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Fabrication of one-dimensional mesoporous CoP nanorods as anode materials for lithium-ion batteries

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Abstract: One-dimensional mesoporous CoP nanorods have been successfully synthesized via a facile hydrothermal method and subsequent low temperature thermal phosphorization treatment. At a current density of 500 mA g^{-1} , CoP nanorods as anode materials for lithium ion batteries deliver a high discharge capacity of 894 mAh g^{-1} after 300 cycles with a coulombic efficiency over 99%. Even at a high current rate of 4000 mA g^{-1} , the discharge capacity of the CoP electrode can still retain 467 mAh g^{-1} . The results suggest that the introduction of Co element and the special mesoporous nanorods play important roles in enhancing the electrochemical property. Therefore, this rod-like CoP electrode is competent as promising anode materials for high-performance lithium-ion batteries.

Introduction

At present, continuous development of the economy companied with the fossil fuel consumption of the industrialization has brought about increasingly serious environment and energy crisis.^[1-3] To deal with these dilemmas, eco-friendly and sustainable energy sources have attracted worldwide concern.^[4-6] Currently, as one of the promising energy storage systems, lithium-ion batteries (LIBs) have been intensively employed in a variety of application fields from mobile devices to transportation industries owing to its desirable energy density, high potential, light weight and environmental friendliness.^[7-10] However, considering connatural disadvantages of relatively low specific capacity (372 mAh g⁻¹) and safety issue, commercial graphite anodes fail to satisfy further application requirements for next-generation high performance LIBs.^[11-13] Thus, exploring novel candidates with high power density, excellent cycle stability and

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good rate capability is the critical factor for the development of LIBs.

In recent years, phosphorus-based anodes have aroused extensive interest due to their promising features of abundant resource, suitable redox potential and high specific theoretical capacity.^[14-15] Among them, non-toxic, inexpensive and chemically durable red phosphorus (R-P) exhibits a high theoretical capacity of 2595 mA h g⁻¹. Nevertheless, the defects of intrinsically low electrical conductivity (<1.0 \times 10-14 S cm⁻¹) as well as severe volume expansion (>300%) commonly cause serious pulverization of the electrode and deteriorated electrochemical performance,[16-18] which definitely hinders the practical applications for LIBs. [19-20] Some effective attempts to address those problems have been focused on designing diversified phosphides by introducing metal elements (Co, Mn, Ni, Cu, Fe, Sn, Mo etc.) and synthesizing various nanostructures (nanorod, nanowire, nanosphere, peapoded shape and so on). ^[21-27] For example, Kwon et al. prepared Co_xP compounds with a good cycling durability of 407 mA h g⁻¹ after 200 cycles. ^[28] Bai et al. reported that peapod-like Ni₂P shows a high reversible capacity of 628 mAh g⁻¹ after 200 cycles at a current density of 100 mA g⁻¹.^[29] Kim et al. synthesized teardrop-shaped SnP_{0.94} with a reversible capacity of 618 mA h g⁻¹ after 100 cycles at 120 mA g⁻¹.^[30] In addition, porous nanostructures are also in favor of lithium ions storage.^[31] The results explicated that these methods are conducive to improving the electrochemical properties of LIBs. Besides, metal phosphides also have a good development prospect in electrocatalytic field.^[32]

Enlightened by above-mentioned approaches, we successfully synthesized one dimensional (1D) mesoporous CoP nanorods by a facile hydrothermal method and subsequent low temperature thermal phosphorization treatment. In particular this strategy is much more controllable and rational by using cost-effective raw materials instead of hypertoxic and costly organophosphorus sources. This 1 D mesoporous nanorods not only provide more active positions and enough free space to mitigate the volume expansion, but also shorten the diffusion path to facilitate fast transport of electron and Li⁺. Thus, assynthesized CoP electrode as anode materials exhibits long cyclic stability and good rate performance.

