



Facile Reversible Displacement Reaction of Cu_3P with Lithium at Low Potential

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The electrochemical reaction of Cu_3P with lithium occurs via a multistep process that leads to the formation of metallic copper, Li_2CuP , and Li_3P , as shown by electrochemical and X-ray diffraction measurements. The structural similarity between these three phases facilitates this topotactic “displacement” reaction that is almost fully reversible on oxidation, re-forming crystalline Cu_3P and expelling Li. The system shows high reversibility during the first cycle, with an irreversibility of only 17%, good cyclability, and a reversible volumetric capacity of 2500 mAh/cm³. These properties suggest it could be an interesting anode material for lithium batteries.

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The search for new negative electrode materials as possible replacements for graphitic carbon in rechargeable lithium batteries remains a major topic in the area of energy storage. Of the many materials investigated over the past years, particular efforts have been devoted to intermetallic compounds, active/inactive composites based on intermetallics, and nitrides. Unlike graphitic carbons, which uptake lithium based on a simple topotactic intercalation process, many of these materials react with lithium involving complex reaction pathways that are based on extensive structural rearrangements. In addition to the large volumetric changes experienced in many intermetallics on Li uptake, this leads to undesirable large irreversible capacity on the first cycle, polarization, and capacity fading on cycling. More advantageous are nitrides possessing a layered structure such as $\text{Li}_{3-x}\text{M}_x\text{N}$, which have been the subject of much interest due to their good electrochemical behavior and large gravimetric capacities. It is, however, necessary to first “charge” them on the first cycle to extract lithium, a process that also results in transformation to an amorphous material that precludes a full understanding of the mechanism of subsequent reversible Li insertion.¹ Along with this detriment, their low volumetric capacity and extreme moisture sensitivity has inhibited commercial implementation.

Some systems that show more promising behavior are based on displacement reactions. These are best known for several intermetallic systems (*e.g.*, Cu_6Sn_5 , InSb, Cu_2Sb , and Mn_2Sb) where a strong structural relationship exists between the starting material and the lithiated phases as shown by Thackeray *et al.*² The reaction of Li with InSb is a classic example, where indium metal is replaced within the fcc lattice of Sb by lithium on uptake, to form $\text{In}_{1-x}\text{Li}_x\text{Sb}$ and ultimately, the end member Li_3Sb . In most cases, the extruded metal (Cu, In, Mn) is sufficiently highly divided that it cannot be detected by diffraction methods and hence its presence must be inferred.^{3,4} In some oxides such as CoO that also operate by a displacement process,⁵ the formation of metal nanoparticles on reduction is in fact thought to be critical to the reversibility of the process.⁶ No examples aside from InSb have been shown to exhibit the formation of detectable, “bulk” metal. Unfortunately, the growth of extensive In whiskers on the surface of the antimonide inhibits the re-assimilation of In on the subsequent cycle, curtailing the cyclability.

Phosphides offer intriguing alternatives to their neighboring members of the group V compounds. Their low intercalation potential resulting from the lower formal oxidation state of the metal and strong covalent character of the M-pnictogen bond, leads to high-lying mixed anion-metal bands, and a high degree of electron delocalization.⁷ Examples, all reported just within the last year, include CoP_3 ,^{8,9} Li_7MnP_4 ,¹⁰ FeP_2 ,¹¹ CuP_2 ,¹² and Li_2CuP .¹³ These

studies have shown that phosphides are characterized by facile bond rearrangements, and a plethora of structural rearrangements that include reversible quasi-topotactic intercalation,¹⁰ and reversible crystalline-amorphous transformations.¹³ None of these materials have displayed unequivocal evidence of a displacement reaction, however. We report here the first example for Li uptake in copper phosphide, Cu_3P . Metallic crystalline copper and Li_3P are clearly extruded and readily re-assimilated in the lattice on charge.

Cu_3P was synthesized using two different techniques. A high temperature form (Cu_3P -HT) was obtained by sealing stoichiometric quantities of metallic copper (99.9%, Aldrich) and red phosphorus in a quartz tube (99.8%, Aldrich) under vacuum. The mixture was placed in a furnace, heated to 1050°C for 1 h, and then quenched in water. The dark ingot thus obtained was ground and sieved to a particle size of 20 μm prior to electrochemical investigation. Copper phosphide was also synthesized by high energy ball-milling (Cu_3P -BM) using stoichiometric amounts of the elements that were sealed in an argon-filled stainless steel bowl. The mixture was ballmilled for 12 h at 550 rpm in a planetary ball mill (Fritsch Pulverisette 6) with a ball:material ratio of 10:1. XRD patterns were collected on samples housed in a specially designed, hermetically sealed sample holder on a Siemens D500 diffractometer equipped with diffracted beam monochromator using Cu K α radiation. To evaluate the electrochemical activity of both materials, Swagelok™-type cells were constructed using the phosphide as the positive electrode. The latter was prepared by mixing Cu_3P with 10 wt % carbon black and 5 wt % poly(vinylidene difluoride) (PVdF) dissolved in cyclopentanone, and casting the slurry onto nickel disks. Electrodes were dried at 70°C for 2 h under vacuum prior to assembly of the cell. Lithium metal was used as both reference and counter electrode, and a 1 M solution of LiPF_6 in 1:1 ethylene carbonate (EC)/dimethylcarbonate (DMC) was used as the electrolyte. A MacPile controller (Biologic S.A., Claix, France) was employed in either galvanostatic or potentiodynamic mode for the electrochemical studies.

