

Facile synthesis of multiporous CuCo₂O₄ microspheres as efficient electrocatalysts for rechargeable Li-O₂ batteries

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ABSTRACT: Multiporous CuCo₂O₄ microspheres have been synthesized via a facile solvothermal method and used as bifunctional electrocatalysts for rechargeable Li-O₂ batteries. The Li-O₂ battery utilizing CuCo₂O₄ shows a higher specific capacity of 5607 mAh g⁻¹ than that with pure Ketjen black (KB). Moreover, the Cu-Co₂O₄-based electrode enables much enhanced cyclability than that of the carbon-only cathode. Such excellent catalytic performance of CuCo₂O₄ could be associated with its inherent catalytic activity and multi-porous microspheres structure.

1 INTRODUCTION

Rechargeable lithium-oxygen batteries have received a great deal of interest in recent years due to its extremely high specific energy, which make them promising energy storage devices for electric vehicles [Abraham K.M.,1996][Girishkumar G.,2010]. A typical nonaqueous rechargeable Li-oxygen battery is composed of Li metal as the negative electrode, a Li ion conducting nonaqueous electrolyte, and porous oxygen diffusion cathode. The basic chemical reactions of non-aqueous electrolyte Li-O₂ batteries involve the formation of Li₂O₂ during the discharge process (oxygen reduction reaction, ORR) and the decomposition of Li₂O₂ during the charge process (oxygen evolution reaction, OER) [Peng Zhangquan,2012]. However, there are a great barrier to making Li air battery practical, including low round-trip efficiency, low rate capability, and poor cycling stability [Girishkumar G.,2010].

Recently, great efforts have been made to improve the charge performance of Li-oxygen batteries by employing bifunctional catalyst in oxygen electrode. These catalysts mainly include noble metals [Peng Zhangquan,2012][Lei Yu,2013], metal nitrides [Shui Jiang-Lan,2012], and also various classes of metal oxides [Xu Ji-Jing,2013][Lee Jin-Hyon,2012].

Among those catalysts, covalent hybrids of spinel metal oxides have higher electrochemical activities as catalysts for Li-O₂ batteries. Cobalt oxides have drawn the most potential because of reasonably good catalytic activity, low cost, ease of preparation and good chemical stability. However, due to the toxicity and high cost of cobalt, one of the worthwhile efforts is to partially replace the Co in Co₃O₄ by cheaper and more eco-friendly alternative metals.

Spinel CuCo₂O₄ nanocrystals have been investigated as a cathode material in Li-oxygen batteries [Liu Ying,2014]. The authors found that the CuCo₂O₄/KB electrode exhibits much lower polarization, better rate capability and longer cycling life. In the simulated air conditions, the battery delivers a high capacity of 7962 mAh g⁻¹ with a discharge-recharge voltage gap of 0.95 V at 50 mA g⁻¹.

Multiporous materials, which not only provide more electrocatalytic sites but also promote mass transport (oxygen and ions) in the electrolyte have been reported as electrocatalysts for rechargeable Li-O₂ batteries [Ma Shunchao,2013].

In this paper, multiporous CuCo₂O₄ microspheres were synthesized via a facile solvothermal method and used as the electrocatalyst for Li-O₂ batteries. Its multiporous structure maximizes the

availability of the catalytic sites and facilitates the diffusion of electrons and reactants. The Li-O₂ batteries which use CuCo₂O₄ microspheres as electrocatalyst display higher discharge capacity and excellent cycling performance.

2 EXPERIMENTAL

2.1 Synthesis of materials

All the chemical reagents were analytical grade and used without further purification. CuCo₂O₄ microspheres were prepared through a modified one-step solvothermal method. In a typical procedure [Ma Shunchao,2013], 1 mmol CuCl₂•2H₂O and 2 mmol CoCl₂•6H₂O were dissolved into 30 mL of ethylene glycol (EG) and 10 mL of distilled water. After magnetic stirring for an hour, 30 mmol of NH₄HCO₃ was added to the above mixture at room temperature. The resultant solution was continually stirred for an hour and transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 24 h. The autoclave cooled to room temperature naturally. The precipitates were collected by centrifugation and washed with distilled water and ethanol three times, followed by vacuum-drying at 70 °C for 10 h. The porous CuCo₂O₄ microspheres were obtained by calcining at 400 °C for 4 h in air.

2.2 Characterization of samples

The samples were characterized by X-ray diffraction (Rigaku Ultima IV, Cu K α radiation, 40 kV, 40 mA), scanning electron microscopy (SEM, QUANTA FEG 250) and transmission electron microscopy (JEOL JEM-2100F, Tokyo, Japan).

