Reversible lithium uptake by CoP₃ at low potential: role of the anion

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Abstract

Although various transition metal compounds in Group V (nitrides and antimonides) have been reported to act as low potential Li insertion hosts, the phosphides have remained unexplored to date. We show here that lithium uptake and extraction in the metal phosphide, CoP₃, provides a reversible capacity of 400 mAh/g at an average potential of 0.9 V vs Li/Li⁺, via a novel mechanism. The latter was revealed using a combination of X-ray diffraction, electron microscopy, and potentiodynamic and galvanostatic intermittent measurements coupled with X-ray photoelectron spectroscopy (XPS). Initial uptake of Li forms highly dispersed cobalt clusters embedded in a matrix of Li₃P; extraction of Li from this ion-conductive matrix on charge yields nano-particles of LiP, with little change evident in the oxidation state of the Co site. This shows that contrary to the case of metal oxides here the anion plays the major role in reduction and oxidation. We expect this is a general phenomenon for phosphides, and to be of fundamental interest and future importance in the search for new negative electrode materials. © 2002 Published by Elsevier Science B.V.

Keywords: Cobalt phosphide; Anode; Lithium-ion battery; Transition metal pnictides; XPS; TEM

1. Introduction

The development and study of new negative electrode materials for rechargeable lithium batteries remains a major topic in the area of the energy storage. Alternatives to commercial carbonaceous materials are eagerly sought to overcome the limitations of low gravimetric and volumetric capacity and safety concerns that these materials exhibit, and to match the higher capacities of new emerging cathode materials. Meeting the requirements of reversibility and low cost is difficult, however. Explorations of transition metal oxides as anode materials, first reported by Idota et al. [1], Nazar and coworkers [2] and by Tarascon and coworkers [3], developed new concepts concerning the mechanism of Li “insertion”. For example, in bulk MoO₃, Li uptake drives the reduction of the metal to form a nano-phase matrix of Li₂O, and metal suboxide particles: on charge, Mo-oxide is regenerated, although “crystalline MoO₃” is not fully achieved. Similarly, reduction of nano-phase CoO produces Co nano-particles in a matrix of Li₂O; and nano-CoO is regenerated on charge [4]. It has subsequently been revealed that the latter reaction can be thought of as a displacement reaction of the Co²⁺ ions within the oxide matrix for Li⁺ on discharge, with the reverse occurring on charge [5]. In these relatively “ionic” systems, reduction is driven by the difference in thermodynamic free energy between the oxidized and reduced states of the metal.

Recent interest has also been piqued by reports of Li uptake in transition metal compounds of Group V, such as nitrides [6] and antimonides [7], which show a lower intercalation potential compared to the respective oxides. This results from the lower formal oxidation state of the metal, and strong covalent character of the M-pnictogen bond, leading to high lying mixed anion-metal bands, and a high degree of electron delocalization [8]. Where a fully lithiated end member exists, conversion between two crystalline phases can occur on lithium insertion, i.e., MnP₄ ↔ Li₇MnP₄ [9]. Here, we report a completely different reversible Li uptake in metal phosphides exemplified by CoP₃. We have found unique behavior in this system: namely the redox behavior is based on shuttling between two different phosphorus oxidation states.
2. Experimental

Synthesis of the cobalt phosphide was performed by heating stoichiometric amounts of metallic cobalt and red phosphorus at 650 °C for 24 h, in a stainless steel tube sealed under argon. Powder diffraction patterns were obtained using a Siemens D500 diffractometer equipped with a diffracted beam monochromator (CuKα radiation). The starting material, CoP₃ was a pure skutterudite phase, as confirmed by Rietveld refinement of its XRD pattern that yielded values (cubic space group IM3; \( a = 7.7082 \AA \)) as previously reported [10]. The structure consists of CoP₆ octahedra corner-shared to form P₄ rings (Fig. 1, inset). The Li uptake properties of the material were evaluated in Swagelok-type cells vs the Li/Li⁺ couple using lithium as the anode. Mixtures of the active material and 40 wt% carbon black were cast on nickel current collectors. The cells were assembled in an argon filled dry-box using a 1 M solution of LiPF₆ in 1:1 EC/DMC as the electrolyte, and examined using a MacPile controller (Biologic S.A., Claix, France).

