Electronic Structure and Properties of Transition Metal Phosphides

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Transition-metal phosphides (TMPs) are commonly employed as conversion anodes used in lithium-ion batteries. In addition to using *ab initio* random structure prediction to identify new high capacity materials, it is also crucial to understand their electronic properties. I have conducted a high throughput search for new bulk crystal structures of Cu-P, and further analysed the electronic properties of a subset of TMPs.

TMP conversion anodes

Graphite, the most commonly employed Li-ion battery anode, is inherently limited in its performance due to its maximal capacity of 372 mAh/g; thus there exists a space for understanding higher capacity active materials to increase the overall battery energy density and improve performance. Transition metal phosphides (TMPs) in general are an attractive class of materials to study within the field of battery anodes given that phosphorus has a high theoretical capacity of 2596 mAh/g. Transition metals are an added benefit to improve structural stability of these compounds [1].

Unlike graphite, which alloys with Li, TMPs are conversion anodes which undergo the following reaction upon lithiation (here M is the transition metal)

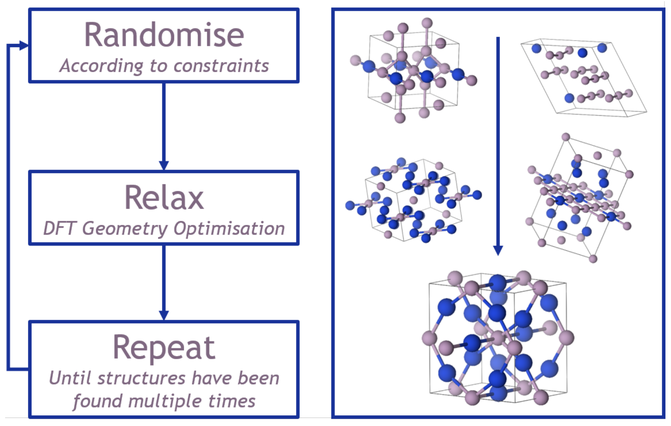
$$MP_x + 3x\,\mathrm{Li} \rightarrow \mathrm{Li_3P} + \mathrm{M}.$$

The benefit of a conversion reaction lies in the ability to use transition metals as a stabilising element for the high capacity phosphorus network. This prevents the anode from breaking down upon successive cycles while maintaining high capacity.

Crystal structure prediction

To determine which of the copper phosphides are most viable in Li-ion batteries, I previously conducted a search of the configuration space of Li-Cu-P as a way to uncover potential binary and ternary phases of this system which may form during battery cycling.

Crystal structure prediction was carried out using the *ab initio* random structure searching technique (AIRSS) [2].



This method generates thousands of random structures subject to constraints such as cell size, number of atoms, and distances between atoms. By then relaxing these structures to their lowest energy ground state using density-functional theory (DFT) in CASTEP [3], I am able to construct a zero temperature hull of each combinations of elements. The structures lowest in energy are thus most likely to form during battery cycling.

I also applied a cut-and-splice genetic algorithm to the Cu-P family using `ilustrado` (documentation at `ilustrado.readthedocs.io`). By using a starting family of AIRSS structures, and successively generating families related to the initial structures this directs the searching process to identify the global minima ground states. Using these predictive techniques I have identified potential high-capacity conversion anodes within the Cu-P system. This method has been successfully applied in other systems as well.

PBE Cu-P Convex Hull

- The AIRSS searches on Cu-P identify four ground state phases, CuP_{10}, Cu_2P_7, Cu_2P, and CuP_2.