2.3 Electrochemical measurements

The Li-O₂ batteries were measured using 2025-type coin battery. The oxygen cathodes were prepared by coating a homogenous ink composed of a mixture of 30 wt% CuCo₂O₄ catalyst, 60 wt% Ketjen black EC600JD (KB), 10 wt% polyvinylidene fluoride (PVDF) or 90 wt% KB, 10 wt% PVDF onto a current collector. The mass loading of the CuCo₂O₄/KB catalyst was 1.1 mg cm⁻². The cell was then assembled in an Ar-filled glovebox. The electrolyte was 1 M LiCF₃SO₃ in tetraethylene glycol dimethyl ether (TEGDME). The discharge/charge tests were controlled by a LAND-CT2001A tester under an oxygen atmosphere. Cyclic voltammetry (CV) was performed between 2.0 and 4.5 V using a CHI660 electrochemical station.

3 RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of CuCo₂O₄ are shown in Figure 1. The results are consistent with the spinel crystalline structure CuCo₂O₄ (JCPDS No. 23-1390). The distinct peaks on wide-angle XRD pattern are observed at 2θ values of 18.88, 31.08, 36.62, 38.31, 44.52, 55.29, 58.96 and 64.79 which correspond to (111), (220), (311), (222), (400), (422), (511), and (440) plane reflections of the spinel CuCo₂O₄ structure, respectively; no other diffraction peaks were found, which indicate that the products were composed of pure CuCo₂O₄.

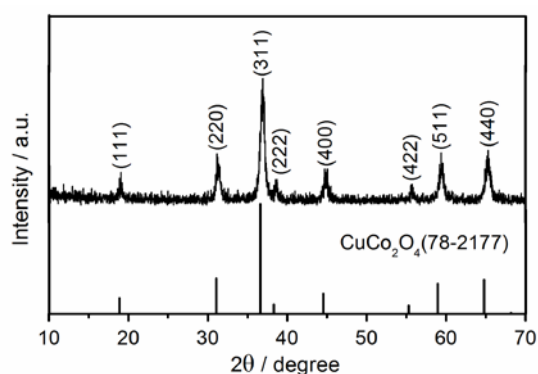


Figure 1. XRD patterns the CuCo_2O_4 microspheres.

As shown in Figure 2a, the product is composed of microspheres with diameter of 0.5-0.7 μm . The microspheres are formed by the aggregation of nanoparticles with typical sizes ranging from 15 to 20 nm. Furthermore, the TEM images (Figure 2b and 2c) obviously reveal that the microstructure of a CuCo_2O_4 sphere composed of numerous nanoparticles, and there are many mesopores that exist in the CuCo_2O_4 microstructure. The representative high resolution TEM (HRTEM) in Figure 2d displays distinct lattice fringes with d-spacing of 0.47 nm and 0.25 nm, corresponding to the (111) and (311) planes of CuCo_2O_4 , indicating that the samples were highly crystallized.

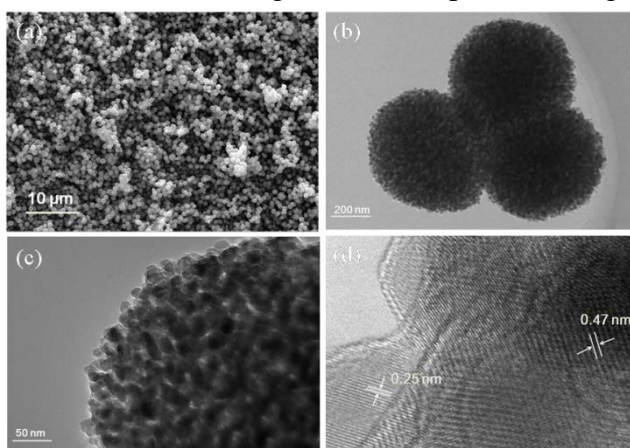


Figure 2. (a) SEM, (b, c) TEM and (d) HRTEM images of as-prepared CuCo_2O_4 microspheres.

Cyclic voltammetry (CV) was employed to investigate the ORR and OER activity of the synthesized CuCo_2O_4 microspheres in nonaqueous electrolyte as shown in Figure 3. The cyclic voltammogram shows a reduction peak, indicating the start of reaction at 2.92 V in the $\text{CuCo}_2\text{O}_4/\text{KB}$ battery, while at 2.76 V in the KB battery. The 0.16 V higher shift in the reduction potential is attributed to the catalytic effect of CuCo_2O_4 microspheres. Besides, the $\text{CuCo}_2\text{O}_4/\text{KB}$ battery shows a much obvious current density during anodic scans (>3.0 V). These results demonstrate efficient catalytic activity of CuCo_2O_4 for both the ORR and OER in aprotic media.

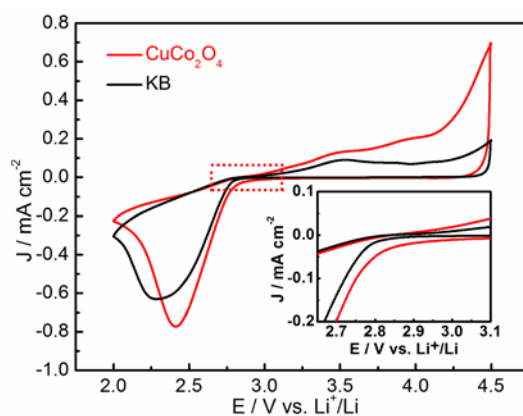


Figure 3. CV curves of CuCo₂O₄/KB and KB carbon-only electrode at a scan rate of 0.1 mV s⁻¹.

