



Cobalt phosphide microsphere as an efficient bifunctional oxygen catalyst for Li-air batteries



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ABSTRACT

An efficient bifunctional catalyst for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is highly desired for the application of rechargeable metal air batteries. Herein, urchin-like CoP microspheres have been synthesized by a facile hydrothermal method with cetrimonium bromide as soft template. In alkaline solution, the as-prepared CoP catalyzes the ORR with an onset potential of -0.11 V (vs. Ag/AgCl) and a potential gap of 62 mV compared with commercial Pt/C catalyst. Meanwhile, the CoP catalyst exhibits better OER activities than the commercial RuO₂ catalyst. Interestingly, when employed as cathodic catalyst for Li-air batteries, the battery shows good discharge capacity of 2994 mAh g⁻¹ at 100 mA g⁻¹, high round-trip efficiency of over 90%, excellent rate capability and cycle stability of sustaining 80 cycles without any capacity degradation at a high discharge current density of 500 mA g⁻¹.

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1. Introduction

As two importantly fundamental electrochemical processes, both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) have attracted tremendous interest in the fields of fuel cell and metal air battery. However, sluggish kinetics hinders the commercialization of these electrochemical devices. Efficient oxygen catalysts are of key importance [1–3]. Noble metal catalysts, such as Pt, Pd and Ru, show the best overall catalytic activity toward the ORR/OER, but, high cost and scarcity make them not feasible for large scale applications. Considerable efforts are desired to explore alternative none-noble metal catalysts for both the ORR and the OER [4–7].

Transition-metal phosphides (TMPs) are an important class of functional compounds due to rich bonding type itself. They have been widely used as efficient catalysts for hydrodesulfurization reaction [8], anode materials for Li-ion battery [9], and active catalyst for hydrogen evolution [10]. In recent years, TMPs have been undergoing intensively research as potential OER and/or ORR

catalyst. Hu firstly reported Ni₂P can catalyze OER in alkaline medium with remarkable activity and stability [11]. Huang systematically studied ORR catalytic properties of M₂P (M = Mn, Co, Ni) @CNTs, and found Co₂P and Mn₂P exhibit better ORR activities, while Ni₂P shows inferior performance [12].

Cobalt oxides have been studied extensively as oxygen catalyst relating to energy devices, but, there are few reports about cobalt phosphides as bifunctional oxygen catalyst. Herein, we present our recent efforts in developing a CoP bifunctional catalyst. Catalytic activities were evaluated through a rotating-ring-disk electrode (RRDE) method, and then CoP based 2032 coin Li-air batteries (LABs) were also assembled and tested.

2. Experimental

Urchin-like CoP was synthesized by a facile hydrothermal method with cetrimonium bromide (CTAB) as a soft template [13]. 1.2 g Co(NO₃)₃·6H₂O, 0.4 g NaH₂PO₄·2H₂O, and 1.0 g CTAB were dissolved in 40 mL deionized water and stirred for 4 h. Then, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 8 h. After cooling to room temperature, the precipitates were filtrated, washed with deionized water and ethanol for several times and then dried at 80 °C

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overnight. The obtained precursor was noted as pre-CoP. Finally, the pre-CoP was calcined at 650 °C for 4 h in a tube-furnace with flowing high purity H₂ to obtain the final CoP.

X-ray diffraction (XRD) measurement was performed with a Bede D1 X-ray diffractometer (Bede Scientific Ltd., UK) equipped with Cu K α radiation. Morphology was characterized by a scanning electron microscope (SEM, Hitachi SU8010). XPS spectra were analyzed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII).

The procedures of electrode preparation and electrochemical tests were similar to our previous work to evaluate ORR and OER activities in 0.1 M KOH solution by a rotating ring-disk electrode (RRDE) equipment (Pine Electrochemical system, AFMSRX rotator, and AFCBP1 bipotentiostat) [14,15]. The RRDE electrode consisted of a catalyst film-coated GC disk (0.196 cm² of geometric surface area) surrounded by a Pt ring (0.125 cm² of geometric surface area). A conventional three-electrode single compartment Pyrex glass cell was used to carry out electrochemical investigations at room temperature. A Pt-wire was used as the counter electrode, and an Ag/AgCl (1 M Cl⁻, 0.197 V vs. SHE) reference electrode was used in a double-junction reference chamber.

The catalyst ink of the CoP microspheres was made by mixing 5 mg CoP powder and 5 mg acetylene black with 95 μ l Nafion solution and 350 μ l ethanol in an ultrasonic bath for 2 h. The working electrode was prepared by applying 7 μ l catalyst ink onto the surface of GC electrode with a micropipette and drying in air for 0.5 h. The catalyst loading was 0.4013 mg cm⁻². For comparison, samples of the pre-CoP, commercial Pt/C and RuO₂ catalysts were also prepared and tested with the same procedure, respectively.

