Low-Temperature Tailoring of Copper-Deficient Cu3−xP – Electric Properties, Phase Transitions and Performance in Lithium-Ion Batteries


Published in:
Chemistry of Materials

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
© 2018 American Chemical Society. This work is made available online in accordance with the publisher's policies. Please refer to any applicable terms of use of the publisher.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.
Low-Temperature Tailoring of Copper-Deficient CuP – Electric Properties, Phase Transitions and Performance in Lithium-Ion Batteries

Alexander Wolff, Thomas Doert, Jens Hunger, Martin Kaiser, Julia Pallmann, Romy Reinhold, Sivatmeehan Yogendra, Lars Giebeler, Jörg Sichelschmidt, Walter Schnelle, Rachel Whiteside, H. Q. Nimal Gunaratne, Peter Nockemann, Jan J. Weigand, Eike Brunner, and Michael Ruck

Chem. Mater., Just Accepted Manuscript • DOI: 10.1021/acs.chemmater.8b02950 • Publication Date (Web): 17 Sep 2018

Downloaded from http://pubs.acs.org on September 25, 2018

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Low-Temperature Tailoring of Copper-Deficient Cu$_{3-x}$P – Electric Properties, Phase Transitions and Performance in Lithium-Ion Batteries

Alexander Wolff,† Thomas Doert,‡ Jens Hunger,† Martin Kaiser,† Julia Pallmann,† Romy Reinhold,‡ Sivatmeehan Yogendra,† Lars Giebeler,‡ Jörg Sichelschmidt,∥ Walter Schnelle,† Rachel Whiteside,‡ H. Q. Nimal Gunaratne,# Peter Nockemann,# Jan J. Weigand,‡ Eike Brunner‡ and Michael Ruck∗,†,∥

† Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany.
‡ Leibniz Institute for Solid State and Material Research Dresden e. V., 01069 Dresden, Germany.
# School of Chemistry and Chemical Engineering, Queen’s University of Belfast, Belfast BT7 1NN, United Kingdom.

ABSTRACT: A convenient approach for a controlled and high-yield synthesis of copper-deficient Cu$_{3-x}$P (0.1 < x < 0.7) is reported that makes use of ionic liquids with highly nucleophilic “naked” halide anions. Halide anions drastically enhance the reactivity of the white phosphorus precursor and kinetically disfavour the formation of phosphorus-rich side products. Cu$_{3-x}$P shows a high degree of tolerance for cation vacancies without major structural reorganisation, as evidenced by X-ray diffraction and solid-state nuclear magnetic resonance spectroscopy. Measurements of the electric properties reveal that Cu$_{3-x}$P is a bad metallic p-type conductor. The resistivity is composition-dependent and displays a distinct anomaly from a phase transition, leading to the discovery and structural characterisation of two hitherto unknown low temperature polymorphs. Electrochemical evaluation of copper-deficient Cu$_{3-x}$P as anode material for lithium ion batteries reveals a drastic change in the cycling mechanism leading to an increase of the initial capacities by about 70 %. This work gives a comprehensive insight into the chemical and structural features of copper-deficient Cu$_{3-x}$P and should lead to an improved understanding of its properties, not only for battery applications.

INTRODUCTION

Metal phosphides are well-known for their interesting structural diversity and their large variation of useful physical properties. Among this group of phosphides, copper(I) phosphide Cu$_{3-x}$P is one binary representative. Although its crystal structure has already been reported in the 1970s by Olofsson, scientific interest has only emerged at the beginning of the 21st century, and subsequently several applications have been developed. Cu$_{3-x}$P can be used, for example, as an oxygen scavenger during the production of copper and its alloys, as anode material in lithium ion batteries, and as catalyst for the splitting of water. Especially the latter example has lately attracted a lot of attention.

Despite this emerging interest, full characterisation and understanding of the structural features of this phosphide are yet to be completed. In particular, it is still frequently considered to have the idealized “Cu$_3$P” composition, although Olofsson had postulated partially occupied copper positions in the crystal structure. This evidence was further substantiated experimentally and theoretically, and confirmed by us recently. However, the impact of this structural feature is not yet widely considered in many investigations, although there are even a few studies using the copper deficiency for application. It was found, for example, that copper vacancies are responsible for plasmonic absorption features of Cu$_{3-x}$P nanocrystals in the near-infrared, which were used for constructing flexible photodetectors. The full potential of this material, however, can only be explored if Cu$_{3-x}$P with defined and chosen composition is accessible. Unfortunately, robustly reproducible synthetic protocols have not been reported so far.

Recently, we reported an ionothermal route to synthesize single-phase Cu$_{3-x}$P by direct reaction of copper metal and red phosphorus (P$_{red}$) in ionic liquids (ILs). Although this synthesis is simple and capable of producing large quantities of high-quality copper-rich Cu$_{3-x}$P in a comparatively short time, the drawback of this method is the formation of X-ray amorphous Cu$_3$P as a second phase when Cu$_{3-x}$P with x ≥ 0.1 is targeted. As evidenced by nuclear magnetic resonance (NMR) spectroscopy, a crucial step during this ionothermal synthesis is the chemical activation of P$_{red}$. In particular, small quantities of P$_4$ molecules are formed when P$_{red}$ is
heated in trihexyltetradecylphosphonium chloride ([P_{66614}][Cl]).\(^{38}\) This initial finding suggested that white phosphorus (P\(_{\text{white}}\)) might be an even better phosphorus precursor in the synthesis of Cu\(_{3-x}\)P, which we subsequently evaluated in this work.

Here we report our results on the syntheses of copper-deficient Cu\(_{3-x}\)P (x > 0.1) via the reaction of copper and P\(_{\text{white}}\) in different ILs. The use of P\(_{\text{white}}\) in chloride-containing ILs suppresses the formation of CuP

imperfections thus making single-phase Cu\(_{3-x}\)P (0.1 < x < 0.7) accessible. Furthermore, we shed light on the relationship between the crystal structure and a selection of composition-dependent physical properties, hence demonstrating that the control of the Cu\(_{3-x}\)P composition is crucial for possible applications to lithium ion batteries.

**EXPERIMENTAL SECTION**

**Starting Materials.** All compounds were handled in an argon-filled glovebox (M. Braun; p(O\(_2\))/p\(_\text{Ar}\) < 1 ppm, p(H\(_2\)O)/p\(_\text{Ar}\) < 1 ppm). The ILs trihexyltetradecylphosphonium chloride ([P_{66614}][Cl], IoLiTec, >95 %), trihexyltetradecylphosphonium bromide ([P_{66614}][Br], IoLiTec, >95 %), Trihexyltetradecylphosphonium bis(trifluoromethylsulfonylimide) ([P_{66614}][NTE], IoLiTec, >98 %) and trihexyltetradecylphosphonium acetate ([P_{66614}][OAc], own synthesis) were dried at 110 °C for 12 h under dynamic vacuum. Copper (ABCR, 99.9 % and 99.999 %, spherical, 100 mesh) was treated with H\(_2\) at 400 °C before use. Following a procedure described by Brauer, P\(_{\text{red}}\) (ABCR, 99.999 %) was washed with sodium hydroxide, rinsed with refluxing water, and finally dried under vacuum.\(^{39}\) P\(_{\text{white}}\) was obtained by heating the purified P\(_{\text{red}}\) in an evacuated silica tube to 450 °C. The opposite side of the ampoule protruded from the tubular furnace to allow condensation of P\(_{\text{white}}\). The crude product was collected under argon and sublimed twice in an evacuated silica tube at 100 °C until a transparent waxy solid was obtained. P\(_{\text{white}}\) is a hazardous form of the element. It is spontaneously combustible upon exposure to air and extremely toxic (estimated human lethal dose: 50-100 mg).

