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Morphology-Directed Synthesis of LiFePO_4 and LiCoPO_4 from Nanostructured $\text{Li}_{1+2x}\text{PO}_{3+x}$

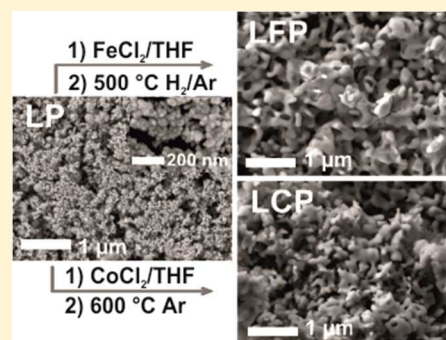
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Supporting Information

ABSTRACT: A LiPO_3 -type nanostructure has been developed using a simple microwave approach at temperatures as low as 200 °C. This phase presents an ideal architecture for the morphology-directed synthesis of the olivine-type phases LiFePO_4 and LiCoPO_4 , through a simple and scalable solution-based technique. Pure and carbon-composited olivine phases of interconnected nanoparticulate morphologies display excellent performance at high rates (up to 20 C) over 500 cycles in Li-ion battery cells.



INTRODUCTION

Olivine-type LiMPO_4 phases present excellent candidate cathode materials for sustainable and scalable lithium ion (Li-ion) batteries. Their high thermal safety, associated with strong P–O covalent bonding in the olivine structure, their excellent Li-reversibility as demonstrated for phases such as LiFePO_4 , and their ability to offer a range of operating voltages (e.g., 3.5 and 4.8 V vs Li^+/Li for LiFePO_4 and LiCoPO_4 , respectively) all present considerable advantages.^{1,2} While in pristine form the poor intrinsic ionic and electronic conductivities of these materials limit electrochemical performance, this performance can be greatly improved by particle-size reduction, carbon coating, and surface modifications.^{3–6} Reducing the particle size of LiFePO_4 , for example, enables high-rate cycling,⁷ attributed to shorter Li-ion path lengths and the formation of a nonequilibrium solid solution phase that inhibits the structural rearrangements typically related to phase transformations during cycling.^{8,9} However, nanosizing may adversely affect the tap density and volumetric energy density of electrode materials. To mitigate these effects, porous materials and extended nanostructured architectures have been recently developed through template-assisted and solvothermal syntheses.^{10–14} Challenges arise with low-temperature solvothermal methods whereby electrochemical performance can be compromised due to the presence of antisite defects in the crystal structure (i.e., appreciable transition-metal occupancy on the Li sites, leading to blocking the 1D Li-ion pathways in the structure).^{15,16} Subsequent postannealing treatments at high temperatures can alleviate this, but typically leads to undesirable particle growth. In this report, we present a new, facile preparation of LiMPO_4 and LiMPO_4/C ($M = \text{Fe}$ and Co) nanoarchitectures engineered

through a morphology-directed synthesis from a nanostructured LiPO_3 -type precursor. These cathode materials retain porous, extended nanostructured morphologies at temperatures up to 500–600 °C, retaining excellent electrochemical properties.

LiPO_3 is conventionally obtained either in a polycrystalline form through high-temperature solid-state reactions or in the form of $50\text{Li}_2\text{O}-50\text{P}_2\text{O}_5$ glass.¹⁷ The material crystallizes in a monoclinic unit cell, characterized by infinite linear chains of metaphosphate groups.^{18,19} Previously, LiPO_3 was reported by Talebi-Esfandarani et al. as a precursor to olivine LiFePO_4 by reaction with iron ore concentrates in graphite crucibles at 1100 °C.²⁰ Such high-temperature treatments can preclude morphology control, resulting in particle growth. Here, we developed a simple approach to synthesize LiMPO_4 phases ($M = \text{Fe}, \text{Co}$) from lithium-rich LiPO_3 at relatively low temperatures, allowing a high degree of control over the final morphology. Nanostructured LiPO_3 -type material is first obtained via the microwave heat treatment of a tetraglyme solution of phosphorus pentasulfide and lithium *tert*-butoxide at temperatures as low as 200 °C (see Supporting Information for experimental details). This colorless precipitate is subsequently dispersed in a solution containing either FeCl_2 or CoCl_2 , followed by solvent evaporation and a final calcination step at 500–600 °C, to produce nanoarchitectures of LiFePO_4 and LiCoPO_4 .

