Computational Investigation of Copper Phosphides as Conversion Anodes for Lithium-Ion Batteries

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ABSTRACT: Using first-principles structure searching with density-functional theory (DFT), we identify a novel $Fm\overline{3}m$ phase of Cu$_2$P and two low-lying metastable structures, an $I\overline{4}3d$–Cu$_3$P phase and a $Cm$–Cu$_3$P$_{11}$ phase. The computed pair distribution function of the novel $Cm$–Cu$_3$P$_{11}$ phase shows its structural similarity to the experimentally identified $Cm$–Cu$_3$P$_2$ phase. The relative stability of all Cu–P phases at finite temperatures is determined by calculating the Gibbs free energy using vibrational effects from phonon modes at 0 K. From this, a finite-temperature convex hull is created, on which $Fm\overline{3}m$–Cu$_2$P is dynamically stable and the Cu$_{1-x}$P ($x < 1$) defect phase $Cm\overline{2}$_x–Cu$_3$P$_3$ remains metastable (within 20 meV/atom of the convex hull) across a temperature range from 0 to 600 K. Both Cu$_2$P and Cu$_3$P exhibit theoretical gravimetric capacities higher than contemporary graphite anodes for Li-ion batteries; the predicted Cu$_2$P phase has a theoretical gravimetric capacity of 508 mAh/g as a Li-ion battery electrode, greater than both Cu$_3$P (363 mAh/g) and graphite (372 mAh/g). Cu$_2$P is also predicted to be both nonmagnetic and metallic, which should promote anodes, given the large volume expansion (between 150 and 300%) exhibited by anodes with high P content, which limits their cyclability. Despite this drawback in volume expansion, TMPs show higher average voltages than graphite, which has an average voltage of 0.1 V. For example, CoP has an average voltage of 0.67 V, the ternary metal phosphide LiFeP$_2$ has an average voltage of 0.4 V, and MnP has an average voltage of 0.62 V. Higher average voltages give the metal phosphides improved safety while sacrificing energy density, making them an ideal choice for large-scale and long-term energy storage.

INTRODUCTION

Graphite is the most commonly employed lithium-ion battery (LIB) anode but is inherently limited by a maximum theoretical capacity of 372 mAh/g upon the formation of LiC$_6$. Phosphorus (black or red) has a significantly higher theoretical capacity of 2596 mAh/g due to the formation of Li$_x$P; however, it suffers from capacity deterioration, primarily caused by deleterious effects from phonon modes at 0 K. From this, a finite-temperature convex hull is created, on which $Fm\overline{3}m$–Cu$_2$P is dynamically stable and the Cu$_{1-x}$P ($x < 1$) defect phase $Cm\overline{2}$_x–Cu$_3$P$_3$ remains metastable (within 20 meV/atom of the convex hull) across a temperature range from 0 to 600 K. Both Cu$_2$P and Cu$_3$P exhibit theoretical gravimetric capacities higher than contemporary graphite anodes for Li-ion batteries; the predicted Cu$_2$P phase has a theoretical gravimetric capacity of 508 mAh/g as a Li-ion battery electrode, greater than both Cu$_3$P (363 mAh/g) and graphite (372 mAh/g). Cu$_2$P is also predicted to be both nonmagnetic and metallic, which should promote efficient electron transfer in the anode. Cu$_2$P’s favorable properties as a metallic, high-capacity material suggest its use as a future conversion anode for Li-ion batteries; with a volume expansion of 99% during complete cycling, Cu$_2$P anodes could be more durable than other conversion anodes in the Cu–P system, with volume expansions greater than 150%. The structures and figures presented in this paper, and the code used to generate them, can be interactively explored online using Binder.

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*Supporting Information

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chemical corrosion exhibited a capacity between 360 and 380 mAh/g over 70 cycles. The capacity of high-temperature-synthesized Cu₃P exceeds that of graphite, and the cyclability of porous Cu₃P is improved relative to other Cu₃P anodes. Cu₃P on the other hand, delivers a higher initial capacity of 815 mAh/g, but can only be cycled stably 10 times before the capacity fades to 360 mAh/g. The main factor in this degradation is the high concentration of P in the Cu₃P, which, while enabling high capacity, also contributes to the structural instability of Cu₃P during cycling as the lithium-rich Li₃P phase forms. To optimize the trade-off between stability and capacity, it would be beneficial to discover a compound with higher P content than Cu₃P to offer higher capacity, and with a Cu content higher than Cu₃P to aid in cyclability.

By performing crystal structure prediction, combining both ab initio random structure searching (AIRSS) and a genetic algorithm (GA), in addition to structural prototyping with known crystal structures of related chemistries, we produced the compositional phase diagram of the copper phosphide system. We describe this approach to structure prediction and the application of open-source Python packages matador (v0.9), for high-throughput first-principles calculations, and ilustrado (v0.3), for computational structure prediction with GAs. Crystal structure prediction for battery anodes is a well-tested method, used for identifying both novel anode materials and unknown phases, which form during battery cycling. AIRSS has been used previously to search for additional phases of Li–P and Na–P, which form during battery cycling. The GA was also employed to search for new phases of Na–P, which were confirmed experimentally by solid-state NMR spectroscopy. As applied here to Cu–P, these methods predict a novel metallic Fm3m–Cu₃P phase at 0 K, within the target composition range of CuₓP₃₋ₓ for a high-capacity, low-volume expansion conversion anode; we compare its electronic structure to other TMPs to show a similarity to Fm3m–Rh₂P and Fm3m–Ir₂P. Two other phases, Cm–Cu₃P₁₁, and I₄3d–Cu₃P, are identified as metastable, both bearing structural similarity to known copper phosphides. We calculate the convex hull of Cu–P at temperatures up to 600 K, confirming the dynamic and chemical stabilities of Cu₃P across this temperature range. A ground-state voltage profile from density-functional theory (DFT) shows that Fm3m–Cu₃P undergoes the same lithiation process as P₆₃cm–Cu₃P; however, Fm3m–Cu₃P has a higher capacity of 508 mAh/g, with an average voltage of 0.86 V versus Li/Li⁺ (compared to 0.91 V for P₆₃cm–Cu₃P).

## METHODS

To search for novel copper phosphides, we first performed structural relaxations of the 13 structures from the Inorganic Crystal Structure Database (ICSD) of Cu₃P (0 < x < 1). The Python package matador was used to query 1053 prototype binary structures from the Open Quantum Materials Database (OQMD), with chemical compositions containing a pnictogen and a transition metal from the first two rows, namely, {Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd}–{P, As, Sb}; each composition was then transmuted to the corresponding stoichiometry of Cu–P, yielding 909 unique structures after geometry optimization. To extend this search beyond existing prototypes, two additional structure prediction steps were performed, namely, AIRSS and an evolutionary search with the GA implemented in the ilustrado package.

When performing AIRSS, one proceeds by generating random “sensible” (symmetry, density, and atomic separation constrained) trial cells and then geometry-optimizing them to their corresponding local minima. All relaxations can be performed concurrently, with no interdependence between calculations. New trial structures are generated until the ground state of each stoichiometry (within the constraints of the search) has been found multiple times.

We initially performed an exploratory AIRSS search consisting of around 5000 trial structures, with constraints on cell size, stoichiometry, and number of atoms in the cell. In this initial search, the total number of atoms in the cell was constrained to be ≤40, and the total number of formula units was randomized between 1 and 4, while still keeping the total number of atoms below 40. The number of atoms of Cu and P were randomized between 1 and 9 in each cell, and the cell volume (V) was constrained based on the total number of atoms in the cell (N) to be 8N / 3 ≤ V ≤ 20N / 3, based on the average densities of Cu–P phases within the ICSD.

