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CNF-grafted carbon fibers as a binder-free cathode for Lithium–Oxygen batteries with a superior performance

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ABSTRACT

In this work, we report the significant enhancement of the electrochemical performance and flexibility of a lithium–oxygen battery by introducing a free-standing, binder-free carbon nano-fibers (CNF) grafted carbon paper cathode with a bimodal pore architecture. The small pore structures (~100 nm) accommodated Li₂O₂, and the large pore structures (~10 μm) enabled effective oxygen diffusion without clogging the pores. This kind of cathode overcame some troubles of the cathode prepared by spraying coating method, such as the low utilization of substrate surface, the unreasonable aperture structure and the aggregation of active carbon material. As a result, this electrode structure imparted stability to active sites during the recovery of discharge products to the initial state, providing long-term cyclability of more than 800 cycles in a 1 M LiTFSI/TEGDME electrolyte system. In addition, the battery output a discharge capacity as high as 20000 mAh g⁻¹ at 468 mA g⁻¹ and exhibited a charge/discharge rate as high as 1136 mA g⁻¹ (0.57 mA cm⁻²). The test results suggest that these CNF-grafted carbon papers have the potential to be used for oxygen/air electrodes for next-generation lithium-oxygen batteries, though the present results need to be improved to achieve performance of practical significance, namely with regard to (i) cathode mass loading to get higher areal capacity, and (ii) cycling performance at higher current density.

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Introduction

Current Lithium–ion batteries (LIBs) with insertion-compound electrodes fall short of the high power and energy densities demanded by multifunctional portable

electronic devices, electric vehicles, and grid storage. For this reason, in recent years non-aqueous lithium–oxygen batteries have received world-wide attention [1–4], since they can theoretically store about 5–10 times more energy than that of lithium–ion batteries [5]. And the oxygen can be absorbed from the environment during discharge, making these

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systems serious contenders to meet the rapid growing requirements.

During these years, as the literature reported [6–10], various electrolyte and electrode materials have been fabricated and tested. The reaction, degradation, and failure mechanisms have been investigated and proposed [11–13]. Advanced characterization techniques and devices have been developed and utilized. Although some breakthroughs have been made [14,15], the development of lithium–oxygen batteries is still in the early stage with many technical difficulties, such as the relatively low obtainable discharge capacity, poor rate capability, low energy efficiency, and limited cycle life.

In the past decade, amount of review papers about lithium–oxygen batteries have been published, and many of them focused on the materials and structures of air electrode [2,3,6,14,16]. In lithium–oxygen batteries carbon-based materials have been extensively studied as cathode materials, and it can be classified into three main groups: commercial carbon materials (Ketjen Black, activated carbon, Super P, etc.) [17–19], functional carbon materials (carbon nanotubes, carbon nanofibers, carbon microfibers, graphene, etc.) [6,20,21], and heteroatom doping carbon materials (N-, P-, S-, doped carbon) [22–24]. It was found that the carbon materials with high mesopore volume, and preferably high surface area, should lead to high specific capacity. Spraying coating as a common method is usually used to prepare lithium–oxygen battery cathodes. However, it is proved that the pore spaces of cathode are easily blocked up during preparation due to the closed-packing nano-materials [25]. In addition, the inevitable application of binder is easy to cause a series of problems, such as surface loss, mass addition, and stability degradation. For example, carbon black, the porous structure is built from carbon black aggregates, which are closely bound together by the binder to form agglomerates. The agglomerate structure unavoidably results in a low- O_2 diffusion rate and limited space for Li_2O_2 deposition [26–28]. To address these issues, in this report we propose to fabricate a cathode via a chemical vapor deposition (CVD) method, where carbon nano-fibers (CNF) were uniformly grown onto commercial carbon papers. Through this method, we can totally utilize the exposed surface of cathode supports and improve the availability of commercial carbon papers. Moreover, the grafted CNF form holes with different apertures, which improve the utilization of void volume of commercial carbon papers leading to a substantially enhanced discharge capacity. The fibrous network of CNF together with cathode support (carbon paper) is also beneficial for retaining the conductive network in the electrode during the deposition/decomposition of the discharge solid-state products. The morphologies of the CNF-grafted cathodes before and after discharge were examined, and the chemical composition of the product was also detected. The rate and cycle performance of the battery with the composite cathode were tested. These experimental results demonstrated that CNF grafted on carbon fibers can be a promising solution to increase the discharge capacity and enhance the reversibility of the air cathode.

Experimental

Synthesis of carbon nano-fibers (CNF) grafted carbon paper

All the chemicals used herein were of analytical purity and used as received without further purification. The CNF was grown directly onto a commercial carbon paper (Hesen, China) by a chemical vapor deposition (CVD) method according to the literature [29,30]. It is known that particle-like active catalytic sites are required for the growth of CNF. The objective of the substrate pre-treatment method is to generate these favorable growth sites, and $Ni(NO_3)_2 \cdot 6H_2O$ (99%, Aladdin) was used as the growth catalyst precursor here. The carbon paper was first soaked into a 0.025 M ethanol solution of $Ni(NO_3)_2 \cdot 6H_2O$, and dried at 100 °C in air for 5 min. After that, many nanoparticles were coated onto the carbon paper uniformly. The carbon paper substrate with catalyst precursor was then placed on an Al_2O_3 boat locating in the center of a quartz tube. Before heat procedure, the protecting gas of Ar (99.999% in purity) was introduced into the tube to let inside air to exchange with Ar. The system was then heated to 700 °C with a heating rate of 50 °C min^{-1} under 15% H_2+Ar . Before CNF deposition, the system was first held at the temperature of 700 °C for 10 min under 50% H_2+Ar in order to reduce precursor to active Ni. CNF was then growing onto carbon paper at the 700 °C, where C_2H_2 was adjusted to 10 sccm and kept for 30 min. Finally, the battery with CNF-grafted carbon paper cathode was assembled in an Ar-filled glove box (Braun, Germany) with O_2 and H_2O levels both below 0.05 ppm. The lithium–oxygen battery was constructed consisting of a commercial Li metal foil (Tansworld Enterprises LTD, China), a glass-fiber separator (Whatman GF/C, America), and the CNF-grafted carbon paper cathode with a diameter of 15 mm 50 μl electrolyte (1 M LiTFSI/TEGDME, Suzhou Chemical Reagent LTD, China) was added in the battery to fully wet the separator and the cathode.

Characterizations

The microstructure of the composite cathode was observed using a field-emission scanning electron microscopy (SEM, Hitachi S-4700). The constituent of CNF-grafted carbon paper was demonstrated and recorded by a Rigaku X-ray diffractometer (XRD, D/max-Ultima IV). In this study, two kinds of cathodes with different CNF loadings were prepared by soaking carbon paper into 0.025 M $Ni(NO_3)_2 \cdot 6H_2O$ solution with different times. By means of weighting the difference before and after the CNF deposition, CNF loadings were determined by 0.18 $mg\ cm^{-2}$ for soaking one time and 0.50 $mg\ cm^{-2}$ for soaking four times, respectively. The mass of CNF was also confirmed by a thermo-gravimetric analysis (TG, TA SDT2960, USA). In this work, all the specific capacities were calculated with respect to CNF loadings, while the current densities were calculated with respect to CNF loadings and/or cathode area.

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