Given their favourable structures as demonstrated above, the multiporous CuCo₂O₄ microspheres were investigated as effective electrocatalysts for rechargeable Li-O₂ batteries. Both the applied current density (mA g⁻¹) and the achieved capacity (mAh g⁻¹) were calculated based on the mass of carbon (KB). For the galvanostatic discharge/charge test, the lower and upper cut-off voltage is 2.2 and 4.4 V (vs. Li), respectively.

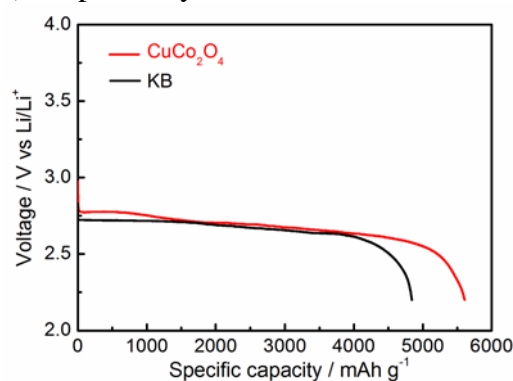


Figure 4. Discharge curves of Li-O₂ batteries at a current density of 100 mA g⁻¹ for CuCo₂O₄-based electrodes (a) and KB-based electrodes (b).

As can be seen in Figure 4, the Li-O₂ battery with CuCo₂O₄ electrode exerts specific capacities of 5607 mAh g⁻¹, which is higher than the battery with bare KB at a current density of 100 mA g⁻¹. To avoid the decomposition of electrolyte on the discharge products during the charge/discharge processes, the capacity-limited cycling method that has been adopted in the literature was used in this work [Peng Zhangquan,2012]. The cycling performance of the CuCo₂O₄ cathode was tested at a current density of 100 mA g⁻¹ under specific capacity limit of 500 mAh g⁻¹ (Figure 5a and 5b). Under this protocol, an energy density of 1350 Wh kg⁻¹ (500 mAh g⁻¹ × 2.7 V) can be achieved, which is about two times the energy density of commercial cathodes in Li-ion batteries (640 Wh kg⁻¹, 160 mAh g⁻¹ × 4 V) [Lim Hee-Dae,2013]. The CuCo₂O₄ electrode could be discharged and charged stably for at least 23 cycles above 2.0 V, on the contrary, the KB electrode can only keep less than 7 cycles. The improved cycling performance of CuCo₂O₄ cathode can be ascribed to the inherent catalytic activity of spinel-type CuCo₂O₄ and its multiporous structure [Liu Ying,2014]. This multiporous structures ensuring can provide many electrocatalytic sites and also promote the flow of gases and infiltration of the electrolyte, and eventually improve the cyclability greatly [Wang Hailiang,2012].

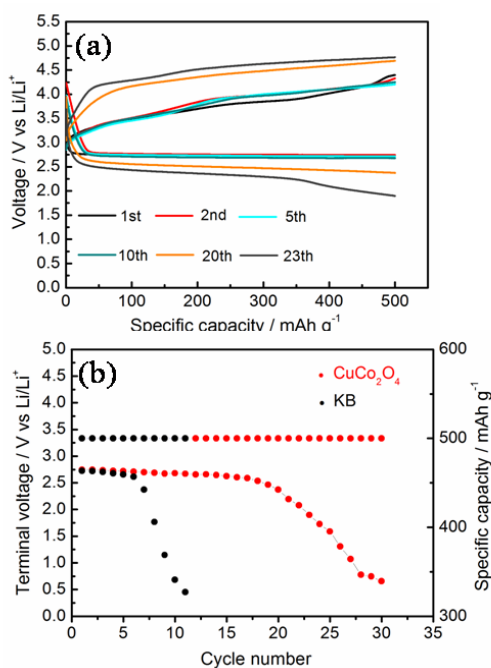


Figure 5. (a) Cycling response and (b) voltage of the terminal discharge vs cycle number of the Li-O₂ cell with the CuCo₂O₄/KB electrode under specific capacity limit of 500 mAh g⁻¹ at a current density of 100 mA g⁻¹.

4 CONCLUSIONS

In summary, we successfully fabricated multiporous CuCo₂O₄ microspheres via a facile solvothermal method. These samples were investigated as electrocatalyst materials for lithium-oxygen battery applications. Compared with the carbon-only electrode, the CuCo₂O₄/C electrode exhibits a significantly enhanced discharge capacity and cycling performance. These results highlight the promising application of such a low-cost multiporous oxide for high performance Li-O₂ batteries.

5 ACKNOWLEDGEMENTS

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