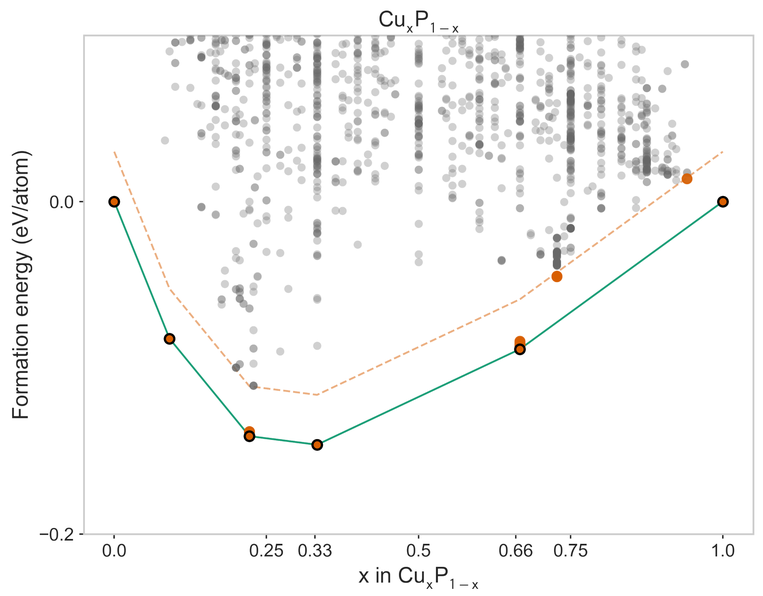


Figure 1: Convex hull of Cu-P using the PBE functional. Orange circles represent structures within 30 meV of the hull tie-line, and grey circles represent AIRSS-identified structures above the tie line. The structures in orange within 30 meV are considered thermodynamically accessible. structures.

- The Cu_2P structure on the hull has not been identified experimentally.
- Other Cu_2-Pnictides have been predicted as 2D materials, such as Cu_2As [4].
- Figure 2 shows the Cu_2P structure which has space group $Fm\bar{3}m$, as do the known structures of Rh_2P and Ir_2P.

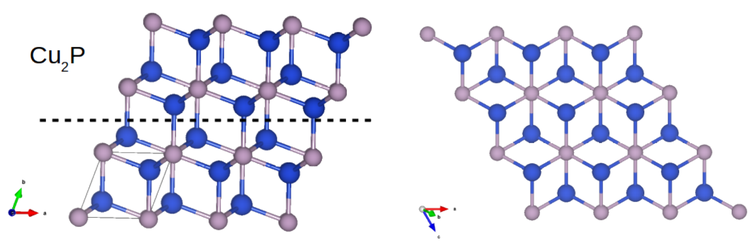


Figure 2: Crystal structure of Cu_2P with $Fm\bar{3}m$ space group in side on and top down view. The cross-section shown on the right is the 2D layer which resembles Cu_2As

Temperature dependent convex hull

- A finite temperature phase diagram using the PBE functional shows that at high temperatures, Cu_2P is most stable.
- Future work will create this phase diagram using the HSE06 hybrid functional in an attempt to understand the long range ordering in Cu_2P and its nearby structures on the hull (Cu_3P and CuP_2)