Structures from the searching and enumeration procedures were then used, with fitness weighted according to their distance from the convex hull, as the initial configurations for a GA implemented in the Python package ilustrado. The ilustrado package uses a simple cut-and-splice crossover operation, supplemented by mutation operators (random noise, atomic permutations, vacancies, and adatoms). To avoid stagnation, each trial structure was filtered for similarity (via pair distribution function, PDF, overlap) against existing structures in the population. Three independent GA runs were performed with 10 generations each, yielding a further 1049 relaxed structures. Finally, a directed AIRSS search of Cu₃P, where x + y < 8, was performed to create a final set of ~20 000 structures within the Cu–P chemical space. In all cases, to constrain the search to physically reasonable structures, a minimum atomic separation of 1.5 Å was enforced and the maximum number of atoms in the cell was constrained to 10 for the initial ~10 000 AIRSS searches and 40 atoms per cell for the final ~3000 trials.

All calculations were performed using CASTEP (v8.1 and v9.1), the plane wave pseudopotential DFT package. To maximize computational efficiency, the initial calculations were performed with loose convergence criteria that ensured formation energies converged to 10 meV/atom. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was used with Vanderbilt ultrasoft pseudopotential, that required a plane wave kinetic energy cutoff of 300 eV to converge energies to within 10 meV/atom. The Brillouin zone (BZ) was sampled with a Monkhorst–Pack grid k-point spacing finer than 2π × 0.05 Å⁻¹; the grid was frequently recomputed to accommodate any changes in the cell shape and size during relaxation. Each structure was geometry-optimized at this accuracy to a force tolerance of 0.005 eV/Å. The structures with a formation energy within 50 meV of the convex hull were then further optimized once more using CASTEP’s on-the-fly (OTF) “C18" library of ultrasoft pseudopotentials, with a finer k-point sampling of 2π × 0.01 Å⁻¹ and plane wave kinetic energy cutoff of 500 eV, which yielded formation energies converged to within 2.5 meV/atom. To predict the voltage profiles with the same convergence criteria (formation energies within 2.5 meV/atom), the relaxation of known Li–P structures required a higher plane wave cutoff of 700 eV. Therefore, to compare ternary phases of Cu–Li–P in the voltage profile, all Cu–Li–P phases were reoptimized at a plane wave kinetic energy cutoff of 700 eV.

To identify stable structures from this search, a convex hull of the copper phosphides was created. The formation energy Eᵱ of each structure CuₓPᵧ, was calculated using

$$Eᵱ(CuₓPᵧ) = E(CuₓPᵧ) − xE(Cu) − yE(P)$$

where E(Cu) is the DFT total energy of the Fm3m–Cu₃ structure, and E(P) is the energy of Cmcm-P (black phosphorus). Black phosphorus was used as the P chemical potential instead of the lower-energy polymorph red phosphorus; as has been previously discussed in Mayo et al., black phosphorus is commonly used when making electrochemical cells. Electrochemical voltage profiles for Li insertion into the stable Cu–P phases were calculated from the computed formation energies from the ternary convex hull of Cu–Li–P. To calculate the voltage profiles shown in the Cu₃P as a Li-Ion Battery Conversion Anode section, the
Results

From the search of ~20 000 trial structures, there are 42 unique phases within 50 meV/atom of the convex hull. Previous computational structure searches have used a distance above the hull of 25 meV/atom,\(^{41}\) and given the accuracy of PBE,\(^{42}\) we chose to increase this cutoff to 50 meV/atom. Furthermore, the experimentally verified \(P_6_{\text{cm}}-Cu_3P\) structure\(^ {43}\) is 37 meV/atom above the convex hull tie-line, further justifying this cutoff. The uniqueness was determined by computing pairwise overlap integrals of the pair distribution functions of phases at each stoichiometry using matador. The set of 42 unique phases contains four experimentally reported copper phosphides from the ICSD: \(P_1-CuP_{10}\) synthesized by a mineralization reaction\(^ {44}\) and \(C2/m-Cu_3P_{17}, 45\) \(P2_1/c-CuP_2\)\(^ {45,46}\) and \(P6_{\text{cm}}-Cu_3P\)\(^ {45,46}\) from high-temperature sintering.

Oloffson’s experiments on single-crystal \(P6_{\text{cm}}-Cu_3P\) synthesized at high temperature, and subsequent work by De Trizio et al.\(^ {47}\) show that \(CuP\) has several defects\(^ {43}\) with a range of stoichiometries between \(Cu_{2.6}P\) and \(Cu_{2.8}P\). DFT studies of the Cu vacancies indicate that \(CuP\) is substoichiometric,\(^ {47}\) and to search this substoichiometric space, unit cells of \(P6_{\text{cm}}-Cu_3P\) were enumerated with 1, 2, and 3 Cu vacancies, resulting in 76 \(Cu_{3-x}P\) structures. The lowest-energy defect was a \(Cm2_1-CuP_1\) (\(Cu_{5.67}P\)) phase 26 meV/atom above the convex hull tie-line, denoted as vacancy enumeration in Figure 1.

The convex hull of \(Cu-P\), with points colored by the provenance of each structure, is presented in Figure 1; the experimentally identified phases, and a new \(Fm3m-Cu_3P\) phase, all lie on the convex hull tie-line and are each labeled with an arrow.

Details of the 24 structures, which are both negative in the formation energy relative to \(Cu\) and \(P\) and are within 50 meV/atom of the convex hull, are given in Table 1. Phases on the convex hull tie-line in Figure 1 are indicated with an asterisk in Table 1, and phases that are experimentally confirmed are denoted by their ICSD Collection Code as “ICSD #”. Phases not reported previously, within 20 meV/atom of the convex hull tie-line, are bolded in Table 1. The provenance of each phase is given in the last column of Table 1. Phases that were found by swapping the elements of a prototype ICSD structure are denoted by the ICSD Collection Code of the prototype used as “prototype #”.

Of the 24 binary structures in Table 1, 9 were discovered by AIRSS, 6 by the GA, 4 from structural prototyping, and 4 were previously known \(Cu-P\) structures from the ICSD. Of particular interest are three new phases, bolded in Table 1, \(Fm3m-Cu_3P\), \(I43d-Cu_3P\), and \(Cm-Cu_3P_{11}\), which are all within 20 meV/atom of the convex hull and will be discussed further in the following sections.

Phosphorus-Rich Phase \(Cm-Cu_3P_{11}\). \(Cm-Cu_3P_{11}\) is a new structure that was found by relaxing the prototype \(Ag_3P_{11}\) (ICSD 26563); it is 17 meV/atom from the hull tie-line and has structural similarity to the ICSD structure \(C2/m-Cu_3P_7\) (ICSD 35281),\(^ {48}\) as shown in Figure 2. Both of these structures have repeating chains of \(P\) atoms, as seen in the supercells in Figure 2, in which alternating patterns of \(Cu\) or \(Cu-P\) are connected to a zig-zag chain of \(P\) atoms. All known phases in the \(P\)-rich \(Cu\) phase, where \(x>1\) region of the convex hull, namely, \(C2/m-Cu_3P_7\) (ICSD 35281),\(^ {45}\) \(P2_1/c-CuP_2\) (ICSD 35281),\(^ {45}\) and \(P1-CuP_{10}\) (ICSD 418805),\(^ {49}\) have long chains of \(P\) atoms, similar to the layered \(P2_1/c-P\) (ICSD 29273,\(^ {54}\) red \(P\)).