X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Scientific XPS Microprobe ESCALab 250 (with focused monochromatized AlKα radiation of energy 1486.6 eV, with a chamber pressure <10⁻¹⁰ mbar) on an irradiated area of 0.4 × 1 mm². The cycled samples were opened in the dry-box, washed with acetonitrile and transferred to the XPS analysis chamber through a sample load-lock system to prevent air exposure. Charge compensation was employed during data collection using a combination of a low energy flood gun and low energy ions (care was taken to avoid charging). These samples were also analyzed by means of transmission electron microscopy (TEM, Philips CM12).

3. Results and discussion

The voltage vs composition curves for the insertion of Li into CoP₃, acquired at a rate of 1Li⁺ per 10 h are shown in Fig. 1. The first discharge process is characterized by a flat plateau corresponding to the uptake of 9 Li (after correction for the carbon contribution; the initial feature in the curve at 0.8 V corresponds to the SEI formation with carbon). On charge, 6 Li are extracted, leading to a reversible capacity of 1000 mAh/g of CoP₃, that fades to 600 mAh/g after 10 cycles and stabilizes at > 400 mAh/g. By means of potentiodynamic cycling with galvanic acceleration, a bell shaped current response associated with a constant voltage (0.35 V; not shown here) during the first discharge shows that the plateau corresponds to a simple two-phase decomposition. We see no evidence for the formation of intermediate ternary phases "Li₃CoP₄," these are also not expected since only a lithium-poor/metal-rich phase, Li₅Co₅P₃, exists in the Li–Co–P phase diagram.

The reaction of CoP₃ with 9 Li⁺ that we propose on discharge: (CoP₃ + 9Li⁺ + 9e⁻ → 3Li₃P + "Co") is comparable to behavior reported by Tirado and co-workers [7] for CoSb₃, which has been proposed to transform into \((\text{Li}_{3}\text{Sb} + \text{Co})\) on Li uptake. In the case of CoP₃, the XRD pattern product at the end of the first discharge (Fig. 2) clearly shows the reflections of the Li₃P phase but not those of metallic cobalt. Any Co particles must be of nano-sized dimensions (well below the limit of detection in both XRD and TEM – see later).

The charge process, corresponding to the extraction of 6 Li, and subsequent cycling behavior is less obvious. The material becomes quasi-amorphous on oxidation,
as shown by X-ray diffraction and only very weak, broad reflections are evident even after data collection for extended periods (Fig. 2) [11]. An important question is whether the cationic or the anionic network plays the major role in the electrochemical redox process. That is, does oxidation result in re-formation of highly dispersed CoP₃ (as in the case of the oxide, CoO) or is the process more complex? To more closely investigate the lithium-driven structural and morphological changes, we examined the CoP₃ electrode at various stages of reduction and oxidation processes by means of transmission electron microscopy and X-ray photoelectron spectroscopy.

The TEM micrograph of the starting material (Fig. 3(a)) shows it consists of particles of dimensions ranging from 200 to 100 nm; as expected, selected area electron diffraction (SAED) patterns taken down the [1 1 1]* zone axis (Fig. 3(a), right) are consistent with the presence of well-crystallized particles in accord with the XRD results. When the CoP₃ is fully reduced (Fig. 3(b)), we observed a complete change of the texture compared to the starting material. The bright field image reveals the presence of 10–20 Å particles embedded within the crystallite, and preservation of the overall shape of the starting particle. In this pseudomorphic reaction, a partially amorphous material is formed, as confirmed by the SAED pattern that consists of broad, weak rings. The reflections were indexed to Li₃P (Table 1) in accord with the XRD pattern. Analysis of the broad ring pattern did not reveal any interplanar spacings assignable to cobalt crystallites (Table 1 and Fig. 3(b), right), indicating that the metal must be very highly dispersed. It is also possible that is weakly bonded to the matrix as highly metal-rich phosphide clusters. Particle dimensions below 10 Å would not be observable by SAED due to extreme broadening.

