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Binder-free nitrogen-doped carbon paper electrodes derived from polypyrrole/cellulose composite for Li–O_2 batteries

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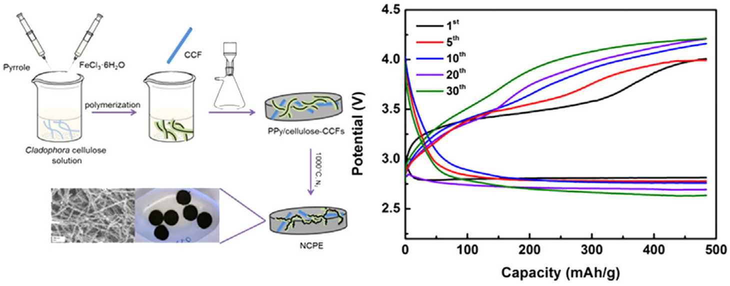
HIGHLIGHTS

- The fabrication of NCPE involves cheap raw materials and easy operation.
- The NCPE holds a bird's nest microstructure and N-containing function groups.
- A Li–O_2 cell with NCPE shows a low overpotential and considerable cyclability.
- Using metal-free and binder-free NCPE could avoid some parasitic reactions.
- The metal-free and binder-free electrode design can increase the energy density.

GRAPHICAL ABSTRACT



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ABSTRACT

This work presents a novel binder-free nitrogen-doped carbon paper electrode (NCPE), which was derived from a N-rich polypyrrole (PPy)/cellulose-chopped carbon filaments (CCFs) composite, for Li–O_2 batteries. The fabrication of NCPE involved cheap raw materials (*e.g., Cladophora* sp. green algae) and easy operation (*e.g.,* doping N by a carbonization of N-rich polymer), which is especially suitable for large-scale production. The NCPE exhibited a bird's nest microstructure, which could provide the self-standing electrode with considerable mechanic durability, fast Li^+ and O_2 diffusion, and enough space for the discharge product deposition. In addition, the NCPE contained N-containing function groups, which may promote the electrochemical reactions. Furthermore, binder-free architecture designs can prevent binder-involved parasitic reactions. A Li–O_2 cell with the NCPE displayed a cyclability of more than 30 cycles at a constant current density of 0.1 mA/cm^2. The 1st discharge capacity for a cell with the NCPE reached 8040 mAh/g at a current density of 0.1 mA/cm^2, with a cell voltage around 2.81 V. A cell with the NCPE displayed a coulombic efficiency of 81% on the 1st cycle at a current density of 0.2 mA/cm^2. These results represent a promising progress in the development of a low-cost and versatile paper-based O_2 electrode for Li–O_2 batteries.

1. Introduction

The rechargeable Li–O_2 battery has recently attracted a great deal of attention because of its significantly higher theoretical

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energy density than traditional lithium-ion battery [1,2,4,5]. A Li–O_2 battery prototype is composed of a lithium metal anode, Li^+-containing nonaqueous electrolyte, and a porous O_2 cathode (normally carbon-based materials with or without catalysts). The key electrochemical reaction in a Li–O_2 battery is $2Li + O_2 \rightleftarrows Li_2O_2$, with a discharge process (oxygen reduction reaction (ORR)) and a charge process (oxygen evolution reaction (OER)) [6]. Although Li–O_2 batteries exhibit a great potential and much progress has been made, the main issues to be addressed are: 1) How to find a long-term stable electrolyte with high O_2 solubility and diffusion; 2) How to design a stable O_2 electrode with excellent electrocatalysts; 3) How to prevent the dendrite formation on the Li metal surface; 4) How to protect the electrodes from CO_2 and H_2O.

The energy storage capacity, rate capacity, and cycle life are strongly determined by the materials and architecture of the O_2 electrode [8]. Carbonaceous materials have been employed as fillers to provide the cathode with porosity and electronic conductivity [9]. It has been well established that a good carbon candidate for Li–O_2 batteries should have characteristics as follows: i) appropriate pore size/volume; ii) large surface area, and iii) high stability. So far, various carbon materials have been systematically studied for Li–O_2 batteries, such as commercial carbon powders [10], one-dimensional carbon nanomaterials [11], two-dimensional graphene [12], mesoporous carbon materials [13], and carbon hybrids and composites [14–16]. To promote the electrochemical performance, the incorporation of heteroatoms in a well-defined way is regarded as a feasible strategy to modify the nature and chemical properties of pure carbon [9]. Among those heteroelements, nitrogen (N), having a comparable atomic size to carbon and five valence electrons for bonding with the carbon atom, has been widely adopted [17,18]. N-doped carbon can not only improve the Li + diffusion and transfer by generating defects and by withdrawing electrons from the carbon atom, but also increase the conductivity of the resulting carbon, which can exhibit a better battery performance than pure carbon materials [19–22]. Many approaches have been reported for the synthesis of N-doped carbon [22–24]. Those synthetic routes normally require multiple or complicate steps, with low yield and high cost, which inevitably limit large-scale fabrication. Therefore, to obtain high-performance N-doped carbon by an easy-to-operate and low-cost method is really a challenge.