In the \(P\)-rich region, five new phases were identified within 50 meV/atom of the convex hull: \(Pmmn-CuP_9\), \(Cm-CuP_{27}\), \(Cm-CuP_{11}\), \(Cm-CuP_{27}\), and \(Cm-CuP\). Using the GA, it was possible to include structures with stoichiometries of \(P\) up to...
Table 1. Phases of Cu–P with a Formation Energy ≤ 0 meV/atom Relative to Cu and P and the Distance from the Convex Hull Tie-Line, ΔE, Less Than 50 meV/atom

| formula | on tie-line | ΔE (meV/atom) | space group | provenance |
|---------|-------------|---------------|-------------|------------|
| Cu      | *           | Fm3m          | ICSD 43493  |            |
| Cu3P    | 31          | I4/mmm        | AIRSS       |            |
| Cu2P    | 28          | P4/nmm        | AIRSS       |            |
| CuP     | 44          | Cm3m          | AIRSS       |            |
| Cu2P    | 11          | I43d          | prototype 67415  |
| CuP     | 30          | P2/m          | GA          |            |
| CuP     | 37          | P6/cm         | ICSD 15056  |            |
| CuP     | 39          | I4 e           | prototype 23560  |
| CuP     | 40          | P1            | GA          |            |
| CuP     | 26          | Cmc21         | AIRSS       |            |
| CuP     | 36          | P6/cm         | AIRSS       |            |
| CuP     | 39          | P1            | AIRSS       |            |
| CuP     | 42          | P1            | AIRSS       |            |
| CuP     | 44          | P1            | AIRSS       |            |
| Cu2P    | *           | Fm3m          | prototype 38356  |
| Cu2P    | 49          | P4/nmm        | ICSD 35282  |            |
| CuP     | 26          | P2/e          | ICSD 35282  |            |
| CuP     | 29          | Cm            | GA          |            |
| CuP     | 43          | Cm            | GA          |            |
| CuP     | *           | C2/m          | ICSD 35281  |            |
| CuP     | 17          | Cm            | prototype 26563  |
| CuP     | 33          | Cm            | GA          |            |
| CuP     | 32          | Cm            | GA          |            |
| CuP     | *           | P1            | ICSD 418805  |            |
| P       | *           | Cmca          | ICSD 150873  |            |

Bold text indicates new phases with ΔE ≤ 20 meV/atom.

*aExperimental lattice parameter for Cu from ref. 48. Structure from single-crystal diffraction.*

*bPrototype structure is I43d–Cu3As. Structure from single-crystal diffraction.*

*cPrototype structure I4–Cr3P by single-crystal X-ray diffraction.*

*dPrototype structure Fm3m–Rh3P by X-ray diffraction.*

*eStructure from X-ray diffraction.*

*fPrototype structure Cm–Ag3P11 by single-crystal X-ray diffraction.*

*gStructure from single-crystal X-ray diffraction.*

|hInorganic Chemistry of Materials pubs.acs.org/cm |

27 atoms in the unit cell and thus found structural variations on CuP, such as CuP11. To compare the new metastable Cm–Cu3P11 structure with other P-rich structures, the pair distribution functions (PDFs) and calculated powder X-ray diffraction (PXRD) peaks of CuP, Cu2P, and Cu3P were calculated and are compared in Figure 3. In all three cases, the initial sharp peak in the PDF between 2.20 and 2.24 Å shows, unsurprisingly, the same Cu–P and P–P distances shared by all three structures. The peaks at radii above 3 Å show the longer-range similarity between CuP, Cu2P, and Cu3P, which is not shared by CuP. Comparison of the PXRD patterns of CuP, Cu2P, and Cu3P shows that Cm–Cu3P11 is distinguished by a peak at a 2θ value of 16°, where Cm–Cu2P has an indistinguishable peak at this point. Given the shared symmetry operations between Cm and C2/m, we expect to see peaks at the same 2θ values, but the intensities will vary between the structures. We deduce that these three phases could be verified using experimental PXRD, by using the peaks at 2θ < 30° to distinguish between the phases.

**Cu3P Phases (x ≤ 1).** Within the stoichiometry range Cu3–P, four unique CuP phases, Cu12P3, Cu7P3, Cu2P7, and CuP, were found. Of these, P6.0–Cu3P was the only phase previously experimentally determined and had a formation energy of 37 meV/atom above the convex hull line. Olofsson identified the stoichiometry of P6.0–Cu3P at 975 K to be between Cu9As2P and Cu17.5P5 due to Cu vacancies within the unit cell of P6.0–Cu3P (shown in Figure S1).43 A study on low-temperature phases of Cu3−xP proposes phases from Cu4P to Cu3P.55 The lowest-energy Cu3−xP (x ≤ 1) phases identified in Table 1, P1–Cu3P (Cm21, P1m), Cm21–Cu3P (C63/m), and P1–Cu3P (C16/c) are all defect structures of P6.0–Cu3P with 1, 2, and 4 Cu vacancies respectively, from the P6.0–Cu3P unit cell of CuP. Of these three P6.0–Cu3P defect structures, Cm21–Cu3P (C63/m) has the smallest distance from the hull (ΔE = 26 meV/atom). This corroborates the previous DFT calculations suggesting CuP has two Cu vacancies.57

In addition to the ICSD phase of P6.0–Cu3P (ΔE = 37 meV/atom), two other CuP phases were found, which are closer to the convex hull line than P6.0–Cu3P; these are the P2/m–CuP (ΔE = 30 meV/atom) and I43d–CuP phases (ΔE = 11 meV/atom). The P2/m–CuP phase is structurally related to the Fm3m–CuP (ΔE = 0 meV/atom) phase (discussed in the following section). These two phases are shown in Figure 4, in which the P2/m–CuP can be described as a stacking of the Fm3m–CuP phase. While the Fm3m–CuP phase has not been observed experimentally, it is likely that the two phases could be distinguished, given their distinct PDF and PXRD patterns shown in Figure S2. The PXRD pattern for P2/m–CuP has additional low-intensity peaks to the right of the 46° peaks and is distinct from the other low-energy phases of CuP as shown in Figure S2, which would further distinguish this phase in experiment.

The lowest-energy CuP phase is an I43d phase 11 meV/atom above the tie-line, which was identified by relaxing the prototype I43d–Cu3As structure (ICSD 64715). The I43d–CuP structure is the highest-symmetry CuP phase and is the only cubic phase in the set of low-energy CuP structures. I43d–CuP contains 8 formula units in the primitive unit cell and has 9-fold coordinated P atoms, whereas P6.0–Cu3P has 8-fold coordinated P atoms. The resulting crystal structures, shown in Figure S1, show two different long-range orderings of the Cu subnetwork. P6.0–Cu3P has only one, 8-fold coordinated, P site, which results in continuous zig-zag chains of Cu atoms surrounding the P, which are at the peaks of the buckles in the zig-zag. In I4–CuP, there are two 9-fold coordinated sites: one at the center of the surrounding Cu (seen in Figure S1) and one at the edges, which together form a hexagonal Cu cage surrounding the P atom in the center. While both phases have high-coordinated P atoms, the I43d–CuP shows a network of Cu atoms surrounding a central P atom, where P6.0–Cu3P contains infinite Cu chains in the c direction.

Another trigonal phase, P31–CuP (ICSD 16841, 59ΔE > 50 meV/atom), has the same structure as P31–CuAs (ICSD 16840); however, it is 82 meV/atom above the convex hull line. To the best of our knowledge, there are no reports of an I43d–CuP phase, either experimentally or in a computational database. The PDF and PXRD patterns of I43d–CuP given in Figure S2 show no relation to any other CuP phase, or the Fm3m–CuP phase; thus, if energetically stable, it could be distinguished using PXRD in the experiment.

**Fm3m–CuP.** The Fm3m–CuP phase was found from the prototype Fm3m–Ir3P (ICSD 640898).59 Comparing the CuP phase to both Ir3P and Rh3P using PDFs in Figure S3 shows that the PDFs are identical between all three structures, and the
PXRD plot of Cu$_2$P has the same peaks, all shifted to slightly higher values of 2θ due to structural relaxations in the geometry optimization of Cu$_2$P.