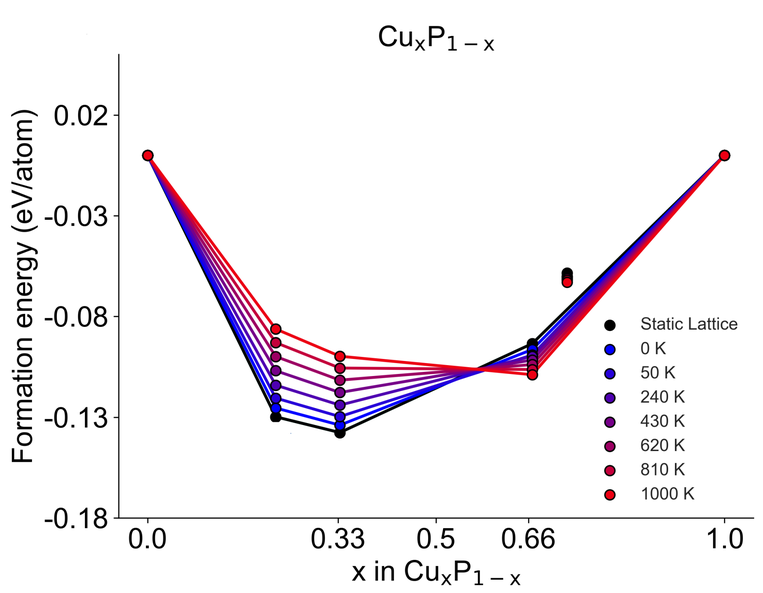


Figure 3: Binary Cu-P hull for selected structures on hull at static lattice. Temperature effects calculated using phonon modes of ground state structures

Band structures of $Fm\bar{3}m$ TM_2P

- Of the 20 TM_2P structures in the ICSD, only Rh_2P and Ir_2P have the same $Fm\bar{3}m$ structure as Cu_2P

Figure 4: Band structures of Cu_2P, Ir_2P, Rh_2P all $Fm\bar{3}m$. Ir_2P ICSD Collcode 640898, Rh_2P ICSD Collcode 38356. Band structures are coloured by the angle projected density of states

- The Cu_2P band structure including long-range effects with the HSE06 functional is not dramatically changed from the PBE band structure from Γ to T

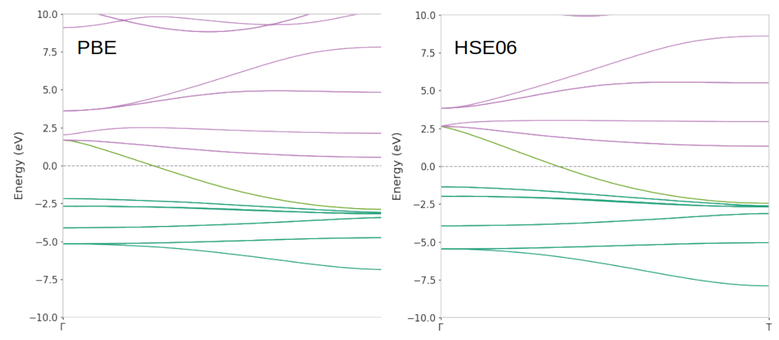


Figure 5: Band structure of Cu_2P using PBE GGA functional and HSE06 Hybrid functional

- Ni_2P is space group $P\bar{6}2m$, and resembles the remaining TM_2P structures including Mn_2P, Fe_2P, and Co_2P.
- The rest of the TM_2P structures are space group Pmna
- Figure 6 shows that compared to Ir_2P and Rh_2P, Ni_2P is a metal with a high density of d-states just below the Fermi level

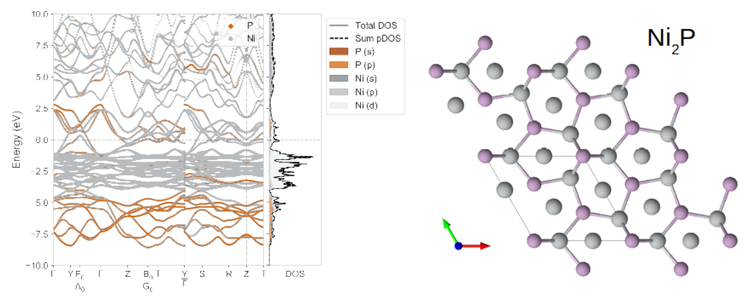


Figure 6: Crystal structure of $P\bar{6}2m$ Ni_2P (left) and band structure of Ni_2P using the PBE functional

Summary & Outlook

- AIRSS searches for novel structures of Cu-P have identified a new Cu_2P structure, which has yet to be made experimentally
- Finite temperature calculations with the PBE functional show Cu-P structures including Cu_2P are stable at high temperatures
- These results are compared to the rest of the family of TM_2P and show that Cu_2P shares electronic features of both Ir_2P and Rh_2P

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