**Synthesis of [P_{66614}][OAc].** The IL was synthesized via anion metathesis. [P_{66614}][Cl] (20.8 g, 40 mmol) and K[OAc] (4.9 g, 50 mmol) were dissolved separately in 20 mL and 50 mL ethanol, respectively. Upon mixing of both solutions, potassium chloride precipitated immediately as a fine white solid. The solution was allowed to stir over night before KCl was filtered off leading to a transparent yellow solution. Subsequently, the ethanol was removed with a rotary evaporator. In the course of this procedure, the excess of K[OAc] precipitates forming a cloudy dispersion. Due to the low viscosity the solid can easily be filtered, leading to a transparent light-yellow filtrate. Finally, the product was dried as stated above. It must be noted, however, that this anion metathesis is not expected to yield quantitative chloride-to-acetate exchange.

**Synthesis of Cu\(_{3-x}\)P (0.1 < x < 0.7).** In a glovebox, stoichiometric amounts of copper and P\(_{\text{white}}\) (total mass ≈ 200 mg) were carefully weighed directly into a glass flask containing a magnetic stirring bar. The starting materials were covered with 1300 mg of [P_{66614}][Cl] (7.5 mmol) and the flask was subsequently sealed with a glass stopper. The flask was rapidly heated to 200 °C in an oil bath and stirred vigorously for 24 h. After cooling to room temperature, the mixture was dispersed in ethanol using an ultrasonic bath and subsequently centrifuged. The solvent was then decanted and discarded. The washing procedure was repeated three times. The resulting fine greyish powder was dried under ambient conditions. To avoid surface oxidation, the material was alternatively washed in a glovebox with dried dichloromethane, provided by a solvent purification system (M. Braun), and dried under argon atmosphere. Cu\(_{3-x}\)P is obtained in yields of 99+ %.

**Crystal Growth of Cu\(_{3-x}\)P.** Single-crystals suitable for crystal structure determination were obtained by annealing polycrystalline Cu\(_{3-x}\)P at high temperature. A sample of Cu\(_{3-x}\)P (~ 100 mg) with the nominal composition of Cu\(_{3-x}\)P was synthesized and dried under argon as described above. In a glovebox, it was transferred into a silica tube, which had previously been dried under dynamic vacuum at 1000 °C for 1 h. After sealing the silica tube under vacuum, the sample was annealed at 900 °C for 2 weeks in a chamber furnace. Adding a small amount of I\(_2\) notably accelerated the recrystallization process. The resulting solid was gently ground to obtain shiny black polyhedra of Cu\(_{3-x}\)P. Energy dispersive X-ray (EDX) spectroscopy showed no iodine in the Cu\(_{3-x}\)P crystals.

**Elemental Analysis.** The Cu\(_{3-x}\)P samples were dissolved in aqua regia with the assistance of microwave irradiation and subsequently diluted with water. The determination of the Cu/P ratio was performed with inductively coupled plasma optical emission spectroscopy (ICP-OES) using a 5100 SVDV (Agilent). The measurement of every sample was independently repeated at least three times.

**Powder X-ray Diffraction.** Powder X-ray diffraction (PXRD) was performed at 296(1) K on an X'Pert Pro MPD diffractometer (PANalytical) equipped with a curved Ge(111) monochromator using CuK\(_\alpha\), radiation (\(\lambda = 154.056\) pm). Le Bail analysis was performed with the software package Jana2006\(^{42-44}\) using an internal LaB\(_6\) standard (660b, National Institute of Standards and Technology, USA).

**Scanning Electron Microscopy.** The dried as-prepared samples were dispersed in ethanol, and a few drops were placed on a polished silicon wafer. After evaporation of the ethanol, the wafer was fixed on a sample holder with a graphite pad. Scanning electron microscopy (SEM) was...
performed by using an SU8020 (Hitachi) instrument with a triple detector system for secondary and low-energy backscattered electrons ($U_e = 3 \text{kV}$).

**Energy-Dispersive X-ray Analysis.** The compositions of the samples were semi-quantitatively analyzed with EDX spectroscopy ($U_e = 20 \text{kV}$) using an SU8020 (Hitachi) instrument equipped with a Silicon Drift Detector X-MaxN (Oxford Instruments). Samples were embedded into an epoxy polymer (Epotin™ 2, Buehler) under vacuum. The pellets were then wet-ground with a MetaServ 250 (Buehler, SiC grinding paper) and subsequently polished with a fleece on the same machine using an alumina suspension (MasterPrep™, Buehler). After coating the polished pellets with carbon, they were fixed on the sample holder with a graphite pad. With respect to the preparation method, the elements C, O and Cl (both of the polymer and the coating) as well as Al (from the polishing suspension) were omitted in EDX quantifications.

**Crystal Structure Determination.** Suitable single-crystals (shiny black polyhedra) were selected with the help of a light microscope in a glovebox. The crystals were attached to 0.2 mm glass capillaries and sealed in larger ones of 0.5 mm diameter to prevent oxidation during the measurements. Temperature dependent screening measurements and complete data sets were recorded on a SuperNova diffractometer (RigakuOxford Diffraction) using graphite-monochromated MoKα radiation ($\lambda = 71.073 \text{ pm}$) with a microfocus source. Lorentz factor, polarization, and multi-scan absorption corrections were applied. The structure at 300 K ($\text{Cu}_2.79(2) \text{P}$) was solved by charge-flipping; atomic coordinates of the low-temperature phases at 200 K (Cu$_{2+6+}$P ($h\text{P}24$)) was solved by charge-flipping; atomic coordinates of the low-temperature phases at 200 K (Cu$_{2+6+}$P ($h\text{P}24$)) and 80 K (Cu$_{2+6+}$P ($t\text{P}288$)) were developed by group-subgroup relations, cf. discussion. Structure refinements were performed with Jana2006. Graphical representations of the structures were drawn with the program Diamond. Crystallographic data of the three polymorphs is summarized in Table S6, the respective atom parameters are stated in Tables S7 – S9. Further details about the crystal structures can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository numbers CSD-434583 (Cu$_{2+6+}$P ($h\text{P}24$), 400 K), CSD-434584 (Cu$_{2+6+}$P ($h\text{P}24$), 300 K), CSD-434585 (Cu$_{2+6+}$P ($h\text{P}66$), 200 K) and CSD-434586 (Cu$_{2+6+}$P ($t\text{P}288$)), 80 K).