Previously, a 2D structure of Cu$_2$P was predicted theoretically as a buckled nonmagnetic material,$^{56}$ in which the magnetism expected was inhibited by the buckled layers. The buckled layers from the 2D phase are also present in the bulk Fm̅3m Cu$_2$P, and the nonmagnetic nature was confirmed in the bulk phase by the lack of spin-polarization in the density of states shown in Figure S4. The bulk Fm̅3m Cu$_2$P structure described above has the same structural motifs as the 2D hexagonal phase predicted by Yang et al.$^{56}$ and has the same electronic properties.

Fm̅3m Cu$_2$P lies on the convex hull tie-line and is energetically more stable than both the experimentally confirmed phase of P63cm Cu$_3$P and its defect structure Cmc2$_1$ Cu$_8$P$_3$. Figure 5 shows the phonon dispersion for the Fm̅3m Cu$_2$P computed as mentioned in the Methods section. No imaginary phonon frequencies were present in the dynamical matrix (interpolated or otherwise), indicating that Fm̅3m Cu$_2$P is dynamically stable.

The electronic structure of Fm̅3m Cu$_2$P is related to the electronic structure of other Fm̅3m TMPs, suggesting that it belongs to the same class of materials as Fm̅3m Ir$_2$P and Rh$_2$P. Of the TMPs in the Materials Project database,$^{59}$ 21 are insulating and 68 are metallic with a high density of transition-metal d-bands below the Fermi level. Figure 6 shows the electronic band structure and density of states of Fm̅3m Cu$_2$P projected by species along the high-symmetry path from SeeK-face to Pack grid. The band structure shows that Cu$_2$P is a metal with P and Cu bands touching at the $\Gamma$ point of $\sim$2.0 eV above the Fermi level. In addition, there is a characteristic high density of flat bands localized on the Cu ions that exhibit a d-character of around 2.5 eV below the Fermi level. Calculating this band structure using the HSE06 functional (shown in Figure S5), a hybrid functional designed to correct for band-gap underestimation, the gap at $\Gamma$ between the Cu and P bands is closed.

Figure 2. (a) Cu$_2$P$_7$ unit cell, (b) Cu$_3$P$_{11}$ unit cell, and (c) Cu$_2$P$_7$ 2$\times$2$\times$2 supercell in which the P–P connectivity is shown to highlight the P chains in the supercell structure. (d) Cu$_3$P$_{11}$ 2$\times$2$\times$2 supercell with the P–P connectivity to show P chains as in the Cu$_2$P$_7$ supercell.

Figure 3. (a) Pair distribution function (PDF) of Cm Cu$_3$P$_{11}$, P2$_1$/c-Cu$_2$P$_7$ (ICSD 35282), and C2/m-Cu$_2$P$_7$ (ICSD 35281) shows all three have a first peak between 2.20 and 2.24 Å, while Cu$_2$P$_7$ has two peaks around 3.6 Å, where both Cu$_3$P$_7$ and Cu$_3$P$_{11}$ have one. All PDFs are artificially broadened with Gaussians of width 0.1 Å, and PXRDs are calculated using a Cu Kα source. (b) Simulated PXRD patterns of both Cu$_2$P$_7$ and Cu$_3$P$_{11}$ share peak positions, as is expected from their shared symmetries. The Cu$_3$P$_{11}$ phase could be identified experimentally by the higher-intensity peaks at 2θ < 30°, including a distinct peak at 16°, not present in Cu$_2$P$_7$. Details of PXRD calculations can be found in the Supporting Information.
Many M₂P phases (where M is a transition metal) have a structure similar to P₆̅₂m–Ni₂P₆ and Fe₂P.₆¹,₆² In which the metal atoms sit in a cage of 3-fold coordinated P and 4-fold coordinated metal atoms. Fm3m–Cu₂P is most similar to the other Fm3m TMPs, as it was derived from the prototype structure Fm3m–Ir₂P, and has a 4-fold coordinated Cu with an 8-fold coordinated P. The Cu₂P band structure in Figure 6 is also similar to those of Ir₂P and Rh₂P. In Rh₂P, there is a directionally opened gap of 1 eV above the Fermi level at the Γ point, not present in Cu₂P or Ir₂P (Cu₂P, Ir₂P, and Rh₂P band structures calculated with spin–orbit coupling are given in Figure S6).

Figure 4. P2₁/m–Cu₃P found by the GA and Fm3m–Cu₂P from a swap with Fm3m–Ir₂P. Here Cu atoms are colored blue and P atoms are colored pink. P2₁/m–Cu₃P structure can be described as a stacking of Cu₂P layers separated by Cu atoms. The stacking pattern, which is present in both structures, is indicated by the black dashed line surrounding the atoms in each structure. This is meant to guide the eye and show the similarity in the two structures. The unit cells of each structure are outlined with a thin gray box. Cu₂P is predicted to be a stable two-dimensional (2D) phase,⁵⁶ which could be layered to produce the Cu₃P phase shown in panel (a) here.

Figure 5. (a) Cu₂P phonon dispersion under the harmonic approximation and the corresponding Brillouin zone. Phonon dispersion and density of states were interpolated from the dynamical matrix calculated using the PBE xc-functional and the C18 pseudopotential library, with a 2π × 0.03 Å⁻¹ k-point spacing, 500 eV plane wave cutoff, in a 2 × 2 × 2 supercell using the finite displacement method (corresponding to a phonon q-point spacing of 2π × 0.046 Å⁻¹). (b) Brillouin zone is a truncated octahedron, with special points on each face labeled here. The dashed hexagon outline indicates the center of the Brillouin zone.

Figure 6. Electronic band structure of Cu₂P projected onto the Cu and P states and density of states projected onto the Cu s, p, d and P s and p states, for Cu₂P using an energy cutoff of 500 eV with a 2π × 0.03 Å⁻¹ k-point spacing and C18 on-the-fly pseudopotentials. The projected band structure is produced by OptaDOS, and band energies are calculated by CASTEP.⁵¹
Both of these structures exhibit spin–orbit coupling due to their heavy metal ions, while Cu has negligible spin–orbit coupling effects. The Rh$_2$P and Ir$_2$P band structures are calculated, including spin–orbit coupling.

**Finite-Temperature Phase Stability.** The temperature-dependent convex hull was constructed by calculating the finite-temperature Gibbs free energies by including vibrational effects at the harmonic level$^{30}$ of several related structures on or near the convex hull from Figure 1. All structures within 20 meV/atom of the hull at 0 K were included in the finite-temperature hull; these were $Fm\bar{3}m$–Cu$_3$P, $I\bar{4}3d$–Cu$_4$P, $Cmc\bar{2}$–Cu$_5$P$_3$ (the structure with 2 Cu vacancies from $P6_{3}cm$–Cu$_4$P discussed previously), Cu$_2$P$_2$, Cu$_{10}$P$_2$, and Cu$_8$P$_3$.

The chemical potentials for this binary convex hull were $Cmc$–P (black phosphorus) and $Fm\bar{3}m$–Cu. Previously, Mayo et al. noted that the inclusion of semiempirical dispersion corrections for black phosphorus changed the energetics of the convex hull,$^{39}$ and therefore, it is not possible to combine optimized structures with and without dispersion corrections on the same convex hull. However, to obtain nonimaginary phonon frequencies of $Cmc$–P, it is necessary to account for dispersion. To account for this, the many-body dispersion correction (MBD) was applied during the geometry optimization and phonon calculation.$^{40}$ Using PBE, the distance between P chains in black phosphorus is 3.95 Å. By applying this correction, the P–P chain distance was reduced to 3.58 Å. To include the MBD correction on black phosphorus in addition to the MBD correction on the black phosphorus chemical potential. (b) Distance from the hull for the four structures that were above the convex hull tie-line at 0 K. All structures except $I\bar{4}3d$–Cu$_4$P get closer to the tie-line as the temperature increases, suggesting that they are stabilized by temperature. This agrees with the experimental evidence for Cu$_3$P and $P6_{3}cm$–Cu$_4$P and suggests that Cu$_8$P$_3$ may form experimentally.