Figure 1 shows the first complete electrochemical cycle of Cu_3P prepared by a conventional high-temperature solid-state route (Cu_3P -HT), collected using the Galvanostatic Intermittent Titration Technique (GITT). The uptake of 3.4 lithium occurs in two distinct steps at 750 and 150 mV vs. Li^+/Li , while on oxidation 3 different processes can be detected at 0.75 V, 1.1 and 1.3 V vs. Li^+/Li , leading to a reversible specific capacity of 340 mAh/g, or 2500 mAh/cm³. A low degree of irreversibility of only 17% is observed. Both HT and ballmilled (BM) Cu_3P gave rise to similar electrochemical behavior under typical galvanostatic conditions (Fig. 1, inset) despite a difference in their particle sizes, although a slightly smoother voltage profile was obtained for the ballmilled material. Analysis of their XRD patterns yielded crystallite coherence lengths of 300 and 150 nm for Cu_3P -HT and BM, respectively, according to the Scherrer formula.¹⁴

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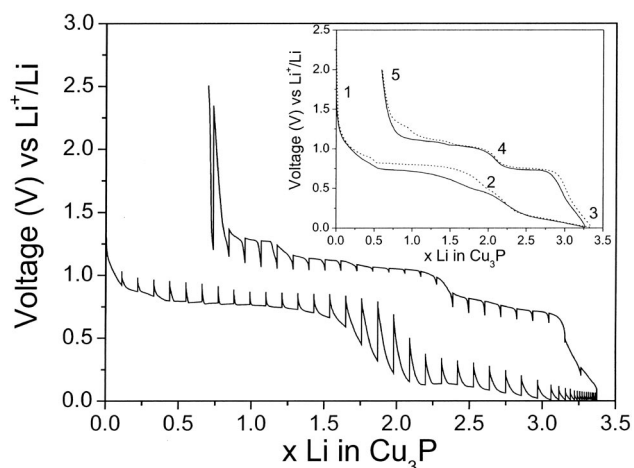
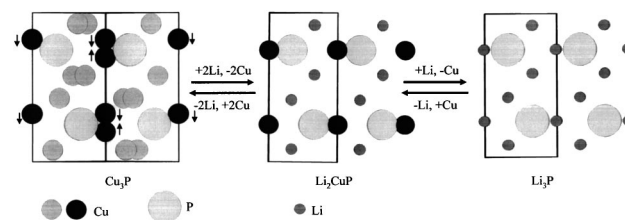


Figure 1. Voltage vs. composition electrochemical curve of $\text{Cu}_3\text{P-HT}$ between 10 mV and 2.5 V vs. Li^+/Li , performed using the galvanostatic intermittent titration technique (GITT) with current pulses of 1 h equivalent to C/9 rate (1 Lithium every 9 h) followed by 5 h relaxation periods. Inset: voltage vs. composition curve of $\text{Cu}_3\text{P-HT}$ (dotted line) and $\text{Cu}_3\text{P-BM}$ (smooth line) cycled at a C/10 rate.

To further understand the chemical processes that occur within the material upon cycling, *ex situ* XRD experiments were performed on electrodes arrested at different stages during reduction and oxidation. A detailed study of $\text{Cu}_3\text{P-HT}$ is shown in Fig. 2. During the first step of the reduction process ($x < 2$), the lines corresponding to the hexagonal structure of Cu_3P ¹⁵ slowly disappear, indicating a partial amorphization of the starting material. Very weak lines corresponding to metallic Cu can be detected, suggesting progressive copper extrusion of the structure during this first step of the reaction. Because no phosphorus-poor ternary phases appear in the phase diagram,¹⁶ both the X-ray diffraction (XRD) pattern and the observed electrochemical plateau at 0.75 V (indicative of a two-phase reaction) suggest the formation of a metastable copper-deficient “ $\text{Li}_2\text{Cu}_{3-x}\text{P}$ ” phase. Upon further discharge down to 10 mV vs. Li^+/Li ($x > 2$), the formation of metallic copper is clearly demonstrated by the presence of two strong lines corresponding to crystalline cubic Cu.¹⁷ Moreover, weak features can be attributed to both Li_2CuP and Li_3P . This is not surprising since the $\text{Li}_{3-x}\text{Cu}_x\text{P}$ (x



Scheme 1. Proposed mechanism for reversible displacement of copper in Cu_3P with lithium to form Li_3P and metallic copper, showing the close structural relationship of the three phases.