Besides the stability of electrolyte, the composition and architecture of the O_2 electrode also influences the performance of Li–O_2 batteries. Typically, a N-doped carbon-based electrode consists of N-doped carbon powder, polymer binder, and catalyst. The multiple components complicate the cell preparation and the electrochemical reactions, and also impose the challenges on the analysis. In addition, carbon particles in an electrode using chemical binder sometimes display a tight aggregation, which inevitably decreases the O_2 diffusion and limits the space for Li_2O_2 deposition. This consequently leads to a limited capacity and a low energy efficiency of the Li–O_2 battery [25]. Moreover, the binder degradation can clog the O_2 electrode surface and then reduce the space for the desired discharge product Li_2O_2 [7]. Binder-free O_2 electrode, designed to avoid the negative influence of the binder, has been reported and recognized as an appealing alternative for Li–O_2 batteries [18,25,27–29]. We have developed a straightforward approach to the manufacture of sustainable paper electrodes based on a high-porous polypyrrole (PPy)/*Cladophora* cellulose composite, and thus the possibility to use the carbonized derivative as binder-free electrodes for Li–O_2 batteries is highly appealing [30–33].

Herein, we report a novel design of a binder-free N-doped carbon paper electrode (NCPE) in the Li–O_2 battery derived from a N-rich PPy/cellulose-chopped carbon filaments (CCFs) composite. The synthetic strategy combines the low-cost and easily accessible raw materials, and a facile operation. The NCPE displays a bird's nest microstructure, which can provide the electrode with considerable mechanic durability, fast Li^+ and O_2 diffusion, and enough space for the discharge product deposition. The rate performance, coulombic efficiency, and cyclability of the Li–O_2 batteries with NCPEs were investigated. The function of the NCPEs is related to their N-containing function groups and self-standing bird's nest microstructure. We expect that this new designed NCPE can be manufactured and used as an electrode material for broad applications (*e.g.,* Li-ion batteries, fuel cells, supercapacitors, *etc.*).

2. Experimental

2.1. Materials

All chemicals were of analytic grade and used as received without any further purification. *Cladophora* green algae was collected from the Baltic Sea, and the *Cladophora* nano-cellulose was extracted from the algae by grinding and acid hydrolysis as previously described [34]. Iron (III) chloride nonahydrate ($FeCl_3 \cdot 6H_2O$), hydrochloric acid (HCl) and pyrrole (Py) were purchased and used as delivered from Sigma-Aldrich. The carbon filaments (CFs) were obtained from Goodfellow, UK. The CFs were simply chopped with a kitchen herb-cutter knife on a wooden block so as to obtain a fluffy mass consisting of individual CCFs with a maximum length of 5 mm. 1 M lithium perchlorate ($LiClO_4$, GFS, $\geq$ 99%) in dimethyl sulfoxide (DMSO, Aldrich, $\geq$ 99.9%) was prepared as electrolyte in the Li–O_2 battery.

2.2. Preparation of the NCPE

Cladophora cellulose (200 mg) was dispersed in water (40 mL) by sonication for 10 min with water cooling. The sonication was carried out with a high-energy ultrasonic equipment (Sonics and Materials Inc., USA, Vibra-Cell 750) at an amplitude of 30% with a pulse length of 30 s and pulse-off duration of 30 s. Pyrrole (0.65 mL) and 0.5 M HCl (40 mL) were mixed with the cellulose dispersion by magnetic stirring for 5 min. PPy was then formed on the *Cladophora* cellulose fibers *via* polymerization with $FeCl_3 \cdot 6H_2O$ (5.9 g) dissolved in 0.5 M HCl (40 mL) as an oxidant. The polymerization proceeded for 30 min under stirring, after which the composite was collected in an Büchner funnel connected to a suction flask, and washed with 0.5 M HCl (3 L) and 0.1 M HCl (0.5 L). The PPy/cellulose composite precursor has been extensively characterized in our previous work [30–32]. The PPy/cellulose composite and 200 mg of CCFs were suspended in 200 mL of water using a mechanical homogenizer (IKA T25 Ultra-Turrax, Germany) at 6200 rpm for 10 min. The mixture was drained on a polypropylene filter and then dried to form a PPy/cellulose-CCFs paper sheet. As-prepared paper was heated to 1000 °C at a heating rate of 3 °C/min and kept for 1 h under a nitrogen atmosphere to form the NCPE. The schematic illustrating of the synthetic procedure of the NCPE is shown in Scheme 1. The obtained NCPE was then punched into a disc with a diameter of 1.2 cm for directly using as an O_2 electrode (Fig. S1a in Supplementary Information (SI)). In addition, in order to investigate the influence of the doping N on the Li–O_2 battery performance, a reference precursor of cellulose-CCFs paper sheet was also prepared under the similar conditions without the addition of PPy. Thus an undoped carbon paper electrode was obtained after annealing.