The previous sections predict the stability of Cu$_3$P discussed previously), Cu$_2$P$_2$, Cu$_{10}$P$_2$, and Cu$_8$P$_3$. The convex hull in Figure 7a was constructed up to 600 K, above which no changes to stabilities are observed. A maximum value of 600 K was chosen so as not to approach the melting point of any phases, as the known phases of Cu$^-$P typically have a melt between 800 and 1200 K. Furthermore, the harmonic approximation is a limited approach, and at higher temperatures, anharmonicity should be accounted for. $Fm\bar{3}m$–Cu$_3$P remains on the hull at 600 K, suggesting that it could be synthesized at high temperature. The convex hull is a confirmation that the $Cmc\bar{2}$–Cu$_5$P$_3$ phase formed from two Cu vacancies in $P6_{3}cm$–Cu$_4$P is the more stable phase at room temperature, as at 300 K, $Cmc\bar{2}$–Cu$_5$P$_3$ is within 10 meV/atom of the convex hull, as shown in Figure 7b. In addition, the destabilization of $I\bar{4}3d$–Cu$_4$P at high temperatures, shown in Figure 7b, suggests that this phase is not experimentally realizable and provides an explanation as to why it has not yet been experimentally synthesized. We can clearly see that $P6_{3}cm$–Cu$_4$P is stabilized at higher temperatures, as shown in Figure 7b, in which it is within 10 meV/atom of the convex hull at temperatures higher than 450 K.

Previous work on the Cu$_{3-x}$P phases of $P6_{3}cm$–Cu$_4$P$^{37}$ confirms that the formation of two vacancies in Cu$_4$P is energetically stabilizing. By enumerating all of the possible structures with two Cu vacancies using the vacancy enumeration procedure described in the Methods section, we have determined that the $Cmc\bar{2}$–Cu$_5$P$_3$ phase with two Cu vacancies in the 6c Wyckoff positions is the lowest-energy vacancy phase. Given the large number of ways to introduce these vacancies into the structure, configurational entropy will further stabilize this phase at high temperatures. To fully understand the nature of vacancy formation in $P6_{3}cm$–Cu$_4$P, a full cluster expansion could be performed, which is beyond the scope of this paper.

**Cu$_3$P as a Li-Ion Battery Conversion Anode.** $Fm\bar{3}m$–Cu$_3$P was computationally predicted to be energetically stable both as a 2D material$^{50}$ and now, in this article, as a bulk phase. The previous sections predict the stability of $Fm\bar{3}m$–Cu$_3$P at temperatures up to 600 K and characterize it as a metal with
dispersive bands and delocalized conduction states at the Fermi level. An intuitive choice of application for Cu$_3$P lies in conversion anodes for Li-ion batteries, where previously both CuP$_2$ and Cu$_3$P were used as anodes with gravimetric capacities between 300 and 800 mAh/g.\textsuperscript{11−14}

The crystal structure of P6$_{3}$cm−Cu$_3$P has a theoretical capacity of 363 mAh/g and experimentally has exhibited a range of capacities based upon the preparation method used.\textsuperscript{13} The powdered Cu$_3$P anodes prepared by Bichat et al.\textsuperscript{15} ranged in the initial capacity from 272 mAh/g using high-temperature synthesis in a silica tube to 527 mAh/g using low-temperature solvothermal synthesis. In the solvothermal route, the Cu$_3$P powders were prepared with copper chloride, water, and NH$_4$OH with white phosphorus, which could have resulted in copper oxide impurities leading to the initial capacity that is above the theoretical capacity of crystalline Cu$_3$P. Pfeiffer et al. synthesized Cu$_3$P powder by a solid-state reaction with red P in an ethanol suspension and Cu foil, and the initial capacity of Cu$_3$P was 415 mAh/g.\textsuperscript{14} Energy-dispersive X-ray analysis showed that the stoichiometry was close to Cu$_3$P (though not exact), suggesting that this initial structure could have been within the stoichiometric range of Cu$_3$P to achieve that initial capacity, in addition to the added capacity from likely oxide impurities.

In contrast, Cu$_2$P has a theoretical capacity of 509 mAh/g, which is above that of graphite at 372 mAh/g. The metallic nature of Cu$_2$P further enhances its use as a Li-ion battery anode, enabling fast electronic transfer through the electrode of the battery. In fact, Cu is already widely used as a current collector in Li-ion batteries, specifically for its properties in resisting Li intercalation, and dead Li is found during cycling rather than Cu−Li phases.\textsuperscript{66} Therefore, no Cu−Li compounds were included in the convex hull.

The volume expansion for a conversion anode with an overall conversion reaction

\[ \text{Cu}_3\text{P} + 3b\text{Li} \rightarrow a\text{Cu} + b\text{LiP} \]  

is calculated as

\[
\text{volume expansion(\%)} = 100 \times \left(\frac{b V(\text{LiP}) + a V(\text{Cu})}{V(\text{Cu}_3\text{P})} - 1\right)
\]

where \(V(\text{Cu}_3\text{P})\) is the volume per formula unit of each phase in the conversion reaction. Using this equation, the volume expansion of Fm$\overline{3}$m−Cu$_3$P is 99%. This is comparable to the calculated volume expansion of P6$_{3}$cm−Cu$_3$P, which is 86%, and far superior to the volume expansion of CuP$_2$, which is 165%. The volume expansion for each binary Cu−P phase is shown in Figure S8, confirming that Cu$_3$P has the lowest volume expansion of the four stable phases on the convex hull. Experimental reports on the cycling of ball-milled CuP$_2$\textsuperscript{12} suggest that volume expansion occurs, as after cycling for 10 cycles, the capacity is reduced by 50%, although they give no estimate of the level of volume expansion in the cell. The expansion is partially mitigated through the use of nanostructuring,\textsuperscript{11} which allows cycling for 200 cycles. However, there is still capacity fading in this case, which reiterates the need for a high-capacity conversion anode with low-volume expansion, so as to reduce the need for nanostructuring or other postprocessing techniques to mitigate volume expansion. As both Cu$_3$P and Cu$_2$P have lower predicted volume expansions, and the synthesized Cu$_3$P shows no evidence of deleterious volume expansion,\textsuperscript{13} it is likely that Cu$_3$P would also have minimal volume expansion in the experiment.

Using the convex hull constructed in Figure 1 and the structures on the ternary hull of Cu−Li−P, a voltage profile was constructed from the DFT ground-state energies for both Fm$\overline{3}$m−Cu$_3$P and P6$_{3}$cm−Cu$_3$P. All of the known ternary structures were included in this hull: P$\overline{3}$m1−Cu$_3$LiP, I4/mmm−Cu$_3$LiP$_3$, I$m$mm−Cu$_3$Li$_2$P$_3$, and Cmcm−Cu$_3$LiP, as well as the binary Li−P structures Cmcm-Li$_2$P, P$_2$1/c-Li$_2$P, P$_2$122121-Li$_2$P$_7$, and I4/$a$cd-Li$_2$P. A plane wave kinetic energy cutoff of 700 eV was used, and all structures on the hull were re-relaxed at this higher cutoff. The ternary hull is shown in Figure S9, in which the pathways from Cu−P to Li are also shown to depict how the voltage profiles for these Cu−P phases were calculated. The hull is shaded with a color map to show the relative formation energy of phases on the hull, indicating that the Li−P phases have more negative formation energies (and thus create a deeper convex hull) than the Cu−P phases.

