



Short communication

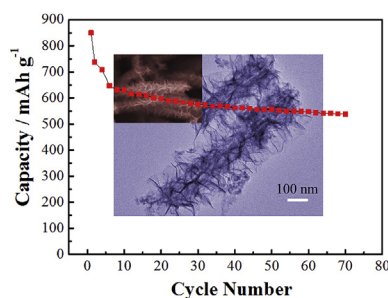
Synthesis of pyrite/carbon shells on cobalt nanowires forming core/branch arrays as high-performance cathode for lithium ion batteries

F. Cao ^{a,*}, G.X. Pan ^a, J. Chen ^{a,b}, Y.J. Zhang ^a, X.H. Xia ^c^a Department of Materials Chemistry, Huzhou University, Huzhou, 313000, China^b College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 313000, China^c State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, and Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, China

HIGHLIGHTS

- Construct self-supported porous Co/FeS₂-C core/branch nanowire arrays.
- Porous Co/FeS₂-C nanowire arrays show high capacity and good cycling life.
- Hierarchical porous array structure is favorable for fast ion/electron transfer.

GRAPHICAL ABSTRACT



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ABSTRACT

Construction of self-supported porous metal sulfide arrays is critical for the development of high-performance electrochemical energy storage devices. Herein we report hierarchical porous Co/FeS₂-C core/branch nanowires arrays by the combination of facile solution-based methods. FeS₂-C nanoflakes branch is uniformly coated on the Co nanowire core forming composite core/branch arrays. The as-prepared Co/FeS₂-C core/branch nanowire arrays possess combined properties of highly porous structure and strong mechanical stability. As cathode of lithium ion batteries, the Co/FeS₂-C core/branch nanowire arrays exhibit good electrochemical performances with initial discharge capacity of 850 mAh g⁻¹ at 0.25 °C and stable high-rate cycling life (539 mAh g⁻¹ after 70 cycles at 0.25 °C). The hierarchical core/branch architecture provides positive roles in the enhancement of electrochemical properties, including fast transportation path of electron, short diffusion of ions and high contact area between the active material and electrolyte.

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1. Introduction

Over the past decades, great efforts have been made to pursue high-performance lithium ion batteries (LIBs) with high energy/

power density to meet the increasing demand of modern electronics and transportation [1,2]. It is well accepted that the whole electrochemical performance of LIBs is mainly controlled by the cathode [3,4]. Tarascon group [5] did a simple calculation and revealed that the energy density of a cell could increase up to 57% by doubling the capacity of the positive electrode, while only an increase of 47% could be achieved as the capacity of the negative

* Corresponding author.

E-mail address: caofengz@126.com (F. Cao).

electrode increased by a factor of 10. So the chances of developing LIBs with high energy/power density rely on spotting better positive electrode materials with larger capacity or higher working voltage [6,7]. In contrast to the fast development of high-capacity anodes (Si [8], metal oxides/sulfides [9,10], metal carbides/nitrides [11,12], Sn and alloys [13], etc.), the advancement of cathode is still not satisfactory and most of the current commercial cathodes (such as LiCoO_2 [14], LiFePO_4 [15], $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ [16]) usually involve one electron reactions and show specific capacities lower than 200 mAh g^{-1} . This greatly limits the further development of advanced LIBs. Therefore, high-capacity cathodes with multi-electron reactions are highly desirable and becoming the research focus of the cathode area.

Pyrite FeS_2 is considered as one of the most promising cathodes of LIBs due to its high theoretical capacity (894 mAh g^{-1}) arising from four electron reduction: $\text{FeS}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Fe} + 2\text{Li}_2\text{S}$ [17,18], low environmental impact and low cost. Though primary Li/ FeS_2 batteries have been successfully commercialized, secondary rechargeable Li/ FeS_2 batteries at ambient temperature are facing great challenges because of rapid drop in capacity during cycling resulting from its complex multi-electron conversion reactions [19,20]. Correspondingly, the conversion reactions cause drastic volume variation and strain, leading to pulverization of electrodes and loss of active materials. In addition, the sluggish kinetics of charge transfer and ionic diffusion (low diffusion of ions and low electrical conductivity) in FeS_2 cathode further accelerate the degradation of high-rate capability and reversibility [21]. To overcome the aforementioned problems, in recent years, integrated array electrodes have been developed to improve the specific capacity and cycling stability of cathodes [22]. Compared with the traditional bulk powder materials, the integrated array electrodes possess three main advantages. First, no extra preparation process of electrode and avoid undesirable supplementary interfaces (that is, polymer binders and additives). Second, it offers better electrical contact and fast reaction kinetics [23,24]. The arrays architectures have combined properties of high surface area, and short diffusion path for ions. The open space between the adjacent nanoarrays allows for better accommodation of large volume changes and strain [25]. Currently, nano/microsized FeS_2 (e.g., nanowires [21], microspheres [26], nanocubes [27], nanooctahedra [20]) powder materials and FeS_2 based composites with conductive matrixes including reduced graphene oxide [28], carbon nanotubes [29], carbon [30], conducting polymers [31], have been reported, and enhanced performances are proven in these systems. Nevertheless, there is no report about FeS_2 nanoarrays and their application as cathode of LIBs.