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Results and Discussion

Figure 1. shows XRD pattern of the obtained CoP nanorods, this product conforms to the characteristic of orthorhombic CoP phase (JCPDS 29-0497). Main diffraction peaks centered at 31.6°, 32.0°, 36.3°, 36.7°, 46.2°, 48.1°, 48.4°, 52.3°, 56.0° and 56.8°, can be well indexed to (011), (002), (111), (102), (112), (211), (202), (103), (020) and (301) planes, respectively. The absent peaks of metallic Co, P and other impurities also indicate a high level of purity in phosphorization process. Moreover, broad peaks with low intensity suggest that as-prepared sample has a fine particle size,^[33] which is beneficial to the electrochemical properties. As a comparison, the XRD pattern of commerical red phosphorus (R-P) is also investigated. As shown in Figure S1 (Supporting Information), R-P represents three peaks centered at about 15°, 33°, and 56°, which are well matched with previous report.^[19]



Figure 1. XRD spectra of CoP nanorods with inset of crystal structure.

The SEM images present morphological aspects of the Coprecursor and CoP nanorods under different magnifications. As shown in Figure 2 (a), The precursor displays well-defined 1D (one-dimensional) shape with smooth outside surface (the inserted image). The morphology of final product CoP shown in Figure 2 (b), manifests rod-like fashion. In detail, these nanorods changes partially with rough surface composed of many nanosized particles (the inserted image) due to the thermal decomposition of the precursor and the recrystallization of the phosphorization process. To further explore nanorod features of CoP, TEM image shown in Figure 2 (c) reveals that nanocrystallites assemble together to generate nanorods. The corresponding HRTEM image shown in Figure 2 (d) exhibits a lattice fringe with a d-spacing value of 0.25 nm, the result is in good agreement with the (111) plane of the CoP phase. While, R-P particles present large size above 50 µm, as depicted R-P in Figure S2 (supporting information). Compared with large-sized R-P material, the nanosized of CoP particles will help to promote electrochemical lithium storage capability in terms of more active sites, convenient ion diffusion pathways and good penetration of the electrolyte. ^[5,34-38]



Figure 2. SEM images of (a) the Co- precursor and (b) CoP nanorods under different magnifications(with insert of magnification, inset scale bar:100 nm), (c) TEM and (d) HRTEM images of CoP

Moreover, porous properties were tested by N₂ adsorptiondesorption isotherm at 77 K based on Brunauer-Emmett-Teller (BET) method. The isotherm in Figure 3 (a) belongs to type IV category with a noticeable hysteresis loop at the P/P_orange of 0.70-0.95,^[39] and BET surface area is estimated to be 16.74 m²/g. Besides, the pore size distribution in Figure 3 (b) was measured by Barrett-Joyner-Halenda (BJH) method, mesopores are mainly situated in the range of 3-9 nm. 1D CoP nanorods with high surface area and sufficient pores could not only afford more electrochemical active sites but also facilitate charge transfer, thus resulting in enhanced lithium-storage capability.



Figure 3. (a) the BET curve and (b) BJH porsize distribution of CoP nanorods

X-ray photoelectron spectroscopy was carried out to elucidate more detailed information about valence states of the CoP. Figure 4 (a) demonstrates a high-resolution Co 2p spectrum, two spin-orbit peaks centered at binding energy of 778.8 and 793.9 eV are ascribed to Co 2p_{3/2} and Co 2p_{1/2} of CoP phase, respectively. And two peaks at 781.8 and 798.1 eV are corresponding to oxidized Co species (Co 2p3/2 and Co 2p1/2), respectively. While the other two peaks (flagged as "Sat.") at 786.5 and 803.2 eV are assigned to satellites due to shake up excitation of the high-spin Co²⁺.^[40] Figure 4 (b) shows a highresolution P 2p spectrum, two peaks are mainly identified as Co-P and P-O chemical bonds. Two peaks at 129.6 and 130.4 eV are attributed to P 2p_{3/2} and P 2p_{1/2} of the CoP phase. While the peak at 133.9 eV puts down to the oxidized surface [41]. The oxidized signals could be assigned to the inescapable surface oxidation when exposed in air, which is the common problem of metal phosphide surface appearing in previous reports. [27, 42-44]



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Figure 4. High resolution XPS spectra of the CoP (a) Co 2p and (b) P 2p

nanorods, electrochemical measurements were conducted.