Although Cu−Li phases are predicted to be stable under the approximation of PBE, the formation energy of the predicted Cu$_3$Li phase is only 26 meV/atom in the OQMD database\textsuperscript{19,64} and no phases of Cu−Li are predicted at finite temperature in the experiment.\textsuperscript{65} Furthermore, Cu is used as a current collector in Li-ion batteries, specifically for its properties in resisting Li intercalation, and dead Li is found during cycling rather than Cu−Li phases.\textsuperscript{66} Therefore, no Cu−Li compounds were included in the convex hull.

There are three ternary compounds on the Cu−Li−P hull in Figure S9; these are I4/mmm−Cu$_3$Li$_2$P$_3$, I$m$mm−Cu$_3$Li$_2$P$_3$, and Cmcm−Cu$_3$LiP. Experiments suggest that a hexagonal Li$_2$Cu$_3$P phase forms during cycling; however, the P$\overline{3}$m1−Cu$_3$LiP (ICSD 659706)\textsuperscript{46} phase of this structure is 39 meV/atom above the hull at a plane wave cutoff of 700 eV.

From this ternary hull, shown in Figure S9, the voltage profile shown in Figure 8 was constructed. This hull is calculated as usual, without incorporating vibrational effects at 0 K. As the
P5̅m1−Cu2LiP phase suggested in the experiment\(^{46,67}\) is 39 meV/atom above the convex hull, it cannot be in the voltage profile calculated in Figure 8. The 0 K voltage profile includes the I4/mmm−Cu2LiP\(_2\) phase, which has been previously synthesized through a solid-state reaction,\(^{68}\) and is a high T\(_c\) pnictide superconductor.\(^{69}\) The I4/mmm−Cu2LiP\(_2\) phase has not, to our knowledge, been identified during cycling in Li-ion batteries previously.

Both CuP and Cu\(_2\)P have the same overall reaction mechanism given by eq 4, and the stable phases during the reaction from charging CuP are given in Table 2. These reactions show that Cu\(_2\)P operates in a narrower voltage window than CuP and has a higher predicted gravimetric capacity. The predicted structures forming at each capacity and voltage are given in Table 2. These phases of Cu\(_3\)P have the same overall reaction as Cu\(_2\)P, but have a higher capacity of 363 mAh/g and an average voltage of 0.91 V. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02054.

Table 2. Reaction Pathways for Cu\(_2\)P + Li → Li\(_x\)P + nCu

| reaction stage | gravimetric capacity (mAh/g) | voltage (V) | reaction pathway |
|----------------|-------------------------------|-------------|------------------|
| Cu\(_2\)P + 3Li → Li\(_x\)P + 2Cu | I | 85 | 1.10 | 1/2Cu\(_2\)LiP\(_2\) + Cu |
| II | 141 | 1.00 | 1/6Cu\(_3\)LiP\(_2\) + 4/3Cu |
| III | 338 | 0.98 | CuLi\(_2\)P + Cu |
| IV | 509 | 0.54 | Li\(_3\)P + 2Cu |
| Cu\(_2\)P + 3Li → Li\(_x\)P + 3Cu | I | 60 | 1.53 | 1/2Cu\(_2\)LiP\(_2\) + 2Cu |
| II | 101 | 1.00 | 1/6Cu\(_3\)LiP\(_2\) + 7/3Cu |
| III | 242 | 0.98 | CuLi\(_2\)P + 2Cu |
| IV | 363 | 0.54 | Li\(_3\)P + 3Cu |

Each plateau in the ground-state voltage profile in Figure 8 represents a three-phase region of the ternary hull in which phases of Cu−Li−P are stable. Here, Cu\(_2\)P was “stabilized” on the ternary hull by artificially excluding the CuP\(_2−CuP\(_2\)\) and CuP\(_2\) phases. This is an approximation of a convex hull in which Cu\(_2\)P is on the tie-line, which does not affect the formation energy (and thus predicted voltages) of the other phases. The experimental voltage curve shown in Figure 8 from ref 67 exhibits a similar trend in phase transitions along the cycle as the theoretical curve for Cu\(_2\)P.

CONCLUSIONS

Using four different computational crystal structure-searching techniques on the copper phosphides, several structures that lie close to the convex hull (within 20 meV/atom) were predicted, including Cm̅−Cu\(_3\)P\(_{11}\), I\(_4\)3d−Cu\(_2\)P, and Fm̅3m−Cu\(_3\)P; the experimentally characterized P\(_1−CuP\(_{10}\), C\(_2/m−CuP\(_7\), and P\(_2\)/c−CuP\(_2\) were all on the convex hull tie-line. By calculating the phonon dispersion curves of all structures within 20 meV/atom of the convex hull above 300 K. Experimental diffractometry on single crystals of Cu\(_3\)P suggests that the phase has a range of

stoichiometries between Cu\(_2.2\)P and Cu\(_2.5\)P\(^{43,47}\) and Cu\(_3\)P (or Cu\(_2.6\)P equivalently) is within these bounds.

In addition to confirming the stability of Cm̅2\(_1−CuP\(_9\), we also confirmed that Cm̅−CuP\(_{11}\) remains metastable up to high temperatures, as shown in the temperature-dependent hull in Figure 7. While Cu\(_3\)P\(_{11}\) is unlikely to be used as a Li-ion battery anode, given its high P content, and therefore susceptibility to volume expansion, it could be a novel phase to consider within the Cu−P phase diagram. Cu\(_3\)P\(_{10}\) was identified experimentally by preparing Cu\(_3\)P\(_2\) in excess P;\(^{10\text{a}}\) given the structural similarity between Cm̅−Cu\(_3\)P\(_{11}\) and C\(_2/m−CuP\(_2\) shown in Figure 2, it is possible that Cm̅−Cu\(_3\)P\(_{11}\) is also formed in excess P. Using the PXRD patterns presented in Figure 3, it may be possible to distinguish the Cm̅−Cu\(_3\)P\(_{11}\) phase from C\(_2/m−CuP\(_2\) experimentally, from the change in the peak intensity at 16° and peak differences at 2θ values < 20°; however, further experimental analysis is likely required given the low intensity of this peak.

Finally, Fm̅3m−CuP\(_3\) is the only phase identified through crystal structure prediction, which was found on the hull at 0 K and which remained on the convex hull at finite temperature, strongly suggesting that it is possible to synthesize Cu\(_3\)P experimentally. Furthermore, its synthesis could provide a novel conversion anode, with favorable properties for Li-ion batteries. Hybrid functional calculations of the electronic properties of Cu\(_2\)P predict it to be isostructural and qualitatively similar electronically to both Rh\(_2\)P and Ir\(_2\)P, which are also Fm̅3m metals with dispersive bands at the Fermi level. This was confirmed using spin-polarized calculations, with both vector and scalar spin treatments, hybrid functional calculations using the HSE06 functional, and finally a projected band structure and density of states using PBE. This confirmation of the metallic nature of Cu\(_2\)P using a wide range of functionals and spin treatments suggests that this could be a better choice for anode than Li−P, which are insulators with wide band gaps. Furthermore, the presence of such dispersive bands suggests high electron mobility within the anode, which would mitigate fast charge transfer between the Cu current collector and Li-ions. Finally, given its higher capacity (509 mAh/g) compared to CuP, Cu\(_2\)P has potential as an experimentally realizable conversion anode, which has a capacity that is competitive with graphite, conductive to promote electronic transfer within the anode, and less vulnerable to degradation compared to high P content conversion anodes due to reduced levels of cyclic volume changes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02054. The input and output files associated with our calculations have been deposited into the Cambridge Repository at https://doi.org/10.17863/CAM.54795 in the Cambridge Repository; and all analysis is on GitHub at harpafl3/data.copper-phosphides and Binder.

