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A binder-free, flexible cathode for rechargeable Na-O_2 batteries

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ABSTRACT

Rechargeable Na-O_2 batteries have attracted significant attention as energy storage devices owing to their theoretically high energy storage capacity and the natural abundance of sodium. However, practical applications of this type of battery still suffer from low specific capability, poor cycle stability, instable electrolytes, and unstable polymer binders. Herein, we report a facile method of synthesizing binder free and flexible cathodes with Co_3O_4 nanowire arrays vertically grown onto carbon textiles. When employed as a cathode for Na-O_2 batteries, this cathode exhibits superior performance, including a reduction of charge overpotential, high specific capacity (4687 mAh/g), and cycle stability up to 62 cycles. These enhanced performance can be attributed to the synergistic effect of the porosity and catalytic activity of the Co_3O_4 nanowire catalyst.

1. Introduction

Rechargeable metal-air batteries have attracted significant attention as energy storage devices owing to their higher theoretical energy density than commercialized Li-ion batteries, especially non-aqueous Li-O_2 and Na-O_2 batteries [1–6]. Na-O_2 batteries are of particular interest as Na exhibits similar physicochemical properties to Li. Considering the limited Li resources that are inadequate to satisfy the increasing demand for batteries based on Li chemistry, many researchers call for using Na to replace Li owing to its abundance and inexpensive nature [7–9]. However, before the practical application of Na-O_2 batteries becomes a reality many significant technical challenges need to be overcome, such as poor rate capacities, low round trip efficiencies (caused by a high overpotential of both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER)), unstable electrolytes and polymer binders (which undergo side reactions), and short cycle lives [10,11]. And, similar to Li-O_2 batteries, the properties of the cathode material (such as morphology, specific surface area, structure, activity, and conductivity) play an important role in the performance of Na-O_2 batteries [12–15]. In response, many scientists have tried to overcome these above mentioned limitations by finding a suitable cathode catalyst to accelerate the ORR and OER kinetics of rechargeable Na-O_2 batteries. They tried to achieve this by adjusting the porous structure of the cathode catalyst to improve cycle stability through providing enough paths for oxygen and ion migration and enough sites for deposition of the discharge product. Additionally, researchers have tried tailoring the cathode structure to enhance its structural stability [16]. For example, carbon supported catalysts, such as mesoporous carbon, carbon fiber, and N-doped graphene

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nanosheets have been widely used as cathodes for Na-O_2 batteries owing to their enhanced electronic conductivity and catalytic activity [17–19]. In general, cathodes are prepared by coating a homogenous slurry containing conductive carbon powder, polymer binder (e.g. PVDF and PTFE), and catalyst onto the current collector. However, the carbon itself and the commonly used polymer binder are reported to be unstable, forming decomposition products during the discharge/charge process [20,21]. To solve these problems, the development of a binder free or non-carbon cathode is of great importance. Prioritizing the mechanical strength of the cathode, we chose carbon textiles as the base owing to their superior flexibility and excellent electrochemical stability.

Herein, we report a facile and efficient hydrothermal synthesis method to fabricate a flexible and binder free cathode with Co_3O_4 nanowire arrays vertically grown onto carbon textiles (this cathode is referred to as COCT throughout the rest of this manuscript). When employed as cathode in a Na-O_2 battery, the COCT cathode endows the Na-O_2 battery with lower overpotential, enhanced specific capacity of 4687 mAh/g (based on weight of Co_3O_4), and enhanced cycling performance (62 cycles).

2. Experimental

2.1. Material preparation

$Co(NO_3)_2·6H_2O$ and NH_4F were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Urea ($CO(NH_2)_2$), tretraethylene glycol dimethyl ether (TEGDME), and sodium triflate ($NaCF_3SO_3$) were purchased from Aladdin Reagent. Carbon textiles (CT) were purchased from Torray.