In this work, we report hierarchical porous Co/ FeS_2 -C core/branch nanowire (CBN) arrays prepared by the combination of chemical bath deposition (CBD), electro-deposition (ED) and glucose decomposition. FeS_2 -C nanoflakes branch is homogeneously coated on the conductive Co nanowires forming composite core/branch arrays. Highly porous structure with conductive core and interconnected composite nanoflakes branch are achieved in the integrated electrode. As cathodes of LIBs, the obtained Co/ FeS_2 -C CBN arrays exhibit high discharge capacity and high-rate capability due to the unique porous array structure with fast ion/electron transfer and large contact area between active materials and electrolyte. The proposed method can be applicable for preparation of other high-performance porous metal sulfide arrays for applications in sensors, catalysis and energy storage and conversion.

2. Experimental

The hierarchical porous Co/ FeS_2 -C CBN arrays were prepared as

follows. First, the Co nanowires were prepared by a CBD method as follows. The clean nickel foil was used as the substrate. In a typical synthesis, the CBD solution was prepared by mixing 1.5 g cobalt nitrate, 15 ml of 28 wt. % ammonia solution and 55 ml of H_2O . Then the CBD solution was transferred to a covered petri dish and the substrate was fixed approximately 2 mm away from the bottom of the petri dish. The CBD solution was kept at 90°C for 6 h for the growth of nanowire arrays. After that, the samples were taken out and rinsed with distilled water, followed by an annealing process at 450°C for 2 h in flowing Ar + H_2 (20%) to form Co nanowire arrays.

Then, the self-supported Co nanowire arrays were used as the scaffold for the growth of FeS_2 -C nanoflakes shell by the combination of a simple ED method and glucose decomposition. The FeS_2 nanoflakes were first prepared in a three-electrode system with a Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode and self-supported Co nanowire arrays as the working electrode. The electrolyte consisted of 5 mM FeSO_4 (ARCOS, 99%) and 0.5 M $\text{CH}_4\text{N}_2\text{S}$ (ARCOS, 99%). The pH value was adjusted to about 6 by adding dilute NH_4OH solution if necessary. The ED deposition was carried out by cyclic voltammetry in the potential range of -1.2 – 0.2 V (vs. Ag/AgCl) at a sweep rate of 5 mV s^{-1} for 20 cycles. After that, the samples were immersed into 0.05 M glucose for 12 h plus an annealing process at 500°C for 1 h in argon to form porous Co/ FeS_2 -C CBN arrays. The mass of Co, FeS_2 and C was about 1.6, 1.5 and 0.1 mg cm^{-2} , respectively. The high-resolution (0.01 mg) balance, inductively coupled plasma-optical emission spectroscopy (ICP-OES, Spectro Arcos) analysis and elemental analysis were used to determine the load weight of different components. We calculated the load weight of Co by the mass difference before and after the loading of Co nanowires on the substrate. The load mass of the Co was about 1.6 mg cm^{-2} . In the same way, we calculated the weight of FeS_2 -C by the mass difference before and after loading of FeS_2 -C branch on Co nanowires backbone. The load mass of FeS_2 -C was about also 1.6 mg cm^{-2} . In order to further confirm the mass of FeS_2 and C, we dissolved Co/ FeS_2 -C by 0.5 M HCl aqueous solution. Then, the inductively coupled plasma-optical emission spectroscopy (ICP-OES, Spectro Arcos) analysis was used to confirm the precise composition of Co and Fe in the solution, and the calculated weight of FeS_2 was found about 1.49 – 1.51 mg cm^{-2} (55 ppm for Fe in solution). We also used elemental analysis to calculate the weight of carbon. It accounted for 3.1% in the whole mass of Co/ FeS_2 -C arrays (3.2 mg cm^{-2}). Then we calculated the mass of carbon was about 0.1 mg cm^{-2} .

The morphology and microstructure of the samples were characterized by X-ray power diffraction (XRD, Rigaku D/max 2550 PC, Cu K α), a scanning electron microscopy (SEM, Hitachi S-4700 and FESEM, FEI Sirion-100), transmission electron microscopy (TEM, JEM 200CX at 160 kV, Tecnai G2 F30 at 200 kV), a NOVA-1000e surface area analyzer (BET measurement), and Raman spectroscopy (WITec-CRM200 Raman system with a laser wavelength of 532 nm).

Electrochemical performances of Co/ FeS_2 -C CBN arrays were investigated in CR2025 coin-type cell. The prepared sample with a diameter of 12 mm was directly used as the working electrode. Test cells were assembled in an Ar-filled glove box with pure lithium foil as both the counter and the reference electrodes. The cells were assembled in an argon-filled glove box using 1 M LiPF_6 in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1: 1 in volume) as the electrolyte and a polypropylene micro-porous film (Cellgard 2300) as the separator. The charge/discharge tests were conducted on LAND battery program-control test system (Wuhan, China) between 1.2 and 2.6 V by applying from 0.25 to 1.5 $^\circ\text{C}$ at room temperature. Cyclic voltammetry (CV), measurements were performed on CHI660c electrochemical workstation. The capacity was calculated based on the mass of active FeS_2 . The mass of Co or carbon was

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