On charge, the bright field image shows the pseudo-amorphous character of the active material is preserved although the particle size is more than halved (Fig. 3(c)). Nonetheless, the weak, broad reflections observed in the XRD pattern are resolvable, and identifiable by SAED in the TEM owing to the smaller crystallite size that can be probed by this method. The crystallites yielded a very broadened SAED pattern consistent with their reduced dimensions (Fig. 3(c), right, inset) in which only a few concentric diffuse “halo” rings were visible, necessitating employment of a larger diffraction diaphragm to improve the image quality 1 2 [12,13]. The resulting SAED pattern (Fig. 3(c), right) was best indexed to LiP (Table 1), but not to CoP₃. 3 As no lines can be ascribed to Li₃P, it has been consumed during oxidation (Table 1). Hence, the electrochemical process appears best characterized as a redox reaction between Li₃P and LiP.

Evidence for the reversibility, and nature of this intriguing process was supplanted by XPS measurements that provide a direct “finger print” of the sample. The binding energy is characteristic of the elements present and their chemical states. Unfortunately, the resolvable Co2p XPS region cannot be used to elucidate the exact role of the cobalt, since metallic and covalent cobalt 2p (1/2,3/2) states are at almost the same energy level; furthermore the binding energy threshold does not

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1 The diffraction diaphragm was increased by a factor of 10 to increase the data sampling area: this explains the brightness of the SAED image associated with a quasi-amorphous phase in the relatively featureless XRD pattern. This technique is commonly used for “amorphous” silicon, for example, where similar effects are seen for nano-sized particles that do not show discrete features in their XRD pattern [12].

2 The co-existence of an “amorphous” XRD pattern, and an indexable ring pattern in the SAED using a standard aperture has also been observed; see [12].

3 Reflection positions matched those of LiP: P21/c, a = 5.582(1) b = 4.941(1) c = 10.255(2), β = 118.150, JCPDF no. 83–1575. Small deviations may result from the presence of defect-laden LiP, owing to its nano-dimensions and method of formation. Note that the two strongest lines of CoP₃: (2 0 0) and (2 2 0), do not match the observed lines, Table 1.
changesignificantlyfromthepristinematerialuponreductionoroxidation (Co2p1/2,3/2 = 2.3 at 793.5/778.4 eV in CoP3; 794.0/779.0 eV on discharge; at 793.7/778.7 eV on charge). Examination of the overlapping Co3p and Li1s region is more revealing, however: Fig. 4 shows the spectra of the fully charged and discharged electrodes, after ion sputtering to clean the surface. In both spectra, the broad feature (P1) at 60 eV is assigned to the Co3p (1/2, 3/2) states, by comparison with reference data [14]. This peak should, of course, remain unchanged in accord with the invariance of the Co3p states (see above). The source of the change in the spectra therefore must lie in the Li 1s states. In both spectra, the signature at 56 eV (P2) corresponds to Li+ from the residual electrolyte (LiPF6) [14]. In the spectrum of the discharged material (Fig. 4(a)), this peak is overlapped with another at 56.87 eV, but is distinguishable in a curve deconvolution. This peak (P3) is assigned to the Li 1s state in Li3P, in good accordance with the literature value of 56.9 eV [14]. It shifts to a higher binding energy (58.2 eV) on charge (Fig 4(b)), indicating the phosphorous oxidation state decreases. This peak is assigned to LiP by comparison with its XPS spectrum (binding energy: 59.03 eV). A simplified mechanism accounting for the initial reversible capacity of 6 Li can therefore be written as follows:

First discharge process:

\[
\text{CoP}_3 + 9\text{Li}^+ + 9\text{e}^- \rightarrow 3\text{Li}_3\text{P} + \text{"Co"}
\]

Subsequent cycling:

\[
3\text{Li}_3\text{P} \leftrightarrow 3\text{LiP} + 6\text{Li}^+ + 6\text{e}^-
\]