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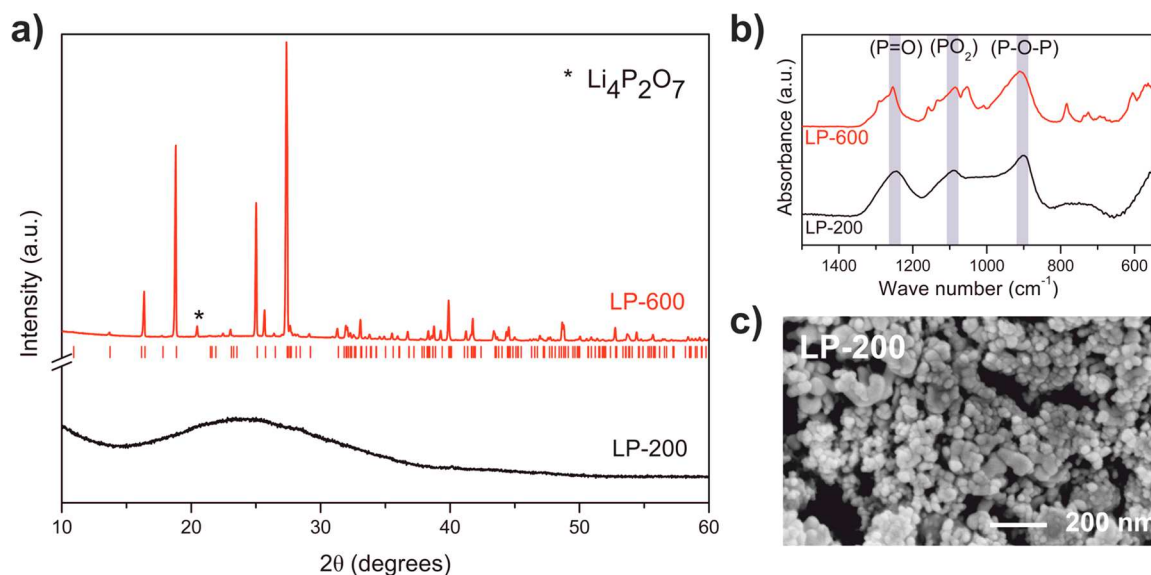


Figure 1. (a) XRD patterns of the LiPO_3 phase, synthesized at 200 °C (LP-200, black line) and after calcination at 600 °C (LP-600, red line), with markers shown for crystalline LiPO_3 .¹⁹ (b) IR spectra of the LiPO_3 phase, synthesized at 200 °C (LP-200, black line) and after calcination at 600 °C (LP-600, red line). (c) SEM image of the LiPO_3 phase synthesized at 200 °C.

RESULTS AND DISCUSSION

The as-synthesized LiPO_3 has been characterized by X-ray powder diffraction (XRD), induced coupled plasma mass spectroscopy (ICP-MS), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). Elemental analysis showed no evidence for the presence of sulfur and reveals a Li:P molar ratio of 1.21(8):1. XRD analysis indicates that an amorphous material is obtained. On heating this sample to 600 °C, a characteristic XRD pattern of crystalline LiPO_3 is found (Figure 1a), suggesting the as-synthesized material is likely an amorphous LiPO_3 -type phase. The appearance of a small impurity of Li-rich $\text{Li}_4\text{P}_2\text{O}_7$ in the XRD pattern after calcination at 600 °C (Figure 1a) is consistent with the ICP-MS analysis, indicating a lithium-rich material (i.e., $\text{Li}_{1+2x}\text{PO}_{3+x}$). Figure 1b shows IR spectra for the as-synthesized material and the material calcined at 600 °C, both displaying characteristic peaks corresponding to vibrational modes of the PO_4 tetrahedra and the P–O–P bonds present in LiPO_3 phosphate chains.^{21–23} Interestingly, SEM images reveal a novel nanoparticulate morphology (Figure 1c), with typical particle sizes ranging from 20 to 35 nm (see Figure S1). The material showed a large specific surface area of 41.6 $\text{m}^2 \text{g}^{-1}$, as determined from nitrogen adsorption using the Brunauer–Emmett–Teller (BET) method. To investigate the potential for this X-ray amorphous and high-surface-area material as a precursor for the synthesis of olivine LiMPO_4 compounds under mild conditions, the as-synthesized LiPO_3 was immersed in suitable metal ion solutions followed by solvent evaporation and calcination. LiFePO_4 and LiCoPO_4 were successfully synthesized using this approach, where LiPO_3 is dispersed in tetrahydrofuran (THF) solutions of FeCl_2 and CoCl_2 , followed by a calcination step after solvent evaporation at 500–600 °C under either inert (Ar) or reducing (H_2/Ar) atmospheres (Figure 2a). Thanks to the relatively low calcination temperature, this approach offers excellent control over the resulting morphology, inhibiting large particle growth. SEM analyses of the obtained LiMPO_4 phases reveal networks of interconnected nanoparticles with open pores enabling shorter path lengths for Li-ion transport and large electrode–