During the ORR process, the transferred electron number (*n*) were calculated using the following equations [16,17].

$$n = 4 \frac{\text{abs}(j_D)}{\text{abs}(j_D) + (j_R/N)} \quad (1)$$

where, *j_D* is the Faradaic current at the disk, *j_R* is the Faradaic

current at the ring, and *N* = 0.22 is the disk electrode collection efficiency.

The ORR and OER measurements were performed in 0.1 M KOH solution at room temperature with a 10 mV s⁻¹ scan rate. During the ORR test, the voltage scanning range was from -0.9 to 0 V. The ring potential was set at 0.6 V, which is considered to be sufficiently high to induce complete peroxide decomposition as reported elsewhere [17]. During the ORR test, the background capacitive current contribution (obtained from N₂ saturated experiment) is subtracted from each voltammogram. For OER test, the voltage scanning range was from 0 to 1.0 V.

CoP microspheres based 2032 coin LABs were assembled and measured. Oxygen cathodes were composed of CoP as active catalyst (30 wt%), super P as conductivity agent (60 wt%) and polyvinylidene fluoride as binder (10 wt%). The homogenous cathode ink was sprayed on carbon paper current collector (Φ 13 mm). The super P and CoP catalyst loading is 0.75 mg cm⁻². LABs were assembled in an argon-filled glovebox, using lithium pellet as counter and reference electrodes, glassfibre as separator (GF/C, Whatman), and 1 M LiTFSI in TEGDME as electrolyte. Galvanostatic discharge-charge tests were conducted within a voltage window of 2.2–4.4 V (vs. Li/Li⁺) with a multichannel battery testing system (LAND CT, 2001A) in a testing glove box filled with a gas mixture composed of 80 vol% pure Ar (99.999%) and 20 vol% pure O₂ (99.999%). Specific capacity was calculated based on the sum mass of super P and CoP catalyst.

3. Results and discussion

Fig. 1(A) shows XRD patterns of pre-CoP and CoP. Compared with the standard PDF card of Co₂P₂O₇ (PDF#49-1091) and CoP (PDF#65-1474), it reveals that the pre-CoP shows characteristic peaks of Co₂P₂O₇ impurity, except some trace peaks of CoP. While, all diffraction peaks could be indexed to well-crystallized CoP after annealing in H₂. Fig. 1(B) and C display SEM images of pre-CoP and CoP. It is clearly seen that urchin-like microsphere of pre-CoP and

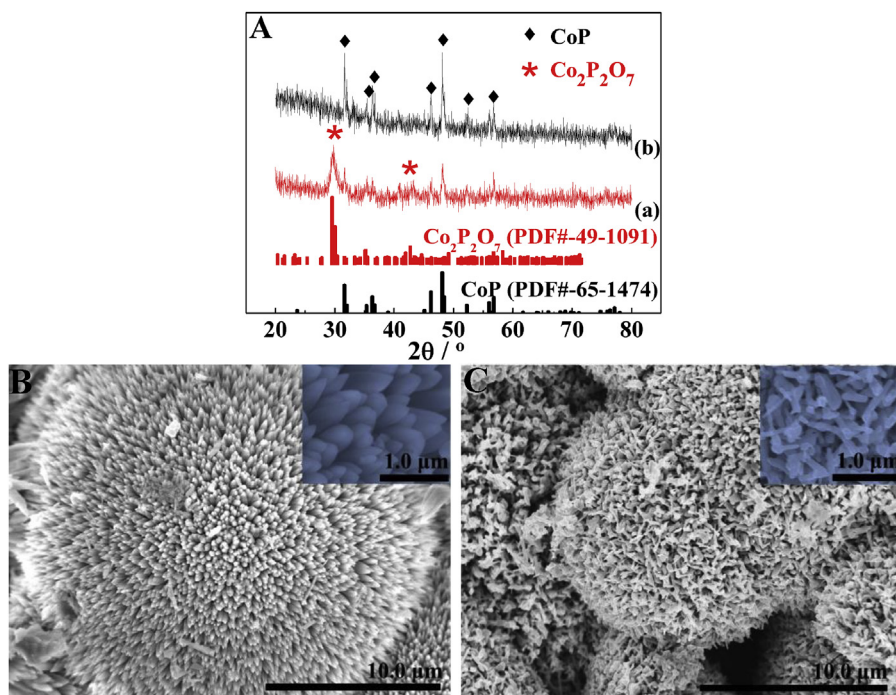


Fig. 1. XRD patterns of (a) the pre-CoP; (b) the CoP (A); SEM images of the pre-CoP (B) and the CoP (C).

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