

Short communication

Phosphides with zinc blende structure as anodes for lithium-ion batteries

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Received 18 February 2005; accepted 13 May 2005

Available online 11 July 2005

Abstract

The phosphides InP and GaP with a zinc blende structure are examined as anode materials for lithium-ion batteries. During discharge, X-ray diffraction phase analysis reveals the formation of Li–In/Li–Ga alloy and amorphous Li₃P. On charge, lithium is extracted from both Li_xM (M = In, Ga) alloy and Li₃P. InP shows a reversible capacity of ~475 mAh g⁻¹ in the voltage range between 0.2 and 1.5 V, whereas GaP exhibits poor capacity retention compared with that of InP.

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Keywords: InP; GaP; Anode; Lithium-ion battery; Reversible capacity; Zinc blende structure

1. Introduction

In recent years, there has been great interest in studying lithium alloy systems and intermetallics as anode materials for Li-ion batteries [1–4]. Although Li–M alloy systems offer high initial discharge capacities, the reversibility is poor. Recently, several transition metals-containing phosphides [5–17] and nitrides [18–20] have been proposed as promising anode materials. Interesting phase transitions and formations have been observed on reaction of lithium with phosphides. In some phosphides such as MnP₄ and Cu₃P, the formation of ternary Li–M–P phases takes place [5,6]. During the discharge and the charge of MnP₄, a transformation between two crystalline phases, viz., Li₇MnP₄ ↔ MnP₄, [5] has been found. On the other hand, the initial discharge of CoP₃ involves complete destruction of the structure and lithium reversibly reacts with P to form Li₃P in the matrix of nanophase Co metal [7–9].

To date, most of the phosphides have contained transition metals. The transition metal is the inactive part in the electrode. The reversible capacity of phosphides can be increased by having a counter cation that can form an

alloy with lithium. With this in view, we have studied the electrochemical properties of Sn₄P₃ [21] and Zn₃P₂ [22]. Kim et al. [23] reported the anodic behaviour of nanophase Sn₄P₃ synthesized by mechanochemical method. It was proposed that lithium is intercalated into the structure during the initial stages of discharge and on complete discharge the formation of Li_{4.4}Sn and Li₃P phases is anticipated. By restricting the cycling voltage window to 0.0–0.72 V, a reversible capacity of 370 mAh g⁻¹ was observed for Sn₄P₃. In a recent article [24], the Sn content is further increased in Sn₄P₃, where by Sn₅P₃ is synthesized by mechanical alloying. Sn₅P₃ displays an improvement in the reversibility to 530 mAh g⁻¹. In the present study, InP and GaP are chosen for study as anode materials. It is known that, In and Ga metals can form an alloy with lithium. Thus, high reversible capacity is expected for InP and GaP due to the electrochemical activity of both the metal and P. Both the compounds have a zinc blende structure and the antimony analogues have been studied as anode materials [25,26]. A reversible capacity of ~225 mAh g⁻¹ was observed in the voltage window 0.5–1.2 V for InSb and a careful in situ XRD study indicated the formation of Li₃Sb and In metal, followed by the alloying of Li with In [27]. In this study, the electrochemical properties of InP and GaP are investigated versus Li metal and a reaction mechanism is pro-

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posed on the basis of results from powder X-ray diffraction studies.

2. Experimental

High purity commercial samples of InP (Cerac, 99.999%) and GaP (Alfa, 99.999%) were used as received for the electrochemical studies. Electrochemical measurements were performed in two-electrode, Swagelok-type cells. The electrodes were prepared by spreading a slurry of 45 wt.% active material, 45 wt.% acetylene black (Denka Singapore Pvt. Ltd) and 10 wt.% PVDF dissolved in NMP on a stainless-steel foil. The electrolyte was 1 M LiPF_6 in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (Chiel Industries Ltd., Korea). The cells were assembled in an argon-filled glove box (m-Braun, ~ 3 ppm H_2O) with lithium metal (Aldrich, 99.9%) as the anode and a Teklon separator (Entek, USA). Galvanostatic charge and discharge cycling was conducted by means of an Arbin battery cycling unit at the C/5 rate (1C corresponds to the reaction of 1Li) over a fixed voltage range. After discharging and charging to a certain voltage, the cell was opened inside the glove box and ex situ XRD of the electrode was performed by covering the electrode with a mylar film to avoid reaction with moisture/air. The XRD patterns were recorded with a Rich Seifert XRD unit (P3000, $\text{Cu K}\alpha_1$ rad.).