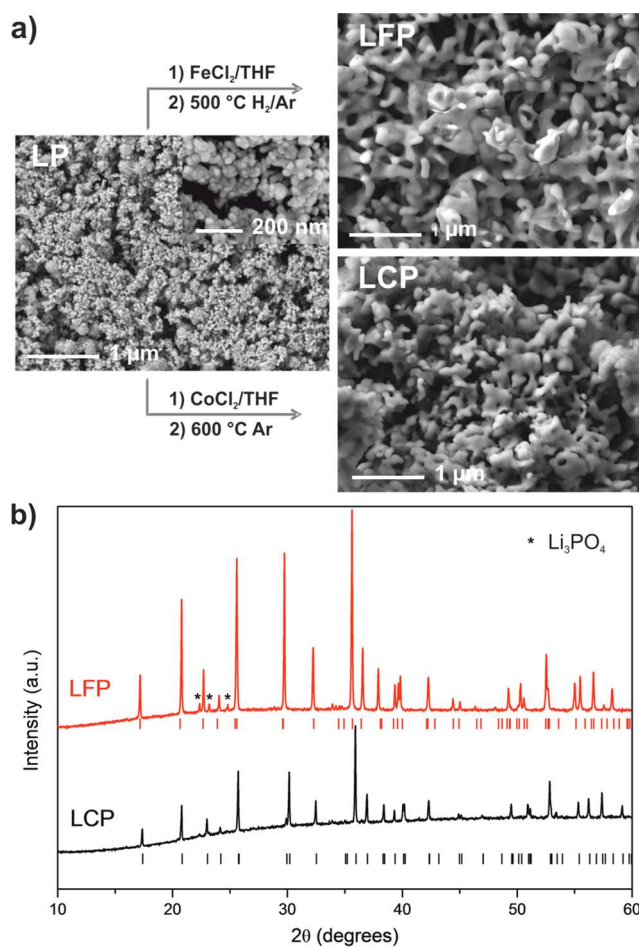


Figure 2. (a) Morphologies of the as-synthesized LiPO_3 phase (LP), LiFePO_4 (LFP), and LiCoPO_4 (LCP). (b) XRD patterns of LiFePO_4 (LFP) and LiCoPO_4 (LCP). The top markers (red) are for LiFePO_4 , and the bottom markers (black) are for LiCoPO_4 .

electrolyte contact areas (Figure 2a).^{10–14} BET surface analysis revealed specific surface areas of 18.1 and 12.6 $\text{m}^2 \text{g}^{-1}$ for