Figure 5 (a) and (b) present cyclic voltammetry (CV) curves of

CoP and R-P in the first five cycles at a scan rate of 0.2 mV s⁻¹

between 0.01 and 3.0 V, respectively. For CoP, it is noted that

the redox peaks of the first cycle are visibly different from the

following CV curves, especially in the cathodic branch. A broad

irreversible reduction peak located at ~0.40 V could be related to

the lithium intercalation of the CoP and the formation of solid

electrolyte interphase (SEI) film [21, 45], as well as other

irreversible reaction In the anodic process during the first cycle,

two peaks at ~1.05 V and ~1.16 V are ascribed to continuous

lithium extraction. While in the second cycle, the previous

cathodic peak (~0.4 V) shifts to 0.6 V, this phenomenon is

probably caused by the structural rebuilding during the activation

process. For R-P, in the initial cathodic scan, a broad peak at

around 0.57 V can be attributed to the generation of SEI film and insertion of Li⁺. In the anodic process, the peak at around 1.15 V resulted from the lithium extration reaction.^[14] In subsequent

To best understand lithium storage capability of CoP

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insertion/extraction process without apparent peaks. Compared with R-P, the CV profiles of CoP overlap better after the initial cycle, it suggests that the introduce of Co element is helpful to improve the electrochemical stability, charge transfer kinetics and coulombic efficiency.

Figure 5 (c) and (d) show the Galvanostatic charge/discharge profiles of the CoP and R-P electrodes for the 1st, 2nd, and 100th cycle at a current density of 500 mA g⁻¹. At the 1st cycle of CoP, it is observed that there is a sloping potential plateau around ~0.40 V, followed by slowly translating into the cutoff voltage of ~0.01 V. In the latter cycles, the discharge potential plateau rises to ~ 0.6 V, this changing trend is in keeping with the CV curve. Furthermore, the charge/discharge specific capacities are 825.7 and 956.8 mAh g ¹, respectively, showing an initial columbic efficiency of 86%. Compared with the theoretical capacity (894 mAh g^{-1}), the extra capacity could be attributed to the formation of SEI film during the initial charge /discharge process, and that is common reported phenomenon of anode materials in previous literature.[23,29,46-47] At the 2nd cycle, the specific charge/discharge capacities of 721 and 769 mAh g⁻¹ are observed, and the columbic efficiency reaches 93%. Up to the 100th cycle, a high discharge capacity of 655 mAh g⁻¹ is still maintained, and the columbic efficiency is almost above 99%, while commerical R-P only delivers the first charge/discharge capacity of 155/1131 mAh g⁻¹ with a very low coulombic efficiency of ~13.7% on account of poor electrical conductivity and huge volume expansion. After 100 cycles, the capacity retention of R-P is only 137 mAh g⁻¹. The result that the CoP electrode has better cycling reversibility and stabliity than that of R-P would be ascribed to the special mesoporous structure which provides big buffer space to alleviate volume change during the charge and discharge process.





the 1 D CoP and R-P in the first five cycles at a scan rate of 0.2 mV s⁻¹ between 0.01 and 3.0 V. (c) and (d) Galvanostatic charge/discharge profiles of the CoP and R-P for the 1st, 2nd, and 100th cycle at a current density of 500 mA g^{-1} .

Figure 6 (a) displays long cyclic performance of as-prepared CoP nanorods and commercial R-P at a constant current density of 500 mA g^{-1} . Compare with R-P, CoP nanorods show excellent cyclic capacity, the discharge capacity of 894 mA h g^{-1} is still retained after 300 cycles, corresponding to ~93% of the initial capacity. And during 10-300 cycles, the columbic efficiency of CoP electrode consistently sustains above 98%, indicating a

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good electrochemical stability and reversible capacity. The capacity increasing after 40 cycles could be attribute to the activation process of materials during the charge discharge process. In addition, we compared the discharge capacity of CoP nanorods with previously reported metal phosphide anodes. As shown in table 1, rod-like CoP electrode shows high lithium strorage capability and good cycling stability, which will be an attractive anode material for lithium ion batteries. In conclusion, the reasons for CoP nanorods with achieved electrochemical properties may be explained as follows: (1) The introduction of metallic Co promotes the electronic conductivity; (2) Large specific surface and high porosity offer additional lithium storage active sites and sufficient free space, which is conducive to buffering the dramatic volumetric expansion and restraining the pulverization of the electrode; (3) 1D nanosized architecture effectively shortens the diffusion path, facilitating fast transport of electrons and Li⁺ ions.