In this system, the relatively high electronic conductivity of CoP3 enhances initial electronic transport within the electrode material and facilitates the decomposition process. After discharge, the high ionic conductivity of Li3P of \(\sim 10^{-3} \text{ S/cm}\) (that has spurred its investigation as a solid electrolyte [15]) promotes Li ion transfer within the composite matrix. The role of the cobalt in the redox process (if any) is still unclear; since the cobalt is in a highly dispersed state in both the discharged and charged materials which preclude investigation of its nature, we can only conclude that it acts as an “active spectator” after initial discharge as bulk metallic cobalt is not formed. This is also in accord with the high levels of carbon that are needed in the compound electrode to promote electronic conductivity. The high degree of Co dispersion and bonding to the Li–

| Table 1 |
| List of expected and observed d-spacings from XRD and SAED patterns for the products after discharge and charge |

<table>
<thead>
<tr>
<th>Li3P, calculated reflections (Å)</th>
<th>d-spacing, SAED pattern (Å)</th>
<th>d-spacing, XRD pattern (Å)</th>
<th>Co metal, calculated reflections near observed (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) discharged state</td>
<td>3.69 (101)</td>
<td>3.69</td>
<td>~3.5</td>
</tr>
<tr>
<td>2.14 (110)</td>
<td>2.14</td>
<td>~2.1</td>
<td></td>
</tr>
<tr>
<td>1.86 (112)</td>
<td>1.85</td>
<td>~1.8</td>
<td></td>
</tr>
<tr>
<td>1.42 (210)</td>
<td>1.40</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>1.22 (300)</td>
<td>1.23</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>LiP, calculated d-reflections (Å)</td>
<td>d-spacing, SAED pattern (Å)</td>
<td>Approximate d-spacing (XRD) (Å)</td>
<td>CoP3, calculated reflections near observed (Å)</td>
</tr>
<tr>
<td>(b) charged state</td>
<td>3.40</td>
<td>~3.4</td>
<td></td>
</tr>
<tr>
<td>2.94 (111)</td>
<td>2.94</td>
<td>~3.0</td>
<td></td>
</tr>
<tr>
<td>2.46 (200)</td>
<td>2.46</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>2.27 (114)</td>
<td>2.21</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. XPS Lithium-1s spectra of LixCoP3 in its (a) fully discharged and (b) fully charged states.
P matrix may nonetheless enhance Li transport by grain boundary effects.

The fact that neither CoP\(_3\) nor an amorphous form of lithium cobalt phosphide are regenerated on charge sets this mechanism apart from transition metal oxides, where partial or complete recuperation of the oxide structure occurs. This can be understood since the reformation of CoP\(_3\) nano-crystallites is unlikely in the more covalently bonded phosphides, owing to the thermodynamics of the Li-Co-P system which should favor LiP formation on charge as a result of its high lattice energy. Nonetheless, the fully reduced material can be considered as a highly dispersed, phase-separated metastable analog of ‘‘Li\(_6\)CoP\(_3\)’’. In this respect, the process is different from Li uptake in phosphides where ternary lithiated phases do exist, such as MnP\(_4\). In this case, reversible conversion to crystalline Li\(_7\)MnP\(_4\) results [9]. Both processes, however, are initiated by electron uptake that primarily occurs at the anion centre, giving rise to scission of the P-P bonds.

4. Conclusions

This work highlights the importance of the anion in the electrochemical process, proving that the redox active centers are not necessarily cationic in transition metal compounds but can be based almost uniquely on the anionic network. In this regard, it is worthwhile recalling that the anion alone also acts as the redox center in the well-known Li–sulfur battery. This cell is based on reactions of Li and sulfur that reversibly yield Li\(_2\)S. Development of those cells has been hampered by the high ionic and electronic resistivity of sulfur, solubility of polysulfide products, and other factors [16]. Investigations of transition metal pnictides as anodes for Li-ion batteries may re-open new opportunities in this fascinating area. Such studies would also focus on the aspect of microstructural control that would lead to improve cycling stability in these materials, work that is currently in progress in our lab.

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H. Tomyama, Jap. Patent, 07-029608 (1995);
[11] Data were collected on a Siemens D500 equipped with a graphite monochromator using Cu-K\(_\alpha\) radiation, and a step size of 0.05\(^\circ\) with a counting time of 30 s on each step.