**Nuclear Magnetic Resonance Spectroscopy.** Liquid samples were transferred into tubes with polytetrafluoroethylene valves (Deutero) in a glovebox. The tubes were evacuated and the valves were closed prior to the measurement. To avoid any solvation influences, dimethyl sulfoxide-d$_6$ was provided inside a sealed capillary in the NMR tubes as external lock. The liquid-state NMR experiments were performed using a Bruker AVANCE III HDX, 500 MHz Ascend spectrometer at 333 K. The $^3\text{P}$ NMR spectra were recorded at the resonance frequency of 202.45 MHz by using a 5 mm high-resolution CryoProbe Prodigy probe head. Solid-state magic angle spinning (MAS) NMR experiments were performed on a Bruker Ascend 800 MHz spectrometer using a double-resonance 1.3 mm MAS NMR probe operating at the resonance frequency of 323.9 MHz and the MAS frequency of 40 kHz. The chemical shifts were referenced externally to $\delta$(H$_2\text{PO}_4$; 85 %) = 0.00 ppm. For the determination of the chemical shift of signals in the $^3\text{P}$ MAS NMR spectra, the centers of gravity of the signals were used.

**Electron Spin Resonance.** For the characterization with electron spin resonance (ESR) spectroscopy, it was required to synthesize Cu$_{2+6+}$P without paramagnetic impurities. The material was therefore prepared with freshly reduced Cu (99.999 %) and the samples were washed and stored in a glovebox. The ESR experiments were carried out with a standard continuous-wave spectrometer at temperatures between 5 K and 300 K. We measured the power ($P$) absorbed by the sample from a transverse magnetic microwave field at X-band frequency ($\approx 9.4$ GHz) as a function of an external, quasi-static magnetic field ($B$). A lock-in technique (modulating the field with 0.5 mT at 100 kHz) was used to improve the signal-to-noise ratio, which yields the derivative of the resonance signal $dP/dB$.

**Electrical Resistivity and Hall Effect Measurements.** For the determination of the electronic transport properties, two samples with the compositions Cu$_{2+6+}$P and Cu$_{2+6+}$P were selected. The powders were checked for purity by PXRD and SEM, their compositions were determined by elemental analysis. The fine ground powders were compacted with spark plasma sintering (SPS) using an SPS-515 ET setup (Fuji Electronic Industrial) under a pressure of 100 MPa with the heating rate of 50 K-min$^{-1}$ to the final temperature of 350 °C, which was subsequently held for 10 min until the sample was cooled to RT. PXRD and SEM investigations proved the material to be unchanged after the SPS. Rods of about 8 mm length were cut from the pellets. Thin Pt wires (25 μm) were attached to the samples by spot welding. Resistivity ($\rho$) was measured in a conventional four-probe arrangement while for the Hall resistivity ($\rho_H$) a five-wire configuration was used. Measurements were performed using low-frequency alternating current in a measurement system PPMS 9 (Quantum Design, ACT option) with magnetic fields up to $B = 9$ T and temperatures between 2 K and 300 K. The transverse magnetoresistance $\rho(B)$ and the Hall resistivity $\rho_H(B)$ were measured at fixed temperatures. The $\rho_H(B)$ was found to vary linearly with field up to $\pm 9$ T.

**Heat Capacity Measurements.** For the heat capacity measurements, the SPS sintered sample with the composition of Cu$_{2+6+}$P was chosen. The sample was crushed and a thin platy piece (1.00 mm x 0.83 mm x 8.24 mm) was selected with the
help of a microscope. Heat capacity measurements were conducted on a 9T CFMS micro-chip calorimeter (Cryogenic Ltd.) using the a. c. method (f = 5 Hz, U = 0.8 V) with Apiezon N grease as thermal contact.

**Electrochemical Characterization.** To minimize the influence of a possible surface oxidation of Cu$_{3-x}$P, all samples for the electrochemical characterization were washed and handled exclusively under argon atmosphere in a glovebox. For the preparation of the electrodes, 80 wt.% of Cu$_{3-x}$P and 10 wt.% Super P (Timcal) were mixed in a stainless-steel shaker for 20 min at 25 Hz. The binder solution was prepared by dissolving 10 wt.% PVDF 1013 (Solvay) in N-methylpyrrolidone (NMP). Subsequently, 0.3 ml of the binder solution and 100 mg powder were mixed and sonicated for 30 min. After doctor blading onto a copper foil in a glovebox, the samples were pre-dried overnight at 80 °C. After cutting electrodes of 12 mm in diameter, the electrodes were again dried overnight at 80 °C under vacuum. The Swagelok cells were assembled in an argon-filled glovebox using a two-electrode configuration. Two glass fiber separators (Whatman) and 250 μL electrolyte were placed between a lithium metal disc (Chempur, 250 μm) as counter electrode and the copper phosphide as working electrode. A mixture of 1 M LiPF$_6$ in dimethyl carbonate/ethylene carbonate (1:1 v/v) (Selectilyte LP30, BASF) was employed as electrolyte. Electrochemical tests were conducted at a constant temperature of 25 °C in a climate chamber using a multichannel VMP3 potentiostat (BioLogic). Galvanostatic cycling with potential limitation (GCPL) was performed between 0.7 and 2.0 V vs. Li/Li$^+$ at a current density of 12 mA∙g$^{-1}$ (C/10 for differential capacity plots). The current density and the specific capacity were calculated based on the mass of copper phosphate.

**RESULTS AND DISCUSSION**

**Synthesis and material characterization.** The reaction of elemental copper with white phosphorus in [P$_{66614}$]Cl yielded a greyish powder of single-phase Cu$_{3-x}$P (0.1 ≤ x ≤ 0.7) according to PXRD (Figure 1) and SEM (Figure S1, Supporting Information). Elemental analysis confirmed that the final composition of the material is in accordance with the targeted nominal composition of the respective synthesis (Table S1, Supporting Information). It was observed that the pristine material is slightly more coarse-grained in comparison to the Cu$_{3-x}$P obtained from the syntheses with P$_{red}$ but can be easily ground to a fine powder. SEM imaging of the samples reveal agglomerated particles with an average size of approximately 50 μm (Figure 2, left). These particles consist of tiny intergrown platelets (Figure 2, right), which rationalizes the observation that the sample can be crushed easily. It was also found that the tendency of agglomeration increases with the ratio of starting material to IL; hence increasing the total mass of the starting materials whilst keeping the amount of IL constant lead to larger agglomerates (Figure S2, Supporting Information).