$= 0 \rightarrow 3$) materials have similar hexagonal close-packed (hcp) arrangements of phosphorus atoms. Scheme 1 illustrates a possible progression from Cu_3P , Li_2CuP and Li_3P structures, showing the minimal change to the hcp P framework that occurs on displacement of Cu/intrusion of Li. However, as Li_2CuP does not dominate the XRD pattern in the two-phase transition region (Fig. 2c), it may be an intermediate on the way to the formation of Li_3P , or simply a side-product. Extrusion of copper from the structure has been suggested for other structurally related copper pnictides such as Cu_2Sb ,¹⁸ and observed for Cu_3N as 60 Å nanoparticles.¹⁹ In the reaction of monoclinic CuP_2 with lithium, the formation of copper is indirectly suggested by the observation of Li_3P in the XRD pattern, but the metal cannot be detected due to its apparently nanosized dimensions.²⁰ The lack of structural correspondence in CuP_2 between reactants and products (which we believe may affect the kinetics of metallic extrusion and growth to some degree), and the higher P/Cu ratio may be responsible for the amorphous state of the metal. In Cu_3P , ready displacement of copper from the structure by lithium is favored by both stoichiometry and topography, hence the growth of larger Cu crystallites ensues.

The same considerations that lead to facile displacement of Cu on reduction also result in ready re-assimilation on oxidation. Upon charge, the Cu metal reflections completely disappear during lithium extraction and reformation of the Cu_3P phase is observed when the electrode is cycled up to 2 V vs. Li^+/Li , as shown in Fig. 2e for the HT material. The same results were obtained for the BM material (Fig. 3). Copper atoms are reinserted into the structure while lithium is displaced, thus recrystallizing the starting material. The Cu_3P that is re-formed for either the HT or BM prepared materials displays a

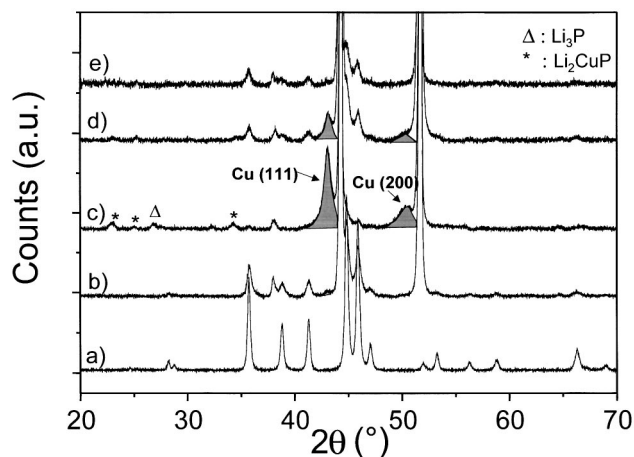


Figure 2. *Ex situ* XRD patterns of $\text{Cu}_3\text{P-HT}$ electrode at different stages: (1) pristine material, (2) stopped at 0.5 V during discharge, (3) at the end of full discharge, (4) stopped at 0.8 V during charge, (5) after one complete cycle. Indexed reflections are marked on the figure; additional peaks correspond to the cell hardware.

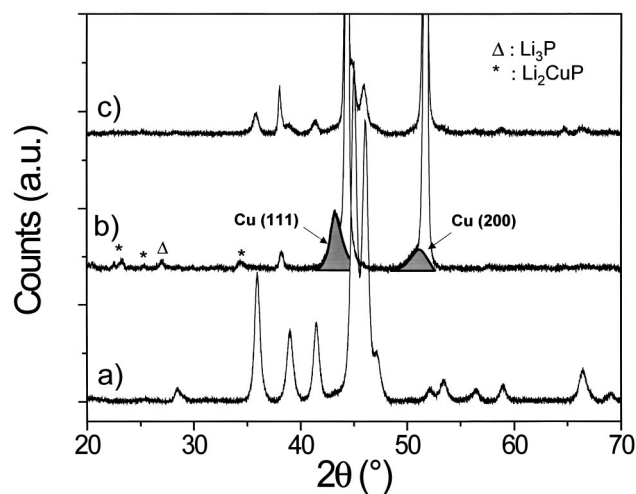


Figure 3. *Ex situ* XRD patterns of $\text{Cu}_3\text{P-BM}$ electrode (a) prior to cycling, (b) stopped at 10 mV vs. Li^+/Li during the first discharge, and (c) stopped after a complete cycle. Additional peaks correspond to the cell hardware.