This special architecture also plays an important role in ameliorating rate performance of the CoP electrode. It was evaluated at different current densities ranging from 200 to 4000 mA g⁻¹. As shown in Figure 5 (d), the CoP electrode shows admirable rate capability even at large current density, yielding average discharge capacities of 856, 690, 624, 565, 527 and 467 mAh g⁻¹ with gradually increasing current densities of 200, 400, 800, 1000, 2000 and 4000 mA g⁻¹, respectively. During following cycles, the specific capacities become 549, 602, 655 and 726 mAh g⁻¹ as altering current densities back to 2000, 1000, 800 and 400 mA g⁻¹. Particularly, the reversible capacity can rebound to 818 mAh g⁻¹, nearly approximating its theoretical capacity when the current density returns to 200 mAg⁻¹ after 110 cycles. All results clearly indicate good rate performance and high cycling stability.





Figure 6. (a) Cycling performance of the CoP and R-P at a constant current density of 500 mA g⁻¹. (b) Rate performance of the CoP at various current densities from 200 to 4000 mA g⁻¹.

Table 1. Comparison of discharge capacity of CoP nanorods in this work and the previously reported metal phosphide anodes.

Materials	Initial discharge capacity (mAh g ⁻¹)	Reversible capacity/ cycles	Current density	Ref.
CoP nanorods	956.8	894 /300	100 mA g ⁻¹	This work
MnP	1104	287/50	50 mA g ⁻¹	[22]
Ni ₂ P/Graphene	973.9	450/50	54.2 mA g ⁻¹	[48]
Peapod-like Ni ₂ P	1027	630/200	100 mA g ⁻¹	[29]
CoP thin film	1055.7	788/25	5 µA cm ⁻²	[21]
Nanorod-FeP@C	986	480/200	30 mA g ⁻¹	[49]

To futher explore the influences of introduction of Co element and mesoporous nanorods on the charge transfe kinetics of electrode, the electrochemical impedance spectro scopy (EIS) was performed, the Nyquist plots are shown ir Figure 7. It can obviously observerd that both the Nyquist plots are composed of semicircle in the middle-high frequency rang and inclined line in low-frequency areas. The diameter o semicircle is related to the charge-transfer impedance (Rct).The inclined line is associated with warburg impendence (Wo), which is associate with the diffusive resistance of lithium ions. the diameter of CoP is obviously smaller than commercial R-P indicating lower Rct and good electron transport in CoF electrode. The improved charge transfer could be attributed to the introduction of Co element enhancing the electricity conductivity of the electrode, and the mesoporous nanorod could shorten the pathway of electron transmission.

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Figure 7. Nyquist plots of the CoP and R-P bef ore cy cles in the frequency range from 100 KHz to 0.01 Hz.

In order to further understand the influence of special 1D architecture on electrochemical performance. The SEM images of the CoP electrode was tested after 100 cycles at the current density of 500 mA g⁻¹. As shown in Figure 8, although the texture of CoP nanorods are maintained in some degree, it is apparent that pristine CoP nanorods transform into coral-like nanorods with much coarser surface due to the partial pulverization during charge/discharge process. Meanwhile, there are also numerous tiny nanoparticles on the surface of the electrode, caused by repetitive lithium intercalation/extraction. These morphological changes may provide more contact areas of electrode/electrolyte and more active sites as well as enough free space, which will help to enhance lithium storage capability and alleviate severe volume expansion.



Figure 8. SEM images of the CoP electrode after 100 cycles at a current density of 500 mA $\mathrm{g}^{\text{-1}}$

Conclusions

1D mesoporous CoP nanorods were successfully synthesized and evaluated as anode materials for LIBs. The CoP electrode delivers high specific capacity, good cycling stability and rate capability. The excellent electrochemical property is due to the unique architecture with additional storage sites, convenient diffusion channels and enough free space. For example, a reversible specific capacity of 894 mAh g⁻¹ can be maintained after 300 cycles at a current density of 500 mA g^{-1} . Even at a current density of 4000 mA g^{-1} , the rate capacity still retains 467 mAh g^{-1} . Consequently, CoP nanorods may be promising applications in LIBs.