Details of the simulation of powder X-ray diffraction patterns and pair distribution functions, as well as the electronic band structure calculations using spin–orbit coupling (PDF)
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Notes
The authors declare no competing financial interest.

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ADDITIONAL NOTE

“OTF pseudopotential strings are Cu: 3l2.2l2.01.010l12l13l 40:41:32 (q=6), P: 3l1.8l4l4l5l30:31:32, and Li: 1l1.0l14l16l18l 10u:20 (q=7).

REFERENCES
(1) Ramireddy, T.; Xing, T.; Rahman, M. M.; Chen, Y.; Dutercq, Q.; Gunzelmann, D.; Glushenkov, A. M. Phosphorus-carbon nano-composite anodes for lithium-ion and sodium-ion batteries. J. Mater. Chem. A 2015, 3, 5572–5584.
(2) Bhatt, M. D.; Lee, J. Y. High capacity conversion anodes in Li-ion batteries: A review. Int. J. Hydrogen Energy 2019, 44, 10852–10905.
(3) Tarascon, J.-M.; Armand, M. Issues and challenges facing rechargeable lithium batteries. Nature 2001, 414, 359–367.
(4) Kirklin, S.; Meredig, B.; Wolverton, C. High-throughput computational screening of new Li-ion battery anode materials. Adv. Energy Mater. 2013, 3, 252–262.
(5) Sun, M.; Liu, H.; Qu, J.; Li, J. Earth-rich transition metal phosphate for energy conversion and storage. Adv. Energy Mater. 2016, 6, No. 1600087.
(6) Feng, L.; Xue, H. Advances in transition-metal phosphate applications in electrochemical energy storage and catalysis. ChemElectroChem 2017, 4, 20–34.
(7) Lu, Y.; Yu, L.; Lou, X. W. D. Nanostructured conversion-type anode materials for advanced lithium-ion batteries. Chem 2018, 4, 972–996.
(8) Boyanov, S.; Bernardi, J.; Gillot, F.; Dupont, L.; Wornes, M.; Tarascon, J.-M.; Moncoutout, L. Doublet, M.-L. Fel. Another attractive anode for the Li-ion battery enlisting a reversible two-step insertion/conversion process. Chem. Mater. 2006, 18, 3531–3538.
(9) Zhang, Y.; Zhang, H.; Feng, Y.; Liu, L.; Wang, Y. Unique Fe2P nanoparticles enveloped in sandwichlike graphitized carbon sheets as excellent hydrogen evolution reaction catalyst and Lithium-ion battery anode. ACS Appl. Mater. Interfaces 2015, 7, 26684–26690.
(10) Lu, Y.; Wang, X.; Mai, Y.; Xiang, J.; Zhang, H.; Li, L.; Gu, C.; Tu, J.; Mao, S. X. Ni,P/graphene sheets as anode materials with enhanced electrochemical properties versus lithium. J. Phys. Chem. C 2012, 116, 22217–22225.
(11) Kim, S.-O.; Manthiram, A. Phosphorus-rich CuP2 embedded in carbon matrix as a high-performance anode for Li-ion batteries. ACS Appl. Mater. Interfaces 2017, 9, 16221–16232.
(12) Wang, K.; Yang, J.; Xie, J.; Wang, B.; Wen, Z. Electrochemical reactions of lithium with CuP2 and Li1-xCuP2,2P2, synthesized by ballmilling. Electrochem. Commun. 2003, 5, 480–483.
(13) Bichat, M.-P.; Politova, T.; Pfeiffer, H.; Tancret, F.; Moncoutout, L.; Pascal, J.-L.; Brousse, T.; Favier, F. Cu2P as anode material for lithium ion battery: powder morphology and electrochemical performances. J. Power Sources 2004, 136, 80–87.
(14) Pfeiffer, H.; Tancret, F.; Bichat, M.-P.; Moncoutout, L.; Favier, F.; Brousse, T. Air stable copper phosphide (Cu2P): a possible negative electrode material for lithium batteries. Electrochem. Commun. 2004, 6, 263–267.
(15) Villievieille, C.; Robert, F.; Taberna, P. L.; Bazin, L.; Simon, P.; Moncoutout, L. The good reactivity of lithium with nanostructured copper phosphide. J. Mater. Chem. 2008, 18, 5956–5960.
(16) Ni, S.; Ma, J.; Lv, X.; Yang, X.; Zhang, L. The fine electrochemical performance of porous Cu2P/Cu and the high energy density of Cu2P as anode for Li-ion batteries. J. Mater. Chem. A 2014, 2, 20506–20509.
(17) Chandrasekar, M.; Mitra, S. Thin copper phosphide films as conversion anode for lithium-ion battery applications. Electrochim. Acta 2013, 92, 47–54.
(18) Curtarolo, S.; Setyawan, W.; Hart, G. L.; Jah Natek, M.; Chepulskii, R. V.; Taylor, R. H.; Wang, S.; Xue, J.; Yang, K.; Levy, O.; Meh1, M. J.; Stokes, H. T.; Demchenko, D. O.; Morgan, D. A. FLow: An automatic framework for high-throughput materials discovery. Comput. Mater. Sci. 2012, 58, 218–226.
(19) Saul, J. E.; Kirklin, S.; Aylor, M.; Meredig, B.; Wolverton, C. Materials design and discovery with high-throughput density functional theory: the open quantum materials database (OQMD). JOM 2013, 65, 1501–1509.
(20) Hautier, G.; Fischer, C.; Ehlacher, V.; Jain, A.; Ceder, G. Data mined ionic substitutions for the discovery of new compounds. Inorg. Chem. 2011, 50, 656–663.
(21) Evans, M. GitHub, matador v0.9, 2020. https://doi.org/10.5281/zenodo.3908573 (accessed May 11, 2020).
(22) Evans, M. GitHub, ilustrado v0.3, 2020. https://doi.org/10.5281/zenodo.3904495 (accessed May 11, 2020).
(23) Harper, A. F.; Evans, M. L.; Darby, J. P.; Karasulu, B.; Koçer, C. P.; Nelson, J. R.; Morris, A. J. Ab initio structure prediction methods for battery materials. Johnson Matthey Technol. Rev. 2019, 64, 103–118.
(24) See, K. A.; Leskes, M.; Griffin, J. M.; Britto, S.; Matthews, P. D.; Emby, A.; Van der Ven, A.; and Wright, D. S.; Morris, A. J.; Grey, C. P.; et al. Ab initio structure search and in situ Li NMR studies of discharge products in the Li-S battery system. J. Am. Chem. Soc. 2014, 136, 16368–16377.
(25) Mayo, M.; Morris, A. J. Structure prediction of Li-Sn and Li-Sb intermetallics for lithium-ion batteries anodes. Chem. Mater. 2017, 29, 5787–5795.
(26) Mayo, M.; Griffith, K. J.; Pickard, C. J.; Morris, A. J. Ab initio study of phosphorus anodes for lithium and sodium-ion batteries. Chem. Mater. 2016, 28, 2011–2021.

(27) Marbella, L. E.; Evans, M. L.; Groh, M. F.; Nelson, J.; Griffith, K. J.; Morris, A. J.; Grey, C. P. Sedimentation and desorption via helical phosphorus intermediates in high-capacity anodes for sodium-ion batteries. J. Am. Chem. Soc. 2018, 140, 7994–8004.

(28) Hellenbrandt, M. The inorganic crystal structure database (ICSD)—present and future. Crystallogr. Rev. 2004, 10, 17–22.