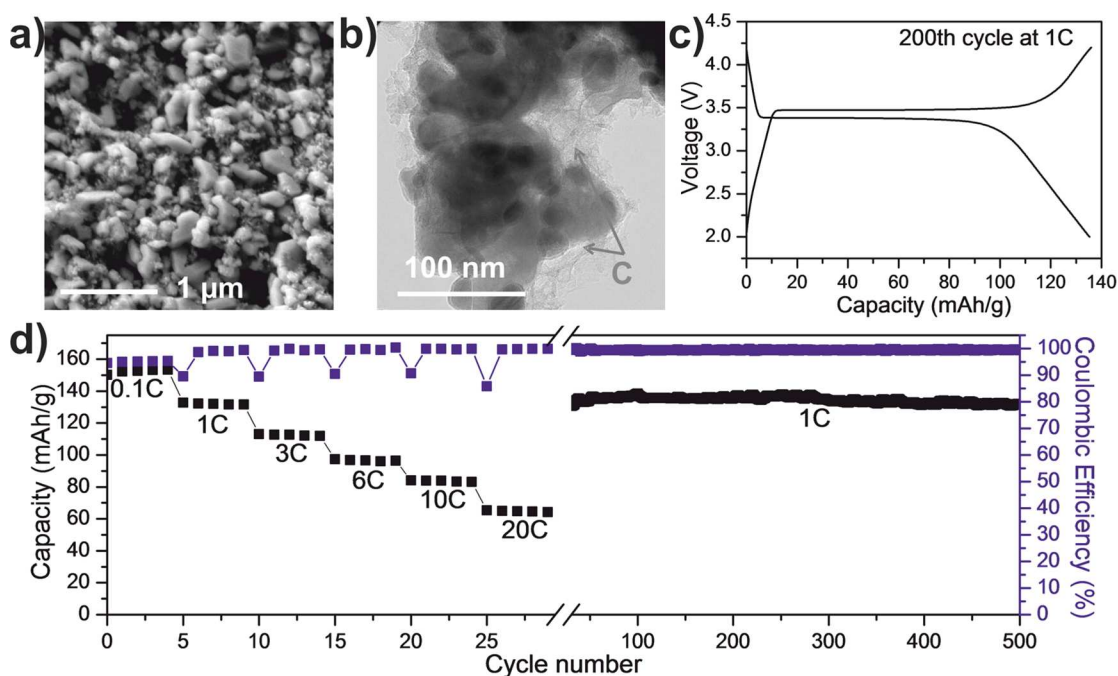


Figure 3. (a) SEM and (b) TEM images of the LiFePO_4/C composite. (c) Representative charge/discharge profile of the LiFePO_4/C composite, represented by the 200th cycle at 1C rate (1C corresponds to 170 mA g^{-1}). (d) Specific capacity as a function of cycle number for LiFePO_4/C at different charge–discharge rates.

LiFePO_4 and LiCoPO_4 , respectively. Samples of LiFePO_4 and LiCoPO_4 were annealed in air at 550°C to ensure removal of carbon prior to surface area measurements. Figure 2b shows XRD data collected from the synthesized materials.

A small amount of Li_3PO_4 (5.0(5) wt %; see Figure S2) is observed in the case of LiFePO_4 , while LiCoPO_4 is obtained predominately as a single phase. Refined data, against olivine-type structure with orthorhombic unit cells (Figure S2), reveal unit cell parameters of $a = 10.3306(1) \text{ \AA}$, $b = 6.0089(1) \text{ \AA}$, $c = 4.69415(8) \text{ \AA}$ and $a = 10.2044(2) \text{ \AA}$, $b = 5.9208(1) \text{ \AA}$, $c = 4.6994(1) \text{ \AA}$ for LiFePO_4 and LiCoPO_4 , respectively, consistent with previous reports.^{24,25} ICP-MS analysis indicated M:Li ratios of 1:0.98(3) and 1:1.13(3) for LiCoPO_4 and LiFePO_4 , respectively, consistent with the presence of a small Li_3PO_4 impurity for LiFePO_4 .

In addition to providing a simple route to controlled LiMPO_4 particle morphology, we demonstrate that the same approach can be modified to obtain LiMPO_4/C composite phases where this nanostructured morphology is retained. FeCl_2 and CoCl_2 form relatively stable complexes with the THF solvent,²⁶ thus enabling the formation of $\text{LiPO}_3/\text{MCl}_2/\text{THF}$ solid precursors through slow evaporation of excess THF at $\sim 70\text{--}80^\circ\text{C}$. These solid precursors are directly converted to LiMPO_4/C nanocomposites after calcination in an oxygen-free atmosphere. Carbon-free materials are achieved through removal of THF from the $\text{LiPO}_3/\text{MCl}_2/\text{THF}$ solid precursors by precalcination in air at suitable temperature ($\sim 300^\circ\text{C}$) prior to a final calcination step under inert conditions.

Interestingly, the LiFePO_4/C composite retains its interconnected nanoparticulate morphology, with carbon homogeneously surrounding the nanoparticles (Figure 3 and Figure S3). Elemental analysis indicates a carbon content of 2.8 wt %. Figure 3c displays a typical discharge/charge profile of the LiFePO_4/C composite at room temperature at a 1C rate, represented by the 200th cycle (Li metal anode; 1 M LiPF_6 in

1:1 EC/DMC). A specific capacity of 153 mAh g^{-1} is observed at 0.1C rate, with capacities of up to 65 mAh g^{-1} at 20C rate. The material also shows an excellent cyclability, retaining a capacity of 130 mAh g^{-1} after 500 cycles at 1C rate. The excellent electrochemical performance suggests this synthetic approach affords materials with a lack of defects that can inhibit Li-ion diffusion. This is consistent with FTIR observations of the LiFePO_4 and LiFePO_4/C phases (see Figure S4), where the P–O vibration of the PO_4 groups at 959 cm^{-1} is very close to the value expected for defect-free LiFePO_4 (957 cm^{-1}), assuming sensitivity of this vibration mode to anti-site defect formation.¹⁶

CONCLUSION

The synthetic approach developed here presents a new route to LiMPO_4 electrode materials through a soft chemical route that maintains the parent LiPO_3 nanostructured morphology. The development of nanostructured LiPO_3 as a precursor material opens up the possibility of chemically tuning the metal content in LiMPO_4 in nanoparticulate forms with high surface areas. The development of this simple and scalable route to nanostructured LiPO_3 provides an alternative to conventional polycrystalline and glass forms, often synthesized at temperatures exceeding 550°C . This morphology-directed approach to electrode nanoarchitectures also demonstrates great promise for obtaining carbon-composited olivines with excellent battery performance and cycling stability up to 500 cycles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00517.

Further details of experimental procedures, Rietveld refinements and diffraction patterns, and FTIR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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