molecular channels; (c) reaction with Li and GaP.



Figure 9. Plot of FT peak variation during the first Li-ion extraction process in region C of Figure 7.

of average bond distance to 2.35 Å. The increase of average bonding distance in the D4 region results from Ga–Li metallic alloying. This is because the atomic radius of a Li atom (1.45 Å) is larger than a Ga atom (1.30 Å). The overall higher bonding shift followed by the random FT peak feature variation during the Li-ion uptake is due to the evolution of a Ga–Li alloying phase. Therefore, the Li-ion uptake mechanism in this region transitions from a Ga⁰ metallic phase to GaLi alloying.

Figure 9 shows the FT peak variation during the first Li-ion extraction process in region C of Figure 7. On charging, the FT peak for the Ga–Li alloying gradually shifts to the lower **r** space region of 2.2 Å for pure Ga–Ga metallic scattering and returns to that of a pure Ga⁰ metallic phase in the successive charged state, indicating volume contraction through Ga–Li

dealloying. The electrochemical reaction is reversibly related to the structural variation of the first discharging process until this region. However, the FT peak shift stops suddenly at ~ 2.2 Å upon further charging to 1.5 V. The FT peak variation could not show the peak characteristics of Ga-P for the initial GaP phase, although the Li-ion extraction proceeds to full charging to 1.5 V. This means that further charging cannot reversibly recover the formation of the GaP phase. There is also no reversible evolution of a GaP tetrahedral polymeric network. The absence of a FT peak at 3.5 Å indicates that the aggregated Ga metallic cluster cannot be pulverized to form chemical bonding with phosphorus atoms. Since an electrochemically inactive Li_nP phase is distributed around a GaLi metallic cluster, the existence of a Li_nP matrix prevents reversible formations of chemical bonding between gallium and phosphorus atoms, as well as molecular pores through the tetrahedral polymeric network. Finally, the Li-ion extraction mechanism can be achieved in a phase change from GaLi alloying to a Ga⁰ metallic phase, but not beyond a GaP phase, which leads to a decrease of the charge capacity ($\sim 800 \text{ mAh/g}$) with respect to the first discharge capacity ($\sim 1690 \text{ mAh/g}$).

Nonreversible structural recovery to the initial molecular pore GaP phase directly affects the successive second dischargecharge process. Because the onset of the second discharge is a Ga metallic cluster, the Li-ion uptake mechanism corresponds to the phase transition to a Ga-Li alloy, as shown in Figure 10a. Unlike the case of the first discharge, the second full discharge shows different spectral behavior. While the first full discharge shows relatively homogeneous chemical bonding for the Ga-Li alloy, the second discharge presents an asymmetric peak feature (denoted by arrows), which means there are two chemical bondings of Ga-Ga and Ga-Li clusters. The existence of Ga-Ga bonding means that not all Ga metal clusters participate in the Li-ion uptake process. The non-electrochemically reactive Ga phase leads to a decrease of the second discharge capacity, in comparison with the corresponding capacity of the first discharge in the D4 region. On the second charge, the FT peak intensity of the higher Ga-Li bonding gradually decreases and, simultaneously, the lower Ga-Ga FT peak intensity increases, showing a symmetric peak feature, as shown in Figure 10b. As a result, it was found that the second discharge-charge process along with the alloy/dealloy mechanism leads to capacity fading due to imperfect GaLi alloying in the Li-ion uptake. This is in good agreement with the electrochemical cycle property in Figure 3, although the charge is electrochemically reversible.

Here, it is necessary to determine the reaction formula evaluated from the chemical composition for each electrochemical-structural step, as shown in Figure 11. On the basis of the EXAFS structural analysis, the change of chemical composition at each discharge region can be inferred from the corresponding discharge capacity. The first overall discharge reaction can be considered as follows: GaP \rightarrow (1) Li_{*a*}GaP (~90 mAh/g) \rightarrow (2) Li_{*a*+*b*}GaP (~522 mAh/g) \rightarrow (3) Ga + *c*Li_{*n*}P (~184 mAh/g) \rightarrow (4) Li_{*d*}Ga + *c*Li_{*n*}P (~894 mAh/g).

Since the initial discharge capacity was ~1690 mAh/g corresponding to 4.5 mol of Li-ion uptake per 1 mol of GaP, Li-ion uptakes evaluated from each discharge capacity can be estimated as 0.24, 1.39, 0.49, and 2.38 mole Li-ion, respectively. The overall discharge is followed by GaP \rightarrow Li_{0.24}GaP \rightarrow Li_{1.63}-GaP \rightarrow Ga + 2.12Li_nP \rightarrow Li_{2.38}Ga + 2.12Li_nP. For the first charge process, only 2.38 mol of lithium of Li_{2.38}Ga can be reversibly alloyed/dealloyed with the Ga phase. Capacity loss during the first charging process may be associated with possible



Figure 10. Spectral variation of Fourier transform magnitudes (FT) for cutoff voltage-resolved Ga K-edge EXAFS spectra during the second charge and discharge.



Figure 11. EXAFS structural analysis of each different scan during the first charge and the second charge and discharge.

electrolyte decomposition reactions between LinP particles with the electrolytes. This reaction is expected to enhance in nanoparticles like our GaP sample with a large surface area and poor crystallinity. Monconduit's group proposed enhanced solubility of the Li₃P into the electrolyte.³¹ The phase transition from the Li2.38Ga alloy to the pure Ga metallic state leads to a charge capacity of ~800 mAh/g, corresponding to ~2.08 mol of Li-ion extraction, as shown in Figure 3. The charge progress goes as $Li_{2.38}Ga \rightarrow Li_{2.08}Ga$, which means the fully charged process could not extract all 2.38 mol of Li-ion and a minor Li-Ga alloy phase distributes in the major pure Ga phase. Further electrochemical reaction involves the phase transition from a pure Ga metallic state to a LiGa alloy and vice versa. However, capacity fading upon prolonged cycling was attributed to volume change between Li_xGa and Ga during lithium alloying and dealloying in the electrochemically inactive Li_nP matrix.

Conclusion

GaP nanoparticles prepared by sodium naphthalenide reduction led to a particle size smaller than 30 nm, and its electrochemical property was better than other metal phosphides, even above 0.75 V. This was due to the formation of an electrochemically stable LinP matrix phase. The phase transition from GaP to Ga–Li alloy by way of a Ga metallic state was the origin for the electrochemically irreversible property. Therefore, a molecular pore GaP phase could be selectively used as two kinds of anode materials, namely, a Li-ion intercalating system into molecular channels in the voltage regions above 0.32 V and a phase transition system of Ga–Li alloy/dealloying until 0.0 V.

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