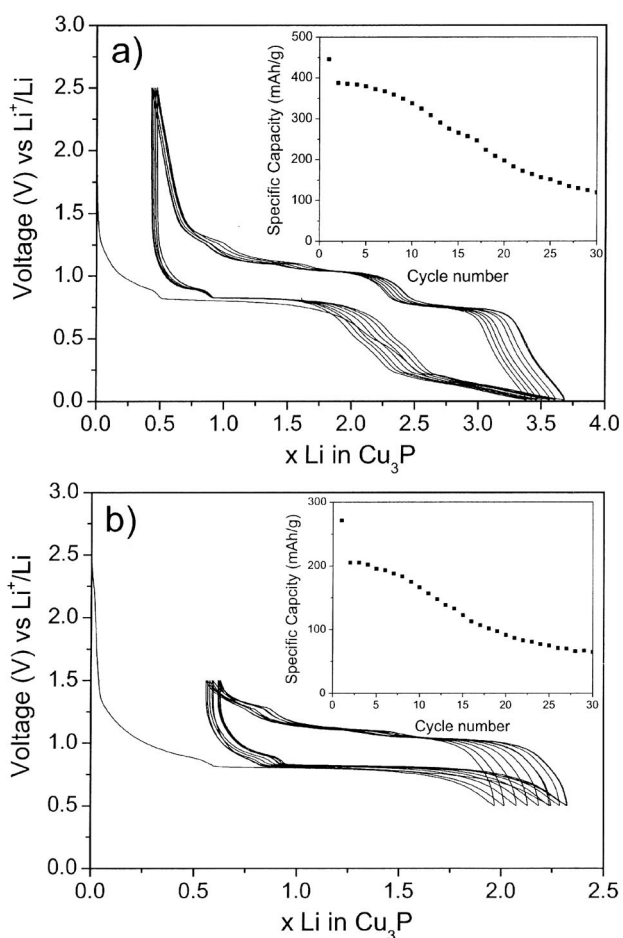


Figure 4. Voltage vs. composition electrochemical curve of $\text{Cu}_3\text{P-HT}$ cycled at a C/10 rate between (a) 10 mV and 2.5 V, (b) 0.5 V and 1.5 V. Inset: Specific capacity vs. cycle number in both voltage windows.

similar degree of crystallinity as the pristine $\text{Cu}_3\text{P-BM}$ compound, according to the linewidth of the Cu_3P reflections after 1 complete cycle (Fig. 2 and 3).

Figure 4 shows the cycling behavior of $\text{Cu}_3\text{P-HT}$ in two different voltage windows. About 85% of the initial capacity is retained at a C/10 rate, although fading is observed after more prolonged cycling. This is probably due in part to electrolyte reactivity at low voltage. The solvent EC/DMC is optimized for carbonaceous negative electrode materials where a protective SEI is formed, but we do not expect this solvent system to necessarily engage in effective SEI formation with phosphides. Identical plateaus are observed on charge and discharge whether a small or a large voltage window is used, confirming the complete reversibility of each step during lithium insertion/deinsertion. Interestingly, the cycling stability of the electrodes is not improved with very small particles ($\text{Cu}_3\text{P-BM}$), indicating that microstructure control does not play a major role in the electrochemical reaction of phosphide materials, contrary to the enhanced properties of nanosized intermetallics.²¹ The Cu_3P cycling stability is also not affected by changing the lower cut-off limit. Similar electrochemical behavior is observed by either

discharging the electrode down to 10 mV, or to 0.5 V vs. Li^+/Li which is just prior to the second plateau that corresponds to full copper extrusion.

In summary, our study shows that Cu_3P reversibly uptakes Li by a process that involves expulsion of copper (as large metallic copper crystallites) from the lattice and its replacement within the phosphorus framework by the alkali ion. It is the first unequivocal demonstration of a “displacement” reaction in a phosphide. Moreover, the extruded copper crystallites are reassimilated into the lattice to re-form crystalline Cu_3P on charge. Good mobility of copper and lithium atoms within the P framework appear to be responsible for this unusual behavior. This leads to lower polarization, better kinetics, and a lower degree of irreversibility. The irreversibility can be compared to other materials that operate via displacement reactions (Cu_2Sb : 30%; Cu_3N : 40%; Ag_3Sb : 30%; CoO : 25%). The high degree of reversibility of the reaction (despite the large length scales required for diffusion) is at least, in part, a direct consequence of the labile metal-phosphorus bonding exhibited by these compounds,¹³⁻¹⁰ in concert with a high degree of structural correspondence between reactants and products. The formation of nanosized metal particles is not necessary for good reversibility of the displacement reaction under these conditions. This, along with the very good electrochemical properties of Cu_3P , illustrates the interesting chemistry displayed by phosphide materials and their possible use as negative electrodes in lithium-ion cells.

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