As discussed, the ionothermal synthesis of Cu$_{3-x}$P (x ≥ 0.1) from P$_{red}$ suffers from the formation of X-ray amorphous CuP$_2$ as a byproduct.$^{35}$ As shown in Figure 3, a sample of the nominal composition Cu$_{3-x}$P synthesized with P$_{red}$ exhibits a large amount of the amorphous CuP$_2$ as impurity, which appears dark relative to the Cu$_{3-x}$P main phase in SEM images captured with a back-scattered electron detector (BSE) and shows a notable difference in composition as evidenced by EDX spectroscopy.$^{35}$ In contrast, CuP$_2$ is not detectable if the synthesis is conducted with P$_{white}$ leaving all other reaction parameters unchanged. This finding is supported by the results of the solid-state $^3$P NMR experiments and the Le Bail fittings of the X-ray diffraction data. As reported recently, Cu$_{3-x}$P exhibits a composition dependent Knight shift, which is proportional to the change of the unit cell dimensions. Both can easily be used to track the change of the Cu$_{3-x}$P composition.$^{35-45}$ Comparing Cu$_{3-x}$P samples from P$_{red}$ and P$_{white}$ precursors with the same nominal composition reveals a significant downfield shift of the solid-state NMR signal and a smaller unit cell volume for all samples synthesized with P$_{white}$ (Figure 4). This indicates that Cu$_{3-x}$P samples

![Figure 1. PXRD patterns of Cu$_{3-x}$P from the reaction of Cu and P$_{white}$ in [P$_{66614}$],Cl with nominal compositions.](image)

![Figure 2. SEM micrographs of Cu$_{3-x}$P (after washing and drying).](image)
Figure 3. SEM (BSE) micrographs of Cu₃₋ₓP synthesized from a molar ratio Cu:P = 2.5:1 with P_red (left) and P_white (right). Bright areas: Cu₃₋ₓP; dark areas: CuP₂; black areas: organic polymer.

Figure 4. ³¹P MAS NMR spectra (left) and unit cell volumes fitted from the PXRD data (right) of Cu₃₋ₓP with different nominal compositions. Black symbols: samples synthesized with P_red. Blue symbols: samples synthesized with P_white. For detailed data see Table S2, Supporting Information.

obtained from reactions with P_white exhibit a higher Cu:P ratio than their counterparts synthesized from P_red because no phosphorus is consumed by the formation of the undesired phosphorus-rich CuP₂ impurity. The shapes of the ³¹P solid-state NMR signals of the Cu₃₋ₓP samples differ significantly depending on which allotrope of phosphorus was used as starting material. Cu₃₋ₓP synthesized from P_red exhibits narrow but asymmetric signals whilst samples obtained from P_white show broad isotropic signals. This broadening can most likely be attributed to the presence of Cu₃₋ₓP phases with slightly different compositions in one batch, pointing towards a high compositional homogeneity if the synthesis is conducted with P_red and rather low homogeneity if P_white is used. This is in agreement with the results of the EDX analysis. While the Cu₃₋ₓP from P_red shows a very homogenous composition across the sample,³⁵ we found the composition of different Cu₃₋ₓP crystallites varying slightly if P_white is used as indicated by a higher standard deviation of the average composition (Figure S3 and Table S3, Supporting Information). The copper-poor limit of Cu₃₋ₓP seems to be reached at x = 0.7 with the synthesis method presented in this work. This is, on the one hand, indicated by the ³¹P NMR shift, which does not change significantly beyond this composition. Additionally, fluctuations in the NMR shifts and in the lattice constants were found if Cu₃₋ₓP (x > 0.7) was targeted leading to poorly reproducible results, however, the exact reason for this behavior requires further studies. Attempts to synthesize Cu₃₋ₓP using P_white lead to the formation of CuP₂ impurities in the product (Figure S4 and Table S4, Supporting Information) as it was previously observed for the synthesis with P_red.

The impact of different phosphorus allotropes on the phase formation. Our results demonstrate that the co-formation of CuP₂ inevitably leads to copper-richer (i.e. phosphorus-poorer) Cu₃₋ₓP phases. Therefore, the key challenge for the synthesis of copper-deficient Cu₃₋ₓP is to suppress the CuP₂ formation. This applies not only to IL-
Figure 5. Mobilization of the discussed phosphorus allotropes in $[\text{P}_{666\text{Cl}}]$ at elevated temperatures as evidenced by NMR spectroscopy ($s = \text{solid; } l = \text{liquid}$).

![Diagram](image)

Figure 6. Scheme of the proposed mechanism of the Cu$_{3-x}$P and CuP$_2$ formation in $[\text{P}_{666\text{Cl}}]$.

Based syntheses at low temperatures, as similar phase relations have also been observed in high-temperature solid-state approaches. Our results suggest that under ionothermal conditions CuP$_3$ is effectively suppressed if P$_{\text{red}}$ is substituted by P$_{\text{white}}$, which should be attributed to their different allotrope structures and, consequently, their chemical properties. White phosphorus, which consists of P$_4$ molecules, is highly reactive (e.g. spontaneous ignition in air) and soluble in many organic solvents. White phosphorus, which consists of P$_4$ molecules, is highly reactive (e.g. spontaneous ignition in air) and soluble in many organic solvents. In contrast to that, the polymeric structure of P$_{\text{red}}$ is far less reactive, stable in air, and almost insoluble in a majority of common solvents. However, it must be considered that our ionothermal reactions are conducted at approximately 200 °C in an ionic liquid medium. It is therefore crucial to discuss the ways in which the phosphorus precursors are mobilized and changed under the impact of temperature and the IL.

At the reaction temperature $T_{\text{white}}$ is already molten ($T_m(\text{P}_{\text{white}}) = 44.1$ °C) and the P$_4$ molecules are partially dissolved in the IL as evidenced by NMR spectroscopy. This means, the P$_4$ molecules are homogeneously distributed within the reaction medium and diffusion is not rate-determining, especially if of the reaction mixture is continuously stirred. Extensive heating of P$_4$, on the other hand, initiates its polymerization to P$_{\text{red}}$ (Figure S5 and Figure S6, Supporting Information), hence decreasing the reactivity of the precursor. Vice versa, it was found that P$_{\text{red}}$ dissolves slowly as P$_4$ if heated inside the reaction medium, which consequently increases the reactivity of the precursor (Figure 5). It should be noted, that we only have experimental evidence for P$_4$ molecules as mobile species, but we cannot exclude the presence of larger fragments, e.g. phosphorus nanoparticles, which are currently not detectable with NMR spectroscopy undergone in this work.

These results demonstrate the impact of the reactivity of the different precursors on the phase formation of Cu$_{3-x}$P, which is mainly attributed to the rate mobile P$_4$ molecules are provided. Furthermore, we assume that these different reaction behaviors are also related to the crystal structures of Cu$_{3-x}$P and CuP$_2$. The crystal structure of Cu$_{3-x}$P hosts isolated P atoms (or $\text{P}^0$ ions if we consider the ionic limit) without P–P bonds, and the formation of the phase requires a consecutive splitting of the phosphorus precursors into “P” moieties at the reaction sites. This requires less energy when starting from P$_4$ molecules than from the polymeric phosphorus network of P$_{\text{red}}$, and we consequently assume that Cu$_{3-x}$P is preferably formed by P$_4$ molecules (Figure 6, path a).