The COCT cathode was synthesized using a hydrothermal method. The CTs were ultrasonically cleaned several times with acetone, absolute ethanol, and distilled water and then dried at 60 °C in a vacuum oven for 12 h. The precursor solutions were obtained by dissolving a desired amount of mixed salt (the molar ration of $Co(NO_3)_2·6H_2O:NH_4F:CO(NH_2)_2$ = 1:1:2) into 40 mL distilled water at room temperature. After stirring for 1 h, the above solutions were transferred to a Teflon lined stainless steel autoclave (50 mL) and the cleaned CTs were immersed in the precursor solutions. Then the Teflon lined stainless steel autoclaves were heated at 120 °C for 5 h in an oven. After cooling down, the CTs were removed from the autoclaves and rinsed several times with deionized water and ethanol, then dried in a vacuum oven at 120 °C for 12 h. Finally, the samples were annealed in air at 400 °C for 2 h. The synthesis steps for COCT cathodes are schematically illustrated in Scheme 1.

2.2. Characterization

Powder X-ray diffraction (XRD) measurements were performed with a Bruker D8 Focus Powder X-ray diffractometer using Cu K_α radiation (40 kV, 40 mA). Scanning electron microscopy (SEM) was performed using a HITACHI S-4800 field mission scanning electron microscope. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were undertaken on a FEI Tacnai G2 electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried on a VG Scientific ESCALAB MKII X-ray photoelectron spectrometer.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on a Bio-Logic VMP3 electrochemical workstation. Na-O_2 battery measurements were cycled on a LAND CT2001AS2 multi-channel battery testing system.

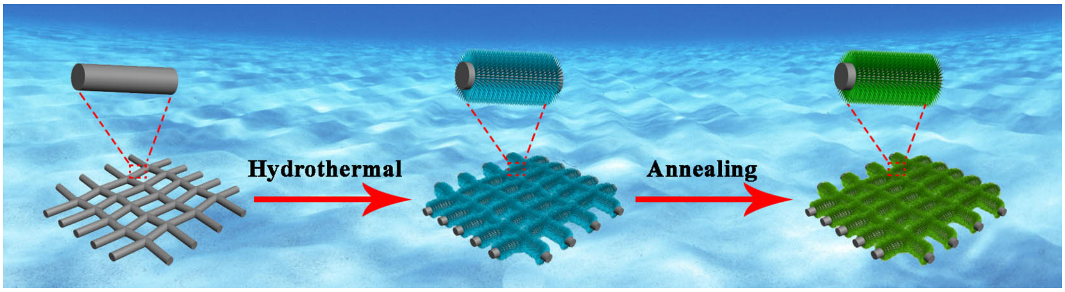
2.3. Na-O_2 battery preparation and electrochemical performance measurements

The electrochemical performance of COCT as a cathode in a Na-O_2 battery was tested using a coin2025 type cell. The cathodes were dried in a vacuum oven at 80 °C for 24 h. All batteries were assembled in a glove box under Ar atmosphere, using a sodium metal foil anode, glass fiber separator, oxygen cathode, and electrolyte containing 0.5 mol/L $NaCF_3SO_3$ in TEGDME. Galvanostatic discharge-charge tests were conducted within a voltage window of 1.8–4.2 V (vs. Na/Na^+) at ambient temperature after a 2–5 h rest period. EIS measurements of the cells were carried out using an AC impedance analyzer within a frequency range of 10^6 to 10^{-2} Hz. The CV curves were measured form 1.8 to 4.0 V at a voltage sweep rate of 0.5 mV/s.

3. Results and discussion

3.1. Materials characterization

We investigated the morphology and structure of the COCT cathode using SEM and TEM. Fig. 1(a) shows an SEM image of the pristine CT, revealing that the CTs are woven by carbon fibers with diameters of about 10 μm. Fig. 1(b) and (c) show



Scheme 1. Schematic illustration of the formation of Co_3O_4 NWs/carbon textiles composite.