

Low Temperature Synthesis of Amorphous FeP₂ and use as Anodes for Li-Ion Batteries

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Supporting Information

General Experimental Information

All manipulations were carried out under inert atmosphere with the rigorous exclusion of air and moisture. Iron(III) chloride and lithium bis(trimethylsilyl)amide were purchased from Sigma-Aldrich and used without further purification. Tetrahydrofuran and hexanes were purchased from Fischer Scientific and distilled from Na/benzophenone prior to use. FTIR analysis was performed on a Thermo Nicolet Avatar 330 spectrometer. PXRD analysis was performed on a Bruker D8 diffractometer equipped with a Ge monochromated Cu K_α source. SEM images were collected with a Zeiss Supra 40 VP scanning electron microscope.

Synthesis of amorphous FeP₂

A solution of Fe(N(SiMe₃)₂)₃ (5.20 g, 9.68 mmol) in THF (100 mL) was treated with PH₃ (25 PSI) in a Fischer-Porter bottle (12 oz.) and the reaction mixture heated at 100 °C while stirring (2 h). The mixture was allowed to cool to room temperature and unreacted PH₃ removed under vacuum. The product was isolated as a black powder via centrifugation. It was washed twice with THF and dried under vacuum. Yield: 1.04 g (91%)

Electrochemical Characterization

Electrochemical performance of FeP₂ was tested using the standard CR2032 coin cell. The cathode was made from a mixture of 75 wt% FeP₂, 15 wt% Super P ® Li and 10 wt% Polytetrafluoroethylene (PTFE) that was dissolved in 7 drops of amyl acetate and rolled into a thin sheet from which circular pellets of usually 5 mg were punched, in a glovebox under argon. Coin cells were assembled with lithium metal as the anode and Celgard® as the separator

saturated in 1M LiPF₆ in 1:1 ethylene carbonate (EC)/ diethyl carbonate (DEC) as the electrolyte. The cells were set to rest for 6 hours before electrochemical testing to ensure complete absorption of electrolyte into the electrode. Discharge/charge experiments were then carried out on a Arbin BT2000 battery tester at a rate of 0.1 C with a potential window between 2.0 and 0.25 V versus Li/Li⁺.

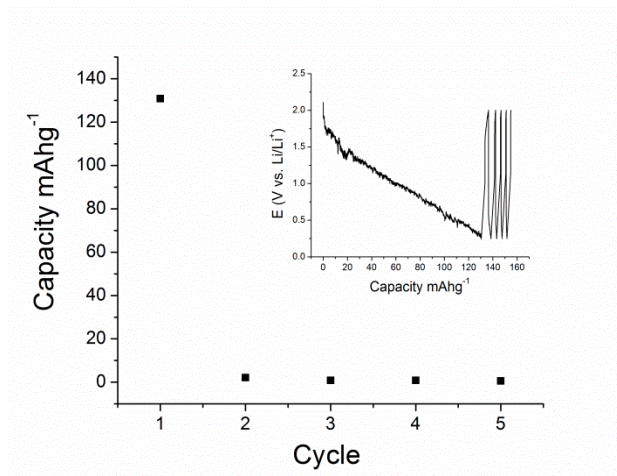


Figure S1. Discharge capacities for the first 5 cycles of air exposed, amorphous FeP₂. Inset is the corresponding discharge/charge plot at 0.1C.

XPS Analysis

All x-ray photoelectron spectra were obtained using a Kratos AXIS Ultra spectrometer equipped with a monochromatized Al K α source, hybrid optics, and a delay line detector coupled to a hemispherical analyzer. The analysis chamber base pressure was typically 2×10^{-9} Torr. All spectra were recorded using a single sweep with a spot size of 300 μm x 700 μm . Survey scans were collected from 0–1200 eV with a pass energy of 80 eV, step size of 1 eV, and a dwell time of 250 ms. The high resolution component spectra were collected with a pass energy of 20 eV, step size of 0.1 eV, and a dwell time of 4000 ms. All binding energies were referenced to the adventitious carbon line (C 1s, 284.8 eV) and charge neutralization was applied during all acquisitions. All samples were prepared in a nitrogen filled glove box and transported directly to the spectrometer using a dedicated interface for transporting air sensitive samples built at the Surface Analysis Laboratory of the Texas Materials Institute (TMI) at UT-Austin. The design of the interface contains a set of built-in figures of merit that were used to verify that samples were not exposed to traces of oxygen and water during transport. Details of the design of the interface

will be published elsewhere.¹ Casa XPS analysis software was used for stoichiometry determination of the samples and Kratos sensitivity factors used for each element of interest.

Surface analysis of the as prepared active material by XPS was consistent with the formation of an iron phosphide²⁻⁵ (Fe 2p_{3/2} BE = 707.8 eV, P 2p_{3/2} BE = 129.4 eV). In addition, surface oxidation was observed as previously reported for bulk FeP₂⁶, with broad peaks of slightly higher binding energy in both the Fe 2p and P 2p regions (Fe 2p_{3/2} BE = 710.0 eV, P 2p BE = 133.1 eV) as well as the presence of an intense O 1s peak (O 1s BE = 531.7 eV). The observed surface phosphorous to iron ratio was 6.88:1 for total atomic content, with 5.33:1 for the components assignable to the iron phosphide.

Table S1. Observed binding energies for Fe 2p, P 2p, and O 1s components from XPS analysis of unexposed amorphous FeP₂.

Component	Binding Energy (eV)
Fe 2p _{3/2} (Fe-P)	707.8
Fe 2p _{1/2} (Fe-P)	720.1
Fe 2p _{3/2} (Fe-PO)	710.0
Fe 2p _{1/2} (Fe-PO)	723.4
P 2p _{3/2} (Fe-P)	129.4
P 2p _{1/2} (Fe-P)	130.4
P 2p (Fe-PO)	133.1
O 1s	531.7

Analysis of Fe:P Ratio

The Fe:P ratio of the bulk material was determined slowly adding concentrated aqua regia (1 mL) to an ampule containing the iron phosphide (0.3024 g) in a liquid nitrogen bath. The ampule was sealed via rotoflow valve and allowed to warm slowly to room temperature. The ampule was again submerged in liquid nitrogen and an additional aliquot of aqua regia (1 mL) added. After slowly warming to room temperature, the excess gas pressure was carefully released. The sample solution was analyzed via ICP-OES (Applied Analytical Inc., Austin Texas).

References

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