On the other hand, the comparatively slow decomposition of P$_{\text{red}}$ creates a “bottle neck” effect in the reaction leading to considerable amounts of unreacted P$_{\text{red}}$ amongst the emerging Cu$_{3-x}$P particles. We assume that the presence of unreacted P$_{\text{red}}$ is causing the formation of CuP$_2$, as an extended covalent phosphorus network is found in the crystal structure of this phase, and it seems reasonable that CuP$_2$ is preferably formed if existing P–P bonds are available (Figure 6, path b). Moreover, it is known from the synthesis of polyphosphides that Cu$_{3-x}$P can be further phosphidized by P$_{\text{red}}$, which makes a reaction of Cu$_{3-x}$P with unreacted P$_{\text{red}}$ also probable (Figure 6, path c). The formation of CuP$_2$ at high P$_4$ concentrations, on the other hand, is reasonably explained by the aforementioned polymerization of P$_4$, which leads to the extended formation of P–P bonds. However, the rate of the CuP$_2$
formation in all these cases is limited due to slower solid-solid diffusions involved in these reactions, which may explain why Cu$_{3-x}$P nevertheless appears as the main phase.

The impact of the ionic liquid anion on the phase formation and the activation of phosphorus. The question remains what exactly the role of the IL is during Cu$_{3-x}$P formation and how it affects the proposed mechanism. Our previous results indicated that the cation does not have a notable influence on the phase formation. In contrast to that, the anions appear to have considerable impact. This can be clearly demonstrated if the Cu$_{3-x}$P synthesis is attempted in [P$_{66614}$][NTf$_2$] (Figure 7). The reaction of copper and P$_{red}$ in this IL is almost completely inhibited, evidenced by the detection of only elemental copper in the PXRD of the solid reaction product. Only the sample surface turns slightly dark during the reaction, most likely due to the formation of an X-ray amorphous phosphide coating. The reaction of copper with P$_{white}$ under the same conditions, on the other hand, leads to the formation of Cu$_{3-x}$P, although elemental copper is still present in the product.

Evidently, chloride ions facilitate the reaction and act as a mineralizer in the same way as has been reported for halide ions in the solid-state synthesis of the aforementioned polyphosphides. Apparently, this mineralizer concept can be transferred to the ionothermal syntheses as well. Similar findings have been already reported by the group of Dehnen, who demonstrated the positive impact of chloride on the crystallization of chalcogenidometalate superspheres.

Besides this mineralizing effect, high concentrations of chloride ions seem to prevent the formation of P–P bonds and, thus, inhibit the formation of the CuP$_2$ impurities. The latter effect is closely related to what we have discussed in the previous section. The phosphorus precursor has to be split at the reaction site, which obviously requires a certain amount of chloride as catalyst. If the P–P bonds are not sufficiently activated, the reaction follows the pathways for polyphosphides, ultimately leading to the formation of CuP$_2$.

Figure 7. PXRD patterns of the products of reacting Cu and P$_{red}$ (top, molar ratio Cu:P = 2.95:1) as well as Cu and P$_{white}$ (bottom, molar ratio Cu:P = 2.7:1) in [P$_{66614}$][NTf$_2$].

To further evaluate the differences of these two anions, a series of Cu$_{3-x}$P model reactions with P$_{white}$ were conducted in [P$_{66614}$]Cl/[P$_{66614}$][NTf$_2$] mixtures (Figure 8, left). The results of the PXRD measurements prove that already 5 mol% of chloride in the reaction mixture lead to a drastic improvement of the phase formation, in particular, no elemental copper can be detected in the products anymore. Remarkably, SEM investigations of the reaction products (Figure 8, right) reveal the formation of X-ray amorphous CuP$_2$, indicated by dark spots in the back-scattered electron images, which only vanish if 60 mol% or more chloride-anion IL is used in the reaction.

Figure 8. PXRD patterns (left) and SEM-BSE micrographs (right) of the products of reacting Cu and P$_{white}$ (molar ratio Cu:P = 2.7:1) in different [P$_{66614}$]Cl/[P$_{66614}$][NTf$_2$] mixtures. The molar ratios of the anions in these mixtures are given in the figure.

Conducting the same model reaction in [P$_{66614}$]Br/[P$_{66614}$][NTf$_2$] mixtures reveals the mineralizing effect also for bromide anions, although CuP$_2$ was found in the product already after reducing the bromide content in the reaction mixture to 80 mol% (Figure S7, Supporting Information). Hence, bromide seems less effective in activating P–P bonds.
The different reactivities of chloride, bromide and \([\text{NTf}_2]^-\) may be explained by their different nucleophilicity or Lewis basicity. \(P_4\), which is known for its electrophilic character, can readily be attacked by nucleophiles.49 This reactivity is, however, not limited to \(P_4\) but is also found for \(P_{\text{red}}\) where nucleophilic attacks on the phosphorus network lead to a cascade of disproportionation reactions and rearrangements. For example, \(P_{\text{red}}\) is degraded by \(K[\text{OEt}]\) and the polyphosphide anions \(P_{11}^-, P_{16}^-,\) and \(P_5^-\) are obtained.38 The nucleophilicity of dissolved anions, on the other hand, depends on the nature of the solvent. In protic solvents, the nucleophilicity of halide anions decreases in the series \(\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-\) due to the strong solvation of the smaller halide ions. In aprotic solvents, however, this trend is inverted and fluoride becomes the strongest nucleophile.59 This trend for aprotic solvents is in general also found for ILs, as demonstrated mainly for alkyl-substituted imidazolium compounds.60-62 The \([P_{66614}]^+\) cation was found to interact even less with anions than any imidazolium cation, owing to its increased steric hindrance and decreased potential to form hydrogen bonds.66 Regarding the different natures of the anions, chloride can be considered to be one of the strongest and \([\text{NTf}_2]^-\) one of the weakest nucleophiles within the commercially available ILs.60,62

The influence of different anions on the decomposition of red phosphorus has been tested, as the aforementioned decomposition yields \(P_4\) which can qualitatively be followed by NMR spectroscopy.38 Indeed, we found that the degradation of \(P_{\text{red}}\) upon heating in the IL under vacuum for several days is far less pronounced in \([P_{66614}]\[\text{NTf}_2]\) compared to \([P_{66614}]\[\text{Cl}\], evidenced by a smaller \(P_4\) signal in the \(^{31}P\) NMR spectrum (Figure 9, left). Moreover, SEM micrographs reveal the surface of \(P_{\text{red}}\) to be strongly etched in \([P_{66614}]\[\text{Cl}\], as indicated by the rough surface of the red phosphorus particles (Figure 9, right). In contrast, the surface of \(P_{\text{red}}\) remains unaffected after being heated in \([P_{66614}]\[\text{NTf}_2]\), explaining the distinctively hindered \(\text{Cu}_{3.793}P\) formation in this IL. Notably, no differences were observed with NMR spectroscopy when \(P_{\text{red}}\) was heated in \([P_{66614}]\[\text{Br}\) or \([P_{66614}]\[\text{Cl}\]. However, the formation of \(\text{CuP}_2\) in the product after reducing the amount of \([P_{66614}]\[\text{Br}\) in the reaction mixture demonstrates the lower nucleophilicity of bromide compared to chloride.

These results suggest that the reactivity might be influenced or even tuned by other anions as well. However, the application of stronger nucleophiles in ILs is limited by the stability of the organic cation, especially at higher temperature.65 Nevertheless, we found that \(P_{\text{red}}\) can be degenerated by \([P_{66614}]\[\text{OAc}\) yielding a dark red-colored solution, which is caused by traces of the \([\text{P}_{66}^+]\) polyanions as evidenced by NMR spectroscopy (Figure S10, Supporting Information).