(29) Pickard, C. J.; Needs, R. Ab initio random structure searching. J. Phys. Condens. Matter 2011, 23, No. 053201.

(30) Deaven, D. M.; Ho, K. M. Molecular Geometry Optimization with a Genetic Algorithm. Phys. Rev. Lett. 1995, 75, 288–291.

(31) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I.; Reson, K.; Payne, M. C. First principles methods using CASTEP. Z. Kristallogr. - Cryst. Mater. 2005, 220, 567–570.

(32) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865.

(33) Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys. Rev. B 1990, 41, 7892.

(34) Sun, L.-Q.; Li, M.-J.; Sun, K.; Yu, S.-H.; Wang, R.-S.; Xie, H.-M. Electrochemical activity of black phosphorus as an anode material for lithium-ion batteries. J. Phys. Chem. C 2012, 116, 14772–14779.

(35) Urban, A.; Seo, D.-H.; Ceder, G. Computational understanding of Li-ion batteries. npj Comput. Mater. 2016, 2, 1–13.

(36) Hinuma, Y.; Puig, G.; Kumagai, Y.; Oba, F.; Tanaka, I. Band structure of Cu2P7 and structure refinements of CuP2 and AgP2. J. Inorg. Gen. Chem. 2005, No. 053201.

(37) Togo, A.; Tanaka, I. Spglib: A Software Library for Crystal Symmetry Search. 2018, arXiv:1808.01590. arXiv.org e-Print archive. http://arxiv.org/abs/1808.01590 (Accessed Feb 19, 2020).

(38) Morris, A. J.; Nicholls, R. J.; Pickard, C. J.; Yates, J. R. OptaDOS: A tool for obtaining densities of states, core-level and optical spectra from electronic structure codes. Comput. Phys. Commun. 2014, 185, 1477–1485.

(39) Nicholls, R. J.; Morris, A. J.; Pickard, C. J.; Yates, J. R. Accurate and efficient method for many-body van der Waals interactions. J. Phys.: Conf. Ser. 2012, No. 012062.

(40) Tkatchenko, A.; DiStasio, R. A., Jr.; Car, R.; Scheffler, M. OptaDOS—a new tool for EELS calculations. Journal of Physics Conference Series. Phys. Rev. Lett. 2012, 108, No. 236402.

(41) Sun, W.; Dacek, S. T.; Ong, S. P.; Hautier, G.; Jain, A.; Richards, W. D.; Ganust, A. C.; Persson, K. A.; Ceder, G. The thermodynamic scale of inorganic crystalline metastability. Sci. Adv. 2016, 2, e1600225.

(42) Zhang, G.-X.; Pei, G.; Kumagai, Y.; Oba, F.; Tanaka, I. Band structure diagram paths based on crystallography. Comput. Mater. Sci. 2017, 128, 140–184.

(43) Olofsson, S. Phosphides of the platinum metals. Nature 1960, 185, 31–32.

(44) Song, M.-S.; Kang, Y.-M.; Kim, Y.-J.; Park, K.-S.; Kwon, H.-S. Nature of insulating phase transition and degradation of structure and electrochemical reactivity in an olivine-structured material, LiFePO4. J. Solid State Chem. 2011, 184, 57–67.

(45) Song, M.-S.; Kang, Y.-M.; Kim, Y.-J.; Park, K.-S.; Kwon, H.-S. Nature of insulating phase transition and degradation of structure and electrochemical reactivity in an olivine-structured material, LiFePO4. Inorg. Chem. 2009, 48, 8271–8275.

(46) Baroni, S.; de Gironcoli, S.; Dal Corso, A.; Giannozzi, P. Phonons and related crystal properties from density-functional perturbation theory. Rev. Mod. Phys. 2001, 73, 535–562.

(47) Van de Walle, A.; Moser, Z.; Gasior, W. First-principles calculation of the Cu-Li phase diagram. Acta. Metall. 2004, 49, 535–544.

(48) Okamoto, H. Cu-Li (copper-lithium). J. Phase Equilib. Diffus. 2011, 32, 172.

(49) Fang, C.; Li, J.; Zhang, M.; Zhang, Y.; Yang, F.; Lee, J. Z.; Lee, M.-H.; Alvarado, J.; Schroeder, M. A.; Yang, Y.; et al. Quantifying inactive lithium in lithium metal batteries. Nature 2019, 572, 511–515.

(50) Owsu, M.; Jawad, H.; Lundström, T.; Rundquist, S. Crystallographic Studies of Cr2P and of the Solid Solution of Hydrogen in Zr2P. Phys. Scr. 1972, 6, 67–70.

(51) Zumbusch, M. On the structures of uranium sulfide and subphosphate of iridium and rhodium. J. Inorg. Gen. Chem. 1940, 243, 322–329.

(52) Moeller, M. H.; Jeitschko, W. Preparation and crystal structure of trisilvere decaphosphide, Ag4P9, an unusual defect tetrahedral compound. Inorg. Chem. 1981, 20, 828–833.

(53) Crichton, W. A.; Mezouar, M.; Monaco, G.; Falconi, S. Phosphorus: New in situ powder data from large-volume apparatus. Powder Diff. 2003, 18, 155–158.

(54) Thurn, H.; Krebs, H. Über Struktur und Eigenschaften der Halbmetalle. XXII. Die Kristallstruktur des Hittorfschen Phosphors. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1969, 25, 125–138.

(55) López, C.; Gauss, B.; Giering, R.; Almqvist, M. An X-ray investigation of the Ni-P system and the crystal structures of NiP and NiP2. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1977, 33, 2787–2797.

(56) Lonsdale, J. N.; Nowacki, W. Refinement of the crystal structure of domeykite, a structure related to the A15 type. Z. Kristallogr. - Cryst. Mater. 1977, 147, 334–345.

(57) Song, M.-S.; Kang, Y.-M.; Kim, Y.-J.; Park, K.-S.; Kwon, H.-S. Nature of insulating phase transition and degradation of structure and electrochemical reactivity in an olivine-structured material, LiFePO4. Inorg. Chem. 2009, 48, 8271–8275.

(58) Baroni, S.; de Gironcoli, S.; Dal Corso, A.; Giannozzi, P. Phonons and related crystal properties from density-functional perturbation theory. Rev. Mod. Phys. 2001, 73, 535–562.

(59) Van de Walle, A.; Moser, Z.; Gasior, W. First-principles calculation of the Cu-Li phase diagram. Acta. Metall. 2004, 49, 535–544.

(60) Okamoto, H. Cu-Li (copper-lithium). J. Phase Equilib. Diffus. 2011, 32, 172.

(61) Fang, C.; Li, J.; Zhang, M.; Zhang, Y.; Yang, F.; Lee, J. Z.; Lee, M.-H.; Alvarado, J.; Schroeder, M. A.; Yang, Y.; et al. Quantifying inactive lithium in lithium metal batteries. Nature 2019, 572, 511–515.

(62) Bichat, M. P.; Politova, T.; Pascal, J. L.; Favier, F.; Monconduit, L. Electrochemical Reactivity of Cu2P with Lithium. J. Electrochem. Soc. 2004, 151, A2074.

(63) Schlenker, H.; Jacobs, H. The Kristallstrukturen des LiCu2P2 und des Li2/3Cu3/2P3. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1972, 28, 327.

(64) Han, J.-T.; Zhou, J.-S.; Cheng, J.-G.; Goodenough, J. B. A new pnicrite superconductor without iron. J. Am. Chem. Soc. 2010, 132, 908–912.

(65) Bawohl, M.; Nilges, T. Phosphorus rich d10 ion polyphosphides and selected materials. Z. Anorg. Allg. Chem. 2015, 641, 304–310.