3. Results and discussion

3.1. InP

The discharge and charge curves for the Li–InP cell cycled in the voltage window 0.05–2.0 V are given in Fig. 1. The initial discharge curve shows a small plateau at ~ 0.8 V followed by a long plateau at ~ 0.3 V. The shoulder at ~ 0.8 V is due to the formation of a solid electrolyte interface (SEI) with acetylene black [8]. After subtracting the capacity contribution from the acetylene black, the initial discharge capacity is 1180 mAh g^{-1} , which corresponds to the reaction of 6.4Li. During charge, the voltage increases smoothly

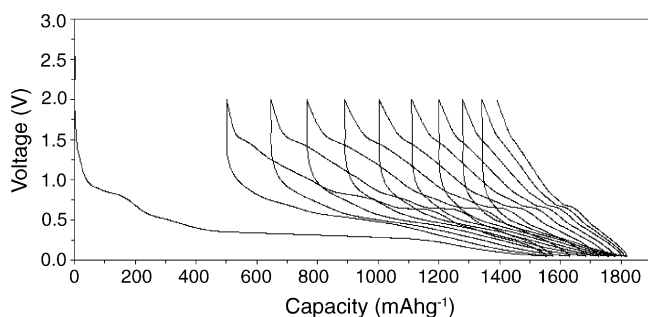


Fig. 1. Discharge and charge curves of Li/InP cell in voltage window 0.05–2.0 V at C/5 rate.

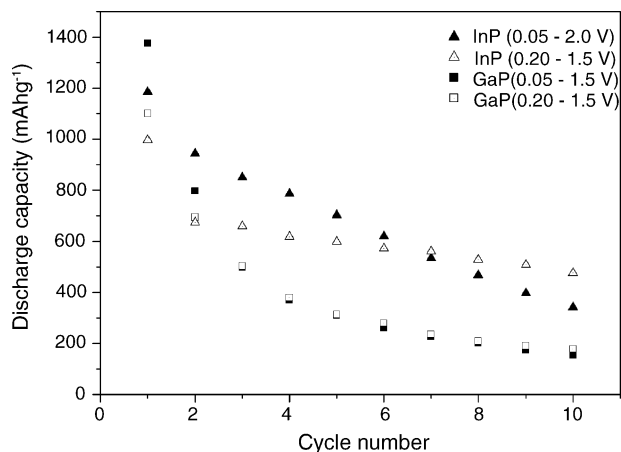


Fig. 2. Discharge capacity vs. cycle number of Li/InP and Li/GaP cells in different voltage windows, capacity corrected for acetylene black.

and a plateau is observed at ~ 0.65 V. The maximum charge capacity is observed in the voltage region below 1.5 V and the voltage increases sharply above 1.5 V. After subtracting the capacity due to acetylene black, the initial charge capacity is 913 mAh g^{-1} , which corresponds to the extraction of $\sim 5\text{Li}$. Thus, Faradaic efficiency for the first cycle is about 77%. Although InP is structurally similar to InSb, the initial discharge behaviour of the two materials is different [27]. Electrochemical studies reported on InSb also shown a plateau at ~ 0.65 V during charge. Hence, the plateau at 0.65 V during charge of InP can be attributed to the extraction of lithium from Li–In alloy. On cycling, the discharge–charge curves shift to the right, which indicates that the discharge capacity is greater than the previous cycle charge capacity. A similar trend in discharge–charge behaviour has been observed previously for InSb [27]. The increase in discharge capacity can be due to the formation of Li-containing passive layers on the surface of the electrode [28]. The cycling behaviour of InP in the voltage window 0.05–2.0 V is presented in Fig. 2. Although, the discharge capacity decreases with cycle number, it reports a promising value of $\sim 300 \text{ mAh g}^{-1}$ after 10 cycles.