**Electrical transport properties.** \(\text{Cu}_{3.793}P\) with small \(x\) was found to be a metallic conductor at room temperature already several decades ago.31,64 We recently confirmed the metallic nature of this compound down to 4 K.35 However, due to a lack of high-quality data, we decided to reinvestigate the electronic transport properties and to extend our characterization to \(\text{Cu}_{x}P\) with lower copper content. The temperature and magnetic field dependence of the electrical resistivity \(\rho(B,T)\) and of the Hall resistivity \(\rho_{xy}(B,T)\) were determined for compacted polycrystalline samples of \(\text{Cu}_{1.793}P\) and \(\text{Cu}_{2.435}P\).
Both samples were found to exhibit metallic $p$-type conductivity with electrical resistivity values at room temperature of 100 and 140 $\mu\Omega\cdot$cm, respectively. Upon cooling (Figure 10), an anomalous decrease of the resistivity is observed to below 190 K ($\text{Cu}_{2.79(2)}\text{P}$) or 180 K ($\text{Cu}_{4.0(3)}\text{P}$) indicating a phase transition. The electric resistivity is lower below the phase transition (more pronounced for the copper-richer phase), suggesting a decrease of the scattering of the charge carriers. Upon heating, the anomalies in both samples are observed at slightly higher temperatures (Figure 10, inset left), hinting at a first order structural phase transition. The transition is accompanied by an anomaly of the heat capacity $C_p(T)$ at this temperature (for $\text{Cu}_{3.76(3)}\text{P}$, see Figure S13, Supporting Information).

The magnetoresistance is positive and small and increases with decreasing temperature. At $T = 2$ K it attains $+5.8\%$ in a field of 9 T. The Hall coefficient $R_{\text{H}}(T)$ (Figure S14, Supporting Information) as derived from the slopes of $\rho_{xy}(B,T)$ is very similar for both compositions and varies weakly with temperature between $1\cdot10^{-9} \text{m}^3\text{C}^{-1}$ and $2\cdot10^{-9} \text{m}^3\text{C}^{-1}$. Within a one-band model this indicates hole concentrations between $6\cdot10^{11}$ cm$^{-3}$ at $T = 2$ K and $3\cdot10^{12}$ cm$^{-3}$ at $T = 300$ K, respectively. An impact of the structural phase transition on the carrier concentration is not visible in the Hall coefficient data, which is, however, also due to the small number of data points.

$\text{Cu}_{3.76(3)}\text{P}$ samples with different compositions were probed by ESR spectroscopy to check if an increasing amount of copper vacancies is mirrored in a partial oxidation of some Cu ions to Cu$^{2+}$. In accordance with the metallic conductivity we found no evidence for Cu$^{2+}$ in the X-band ESR spectra in the range of 300 K to 5 K (Figure S15, Supporting Information). Thus $\text{Cu}_{3.76(3)}\text{P}$ probably adopts the variable composition by creating itinerant charge carriers. In this context we must admit, though, that Cu$^{2+}$ cannot always be detected at the X-band frequencies due to spin-phonon interactions.

Temperature-dependent structure investigations.
Structural phase transitions of $\text{Cu}_{3-x}\text{P}$ below ambient temperature, as indicated by the resistivity and Hall measurements, have not yet been reported in literature. Thus, single crystals were grown to investigate the low temperature polymorphs.

Temperature-dependent diffraction data indicated the presence of two low-temperature phases (Figure S16, Supporting Information). For that, diffraction images were taken in steps of 10 K and complete data sets were recorded at 400, 300, 200, 100, and 80 K. The reinvestigation of the crystal structure at 400 K and 300 K confirms the reported Na$_3$As-type structure in the hexagonal space group $P6_c\text{m}$ (no. 185) with lattice parameters $a = 693.5(1)$ pm and $c = 713.0(1)$ pm (at 295 K) and six formula unit per unit cell. According to its Pearson symbol we call this polymorph $\text{Cu}_{3.76(3)}\text{P} (hP24)$ in the following.

$\text{Cu}_{3.76(3)}\text{P}$ forms a three-dimensional network structure with Cu–P distances between 232 pm and 249 pm and relatively short Cu–Cu distances of 255 pm to 273 pm. Both, Cu–Cu distances and Cu coordination numbers (Table S5, Supporting Information) bear a resemblance to typical intermetallic phases, like AuCu$_3$. The phosphorus atom exhibits an unusual high coordination number of 11.

For simplicity, the structure can formally be divided in two different layers that alternate along the $[001]$ direction. Slightly puckered honeycomb nets are formed by Cu$_1$, Cu$_2$ (Wyckoff site $2a$ and $4b$, respectively) and phosphorus atoms. The Cu$_3$ and Cu$_4$ atoms (Wyckoff sites $6c$) form a strongly corrugated honeycomb net, topologically resembling the structure of grey arsenic (Figure 11). In agreement with de Trizio et al., only the latter Cu positions were found to be partially occupied (Table S7, Supporting Information).
As visible from Figure 11, Cu3 and Cu4 atoms have large displacement parameters in the hexagonal $ab$-plane whereas the displacements of Cu1 and Cu2 atoms are conspicuous along [001]. The conventional refinement with anisotropic displacement parameters taking the statistical copper vacancies on the Cu3 and Cu4 positions into account resulted in reasonable $R$-values but exhibited large atomic displacement values for all Cu atoms and two pronounced peaks in the difference Fourier maps close to the Cu1 and Cu2 positions. The displacement parameters of all Cu atoms are elongated, those of Cu1 and Cu2 along [001], Cu3 and Cu4 in the $ab$-plane (Figure 11). The extrapolation of the principal mean square displacement parameters to $T = 0$ K indicates mainly dynamic contributions so that an anharmonic refinement with up to 4th rank tensors were considered. To minimize correlations, tensor components were set to zero if the refined parameters were within a standard uncertainty of 3σ. As a result, the $R$-values dropped considerably and the difference Fourier map became featureless (Table S6, ESIF). The displacement and occupational parameters of P are unsuspicious. The occupations of the Cu3 and Cu4 positions refined to 88(1)% and 90(1)% respectively, leading to a composition Cu$_{3.96}$P in good agreement to the initial composition of the Cu$_{3.76}$P powder used for growing the single crystals. It should also be noted, that (twin) refinements in subgroups of $P6_5$cm without c-glide planes ($P6_3$, $P3m1$, etc.) do not lead to smooth Fourier maps and incompressible displacement parameters.

Upon cooling below 260 K additional reflections indicated a doubling of the hexagonal $a$ and $b$ lattice parameters (Figure S16, center, Supporting Information). As the symmetry of the diffraction image and the reflection conditions remain unchanged, the cell enlargement can be described by an isomorphic symmetry reduction of index 4 and a starting model for the this superstructure was established using the group-subgroup formalism starting from the Cu$_{3.76}$P ($hP24$) structure model (Figure S17, Supporting Information). The resulting low-temperature structure is called Cu$_{3.96}$P ($hP96$) in the following.