Experimental Section

Analytic grade chemicals purchased from Aladdin Ltd. (Shanghai, China) including Cobalt nitrate hexahydrate (Co(NO₃)₂•6H₂O), urea (CO(NH₂)₂), ammonium fluoride (NH₄F), sodium hypophosphite (NaH₂PO₂), red phosphorus, were used without further purification.

Preparation of Co-precursor and mesoporous CoP nanorods:

The 1D co-precursor was fabricated by a facile hydrothermal route. 1.02 g of $Co(NO_3)_2$ •6H₂O, 0.33 g of NH₄F and 1.05 g of $CO(NH_2)_2$ were uniformly dissolved in 80 mL deionized water, then the solution was transferred to a 100 mL Teflon-lineds autoclave for following thermal treatment at 120 °C for 6 h. When cooled naturally, the pink precipitation was washed several times and dried in a vacuum oven at 80 °C over night. In order to synthesize cobalt phosphide, the subsequent phosphorization treatment was conducted in a tube furnace. In details, 2 g of NaH₂PO₂ and as-prepared Co-precursor were placed into porcelain crucible at the upstream and the downstream position, separately. Whereafter, the reactants were heated to 350 °C at the heating rate of 1 °C min⁻¹ under Ar atmosphere for 2 h and then cooled to ambient temperature. The final product of mesoporous CoP nanorods was harvested

Material characterizations

Crystal phase identification was determined by powder X-ray diffraction (XRD) using PAN alytical X'Pert PRO diffractometer with Cu/K α radiation and λ =1.5406 Å. The morphological features were measured by scanning electron microscope (SEM, ZEISSULTRA55) and transmission electron microscope (TEM, JEM-2100HR). The specific Brunauer-Emmett-Teller (BET) surface area was carried out on a Coulter SA 3100 surface area analyzer. X-ray photoelectron spectroscopy (XPS) measurment was carried out on PHI 5800 ESCA system to reveal the surface chemical valence state with Al K α (150 W, 1486.6 eV) radiation as the probe beam

Electrochemical measurements

CR2430 coin-type cells were assembled in an agron-filled glove box to evaluate electrochemical performance. The working electrode consisted of CoP nanorods or red phosphorus, super-P and LA 133 with the weight ratio of 7:2:1. The average mass loading of active material each electrode was about 1 mg. Metallic lithium foil was utilized as the counter and the reference electrode, Celgard 2400 film was used as the separator and commercial electrolyte was 1 M LiPF₆ in the solution of ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate (1: 1 : 1 by volume). Cyclic voltammetry test was carried out with the scan rate

of 0.2 mV s⁻¹ on solartron 1470 electrochemical workstation. Galvanostatic charge/discharge data was executed on NEWARE battery testing equipment between 0.01 and 3.0 V at various current densities. The electrochemical impedance spectroscopy (EIS) measurement was performed from the CHI604D electrochemistry system in the frequency ranging from 0.01 Hz to 100 KHz.

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Text for Table of Contents

One-dimensional mesoporous CoP nanorods were synthesized by a facile hydrothermal method and subsequent low temperature thermal phosphorization treatment. when used as an anode material for lithium ion battery, CoP electrode delivers a high discharge capacity of 894 mAh g^{-1} after 300 cycles at a current density of 500 mA g^{-1} . Even at a current density of 4000 mA g^{-1} , the rate capacity of CoP electrode still retains 467 mAh g^{-1} , showing high reversible capacity, good cycling stability, and rate capability.



Key Topic*The synthesized 1D mesoporous CoP anode materials have enhanced electrochemical performances of lithium-ion batteries

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Title: Fabrication of one-dimensional mesoporous CoP nanorods as anode

*one or two words that highlight the emphasis of the paper or the field of the study mesoporous CoP nanorods, battery.