Ex situ XRD patterns for InP electrodes are shown in Fig. 3. The pattern for InP discharged to 0.3 V (Fig. 3(b)) indicates the presence of Li–In alloy and a InP phase. During discharge, the formation of In metal is not observed prior to alloy formation. This is in contrast to the reaction mechanism observed for InSb, in which during initial stages of discharge indium metal is produced. The direct development of Li–In alloy in case of InP is due to the low discharge plateau (~ 0.3 V) of the cell. Thus, although indium extrudes from the lattice during discharge, it reacts simultaneously with lithium to form Li–In alloy. The XRD pattern for a completely discharged electrode (Fig. 3(c)) shown the presence of only Li–In alloy; there are no peaks corresponding to the initial InP phase. This indicates that InP reacts completely during discharge. Also, the Li_3P phase is not seen in the XRD pattern, which may be due to the formation of an amorphous

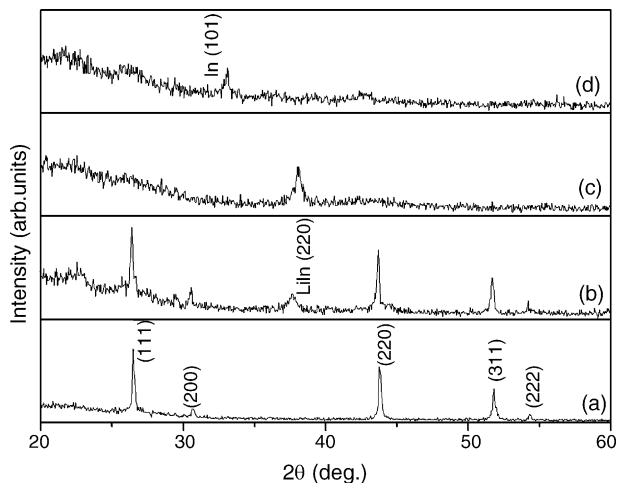
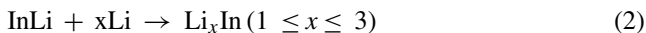
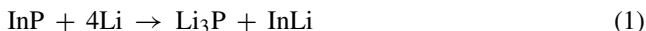
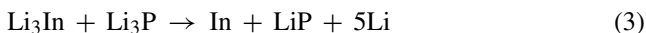


Fig. 3. Ex situ XRD patterns of InP electrode taken (a) before discharge, (b) after discharge to 0.3 V, (c) after initial discharge to 0.05 V, and (d) after charge to 2.0 V.

phase. The XRD pattern for a completely charged electrode (Fig. 3(d)) reveals the formation of an In metal phase and the absence of a Li–In alloy phase. Thus, the reaction sequence of lithium with InP during initial discharge can be written as follows:



The observed lithium content (6.4Li) during discharge is nearly equal to the expected value (6Li). The small excess lithium consumption can be attributed to SEI formation with carbon. The high charge capacity (5Li) indicates that lithium is extracted from both Li_3P and Li_xIn alloy. Pralong et al. [8] have proposed that in CoP_3 , the reversible discharge capacity is due to transformation of $\text{Li}_3\text{P} \leftrightarrow \text{LiP}$. Thus, the charge reaction can be written as:



3.2. GaP

The discharge–charge curves of Li–GaP cycled in the voltage window 0.05–1.5 V are shown in Fig. 4. The discharge voltage behaviour of GaP is similar to that of InP except that during charge no plateau is observed in GaP. During charge, the voltage increases smoothly to 1.5 V. After subtracting the capacity contribution due to acetylene black, the initial discharge capacity is $\sim 1375 \text{ mAh g}^{-1}$, which corresponds to the reaction of $\sim 5.2\text{Li}$. The thermodynamic and electrochemical properties of the Li–Ga system have been studied by Wen and Huggins [29] and it was found that lithium forms an alloy with gallium to a maximum composition of Li_2Ga . The initial discharge reaction can be written as:

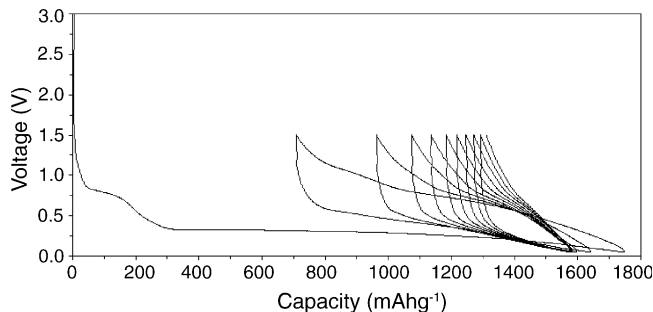
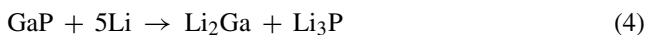


Fig. 4. Discharge and charge curves of Li/GaP cell in voltage window 0.05–1.5 V at C/5 rate.