Noticeably, the Wyckoff positions of Cu1 and Cu2 of the Cu$_{3.96}$P ($hP24$) structure split into two non-equivalent sites in the low-temperature Cu$_{3.96}$P ($hP96$) structure and the P, Cu3, and Cu4 positions split into three sites each.

The Cu$_{3.96}$P ($hP96$) structure model displays similar large and elongated displacement parameters for the Cu atoms so that an anharmonic refinement was performed again. The main difference between Cu$_{3.76}$P ($hP24$) and Cu$_{3.96}$P ($hP96$) structures is, however, that the Cu deficit accumulates on one copper site in the low-temperature polymorph Cu$_{3.96}$P ($hP96$): the refined occupancy for this position, Cu3a, is only 25(1)% whereas all other Cu position are fully occupied within a 3σ uncertainty. In other words, a rearrangement of vacancies in the Cu substructure occurs upon cooling (Figure 12).

The composition was computed to Cu$_{3.86}$P for the Cu$_{3.96}$P ($hP96$) structure. The coordination polyhedra and interatomic distances of Cu3a (occupancy 25%) and Cu3b (fully occupied), both derived from Cu3 in the Cu$_{3.96}$P ($hP24$) structure and adopting the same site symmetry $m$ (Wyckoff site 6c), are hardly distinguishable. As a main difference, Cu3a exhibits four short Cu-Cu distances of less than 250 pm, whereas for Cu3b, all Cu-Cu distances are larger than 260 pm (Figure S19, Supporting Information).

![Figure 11. The Cu$_{3.96}$P ($hP24$) crystal structure (300 K data). The ellipsoids represent 90% probability.](image)

Upon cooling below 190 K a second structural reorganization takes place as evidenced by additional satellite reflections at slightly incommensurate positions along $c^*$ (Figure S16, right, Supporting Information). To establish a first structure model of this second low-temperature polymorph, the satellites were indexed using a modulation wave vector $q = (0, 0, 0.31(1))$. Additional diffuse streaks running between the reflections along the
l-direction were ignored. A starting model was created in the superspace group \( P6_3cm(00\overline{7})000 \) (no. \( 185.1.24.1 \))\(^{20} \) by taking the atomic positions of the \( \text{Cu}_3\text{P} (hP96) \) structure model as average structure. The final refinements were performed using the commensurate option with a threefold c-axis resulting in the 3D space group symmetry \( P31m \). The resulting structure is thus called \( \text{Cu}_3\text{P} (tP288) \) in the following. One harmonic positional modulation wave for all atom positions and for the displacement parameters were refined together with one harmonic wave for the occupation parameters of \( \text{Cu}_3 \). The electron density distribution around the atomic domain of \( \text{Cu}_3 \) is clearly disrupted along the modulation direction, mirroring the occupational modulation (Figure 13).

As a consequence, the resulting puckered grey As-like \( \text{Cu} \) exhibit vacancies in some heights, whereas others are not affected by the positional modulation (Figure 14). In layers with vacancies, the response of the surrounding atoms in terms of positional modulations is much stronger than in fully occupied layers.

**Figure 13.** Fourier maps (\( F_0 \)) around \( \text{Cu}_3 \) of the \( \text{Cu}_3\text{P} (tP288) \) structure indicating the occupational modulation (left) and \( \text{Cu}_2 \) with a strong displacement (right); contour lines in steps of \( \pm 0.5 \) \( e\cdot\text{Å}^-3 \), thick black lines represent the calculated atomic positions.

**Figure 14.** Impact of the \( \text{Cu} \) modulation on the As-like \( \text{Cu} \) substructure of \( \text{Cu}_3\text{P} (tP288) \).

Additionally, \( \text{Cu}_2 \) exhibits a strong positional modulation along the c direction, which may also be interpreted as two \( \text{Cu} \) positions with alternating occupational modulations. \( \text{Cu}_2 \) is generated from \( \text{Cu}_2 \) of the \( \text{Cu}_3\text{P} (hP24) \) structure in the course of the symmetry reductions, which was the atom with the largest displacement parameters along [001] in the \( \text{Cu}_3\text{P} (hP24) \) phase. This is probably due to a certain amount of static disorder underlying the dynamic effects, i.e. local situations where \( \text{Cu}_2 \) is located at slightly different z-positions with respect to the plane of the phosphorus atoms.

Considering the omitted diffuse intensities, the refinements converged to acceptable \( R \)-values for the main reflections and a featureless difference Fourier map. The refined composition of \( \text{Cu}_{2.6(0)}\text{P} \) is in reasonably good agreement with the results of the \( \text{Cu}_{3}\text{P} (hP96) \) and \( \text{Cu}_{3.3}\text{P} (hP24) \) refinements.

The phase transitions are fully reversible. Heating the crystal reveals the same diffraction images and structure models as observed before and during the cooling procedure.

To conclude the crystal structure results, we were able to confirm the proposed copper depleted sites in the \( \text{Cu}_{3}\text{P} (hP24) \) structure experimentally. Atomic displacement parameters of the \( \text{Cu} \) atoms indicate a considerable thermal motion. Upon cooling, two polymorphs were discovered that show substantial redistribution of the copper vacancies coupled to a subtle reorganization of the copper partial structure.

**Electrochemical characterization.** \( \text{Cu}_3\text{P} \) has been intensively studied as anode material for lithium ion batteries since the beginning of the 21\(^{\text{th}} \) century, primarily because its volumetric capacity exceeds graphite by a factor of three.\(^{10-14} \) This advantage initiated a series of detailed mechanistic studies of the \( \text{Cu}_3\text{P} \) reaction with lithium.\(^{14,15,40,71-73} \) The following discussion is based on the most recent study of the mechanism with \( \text{in situ} \) \( ^{3}\text{P} \) and \( ^7\text{Li} \) NMR spectroscopy by Poli et al.,\(^{15} \) which also nicely links in the results of the previous PXRD studies.\(^{46,71} \)

Based on this recent investigation, copper-rich \( \text{Cu}_3\text{P} \) reacts with lithium to form three different products, depending on the applied electrochemical potential: (a) \( \text{Li}_x\text{Cu}_2\text{P} \) (crystal structure unknown); (b) \( \text{Li}_x\text{CuP} \) and (c) \( \text{Li}_x\text{P} \). The chemistry behind this substitution can be understood by comparing the known crystal structures in this system (Figure 15). Formally, \( \text{Li}_x\text{CuP} \) is obtained if the \( \text{Cu}^+ \) ions on the \( \text{Cu}_3 \) and \( \text{Cu}_4 \) positions (Wyckoff site \( 6c \)) of \( \text{Cu}_3\text{P} \) are substituted by \( \text{Li}^- \). These \( \text{Cu} \) positions, which are located between layers of buckled \( [\text{CuP}]^- \) hexagonal nets (including \( \text{Cu} \) and \( \text{Cu}_2 \) positions), were also identified by our crystal structure investigations to host the \( \text{Cu} \) vacancies of \( \text{Cu}_3\text{P} \). Following this argument, the structurally unknown \( \text{Li}_x\text{Cu}_3\text{P} \) should consist of an intermediate structure, where the \( \text{Cu} \) atoms between the nets are only partially exchanged by \( \text{Li}^- \). Upon further lithiation of \( \text{Li}_x\text{CuP} \), the \( \text{Cu} \) atoms of the hexagonal nets are fully substituted, leading to the formation of \( \text{Li}_x\text{P} \).
Lithiation of Li$_2$CuP, however, requires a more complex reorganization of the crystal structure, which was also found to be disadvantageous in regards to cycling stability.\textsuperscript{14} Subsequently, the cut-off potential in our experiments was set to 0.7 V, to prevent the formation of Li$_2$P and to enable a reversible cycling between Cu$_{3-x}$P and Li$_2$CuP. Thus, the following processes should take place:

\begin{align*}
\text{Cu}_{3-x}\text{P} + 0.2 \text{Li} & \rightarrow \text{Li}_{0.2}\text{Cu}_{2.8}\text{P} + 0.2 \text{Cu} \text{ (process 1)} \\
\text{Li}_{0.2}\text{Cu}_{2.8}\text{P} + 1.8 \text{Li} & \rightarrow \text{Li}_x\text{CuP} + 1.8 \text{Cu} \text{ (process 2)}
\end{align*}

\begin{align*}
\text{Li}_x\text{CuP} + x \text{Cu} & \rightarrow \text{Li}_x\text{Cu}_{x+1}\text{P} - \text{Cu}^0 + x \text{Li} \text{ (process 2*)}
\end{align*}

We found that electrodes produced from Cu$_{3-x}$P with various compositions differ significantly (Figure 16). The reaction steps proposed in the mechanism stated above can be accurately assigned to material of a Cu$_{3.05}$P composition. The differential capacity plots (Figure 16, left) obtained for this material matches those reported in literature.\textsuperscript{10,11,14,46} This supports the assumption, that the stoichiometric Cu:P = 3:1 starting ratio in the syntheses of these material resulted in the formation of copper-rich Cu$_{3-x}$P. In contrast to that, some features of the lithiation reactions are found less pronounced or missing for Cu$_{3-x}$P with lower copper content.

Process 1, assigned to the formation of Li$_{0.2}$Cu$_{2.8}$P, corresponds to the signal found at 0.89 V for Cu$_{3.05}$P. Following the proposed mechanism, this phase should not be formed with Cu$_{2.5}$P and Cu$_{2.3}$P, as the copper content of these compounds is below that of the targeted phase. This is indeed proven by the absence of the corresponding signal at 0.89 V. Instead, a broad signal is observed for the copper-deficient compounds, which might be caused by small amounts of copper-rich phases present in the investigated samples. Upon further lithiation, the Li$_x$CuP formation (process 2) is observed for all materials at 0.81 V. The delithiation of Li$_x$CuP (process 2*) is found at 1.05 V for all materials, as expected from the results of the first discharge. In the following reaction, further delithiation (process i* and o*) is only observed for Cu$_{2.09}$P at 1.09 V and 1.26 V, respectively. Apparently, there is not enough copper available to form copper-rich phases, which agrees well with the absence of process 1 during the first discharge.
Our results clearly indicate that copper-rich and copper-deficient Cu$_{3-x}$P reacts differently with lithium. These differences lead to very interesting results in terms of the specific capacity and the cycle stability. The initial capacity of Cu$_{3-x}$P during the first discharge is about 70% higher than the capacity of Cu$_{2.95}$P, vice versa the cycling stability of Cu$_{2.95}$P is much better (Figure 16, right). The performance of our cells can, however, not compete with the excellent results reported by Stan et al. This behavior is most likely caused by the coarse-grained material used in our work which could probably be optimized, but was not in the scope of this work. As the higher capacity of the copper-deficient material is counterintuitive to the mechanism discussed in literature, a different lithiation pathway of the copper-deficient material needs to be considered, which should be investigated by more elaborated experiments in the future. Our results, however, suggest that the optimal composition of Cu$_{3-x}$P for battery applications should not be too close to the stoichiometric Cu$_3$P composition to enable a high specific capacity and reversible cycling.

CONCLUSION

In summary, we have developed a convenient approach to precisely synthesize different Cu$_{3-x}$P (0.1 < x < 0.7) phases in high yields with excellent reproducibility. Our mechanistic investigations reveal the different mineralizing and activating properties of halide anions in ionic liquids. This is in particular interesting for the development of ionothermal approaches for other inorganic materials, as rules for choosing appropriate ionic liquids are only rarely found in literature. The physical characterization of the Cu$_{3-x}$P shows a composition-dependent change in the electric conductivity, which is accompanied by a change of the Hall coefficient. The low-temperature phase transition indicated by the non-linear behavior of the electric properties was followed by single-crystal X-ray diffraction elucidating two hitherto unknown Cu$_{3-x}$P polymorphs. Our analysis of the structural relations of these polymorphs confirms the Cu vacancy accumulation between the Cu/P-layers as suggested in literature. The application of different Cu$_{3-x}$P phases as anode material in lithium ion batteries evidences a composition-dependent change in the lithiation pathway, which might be used to further optimize these devices.

SUPPORTING INFORMATION

SEM images of Cu$_{3-x}$P, EDX data of Cu$_{3-x}$P, data of elemental analysis of Cu$_{3-x}$P, results of lattice parameter fitting, solid-state NMR data of Cu$_{3-x}$P, photography and solid-state NMR spectra of polymerized P$_{\text{white}}$, PXRD data of Cu$_{3-x}$P, liquid-state NMR spectra of P/IL mixtures, resistivity and Hall data of Cu$_{2.79}$P and Cu$_{2.43}$P, heat capacity data of Cu$_{2.79}$P, ESR spectra of Cu$_{3-x}$P, crystallographic data, voltage profiles of Cu$_{3-x}$P. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: michael.ruck@tu-dresden.de

Author Contributions

All authors have given approval to the final version of the manuscript.

Funding Sources

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the Priority Program SPP 1708. J.J.W. thanks the DFG for funding a Rigaku Oxford Diffraction SuperNova system with a dual source (INST 260/618-1).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We would like to thank Dr. F. Haarmann for helpful discussions of the solid-state NMR results. We gratefully acknowledge Dr. G. Auffermann (MPI CPFS, Dresden) for elemental analysis, Dr. I. Veremchuk (MPI CPFS, Dresden) for SPS and V. Charbonneau (IFW, Dresden) for experimental assistance.

ABBREVIATIONS

IL, ionic liquid; P$_{\text{red}}$, red phosphorus; P$_{\text{white}}$, white phosphorus; [P$_{6604}$], trihexyltetradecylyphosphonium; [NTf$_2$][bis(trifluoromethylsulfonyl)imide]; EDX, energy dispersive X-ray; PXRD; powder X-ray diffraction; SEM, scanning electron microscopy; BSE, back-scattered electron; ICP, inductively coupled plasma; OES, optical emission spectrometry; MAS, magic-angle-spinning; ESR, electron spin resonance; SPS, spark plasma sintering; NMP, N-methylpyrrolidone.

REFERENCES


Insert Table of Contents artwork here