The ex situ XRD pattern for the GaP electrode taken after discharge to 0.3 V indicate broadening of the peaks without any change in peak position (Fig. 5(b)). The pattern for the completely discharged electrode (0.05 V) shows a small hump at around $2\theta = 42^\circ$, which can be attributed to the formation of LiGa phase. There are no peaks corresponding to the initial GaP phase and this suggests the complete reaction of GaP. Also, the Li–Ga alloy is expected to form directly during discharge because of the low discharge plateau. The initial charge capacity is $\sim 900 \text{ mAh g}^{-1}$ and corresponds to the extraction of $\sim 3.4\text{Li}$. The Faradaic efficiency of the first cycle is 65.5%. The ex situ XRD of the GaP electrode at the end of first charge (1.5 V) indicates the formation of an amorphous phase and the disappearance of the LiGa alloy peak, i.e., lithium is extracted from the Li–Ga alloy. The high charge capacity (3.4Li) clearly suggests that lithium is also extracted from Li_3P during charge. On subsequent cycles, the observed reversible capacity is due to the reversibility of both Li_3P and Li–Ga alloy. The discharge capacity falls with cycle number and reaches a value of $\sim 150 \text{ mAh g}^{-1}$ after 10 cycles (Fig. 2). The electrochemical performance of the

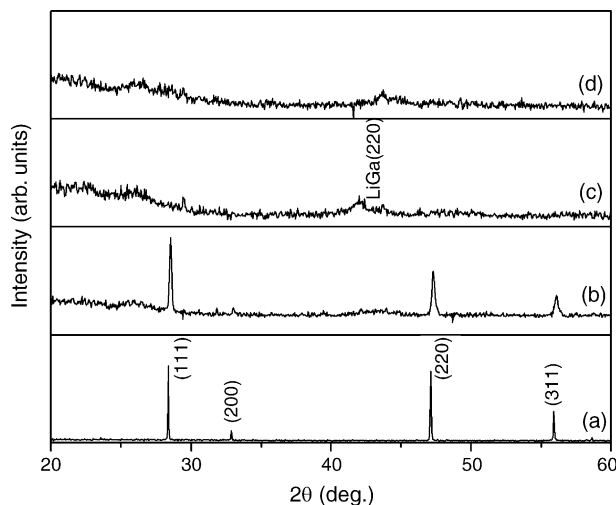


Fig. 5. Ex situ XRD patterns of GaP electrode taken (a) before reaction, (b) after discharge to 0.3 V, (c) after initial discharge to 0.05 V, and (d) after charge to 1.5 V.

isostructural analogue GaSb also shows an inferior capacity retention compared with that of InSb [26].

The capacity retention in intermetallics can be enhanced by choosing a proper voltage window. The cycling of InP and GaP has been carried out in the voltage window 0.2–1.5 V with a view that the volume changes in the electrode can be restricted by increasing the lower voltage limit. The cycling performance does indeed show an improvement in the reversible capacity (Fig. 2). A high discharge capacity of $\sim 475 \text{ mAh g}^{-1}$ is observed for InP. With GaP, however there is not much improvement; the capacity reaches only $\sim 175 \text{ mAh g}^{-1}$ after 10 cycles.

4. Conclusions

The reaction of lithium with InP or GaP occurs at low voltages with low polarization, which is a good reason to select these phosphides as anode materials. The irreversible capacity losses observed on the first cycle of the phosphides are less than those for Sn or other oxide-based compounds. Because of the low average potential ($\sim 0.3 \text{ V}$) of the Li/InP cell, Li–In alloy formation is seen directly in the XRD pattern without prior formation of In metal. Upon charge, lithium is extracted reversibly from both Li_3In and Li_3P . A high discharge capacity of $\sim 475 \text{ mAh g}^{-1}$ is achieved even after 10 cycles when the Li/InP cell is cycled in the voltage window 0.2–1.5 V. The initial discharge plateau and the reaction mechanism of GaP are similar to those of InP, but the charge curves of GaP exhibit a gradual increase in voltage without any plateau. Also, the reversibility due to Li–Ga alloy and Li_3P is poor, which leads to capacity fading with cycling. After 10 cycles, the Li/GaP cell shows a discharge capacity of only $\sim 175 \text{ mAh g}^{-1}$. The long-term cycling stability of phosphides remains a key issue in establishing their practical application in Li-ion batteries.

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