



Boron-doped Ketjenblack based high performances cathode for rechargeable Li–O₂ batteries

Yueyan Li^a, Li Wang^b, Xiangming He^{b,*}, Bin Tang^c, Yunxue Jin^{a,*}, Jianlong Wang^b

^a Faculty of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, Jiangsu, China

^b Institute of Nuclear & New Energy Technology, Tsinghua University, Beijing 100084, China

^c Jiangsu Huadong Institute of Li-ion battery, Zhangjiagang 215600, Jiangsu, China

ARTICLE INFO

Article history:

Received 28 April 2015

Revised 23 June 2015

Accepted 23 June 2015

Available online 3 September 2015

Keywords:

Li–O₂ battery

Rechargeable

Discharge capacity

Boron-doped Ketjenblack

Oxygen reduction

ABSTRACT

Boron-doped Ketjenblack is attempted as cathode catalyst for non-aqueous rechargeable Li–O₂ batteries. The boron-doped Ketjenblack delivers an extremely high discharge capacity of 7193 mAh/g at a current density of 0.1 mA/cm², and the capacity is about 2.3 times as that of the pristine KB. When the batteries are cycled with different restricted capacity, the boron-doped Ketjenblack based cathodes exhibits higher discharge platform and longer cycle life than Ketjenblack based cathodes. Additionally, the boron-doped Ketjenblack also shows a superior electrocatalytic activity for oxygen reduction in 0.1 mol/L KOH aqueous solution. The improvement in catalytic activity results from the defects and activation sites introduced by boron doping.

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1. Introduction

Non-aqueous rechargeable Li–O₂ batteries are promising for energy storage systems because of their excellent energy density [1,2]. However, the practical specific capacity is very limited when compared with the theoretical due to the high irreversibility and poor kinetics of the cathode reaction. Many factors, such as electrolyte, structures of carbonaceous materials and oxygen reduction catalysts, show great effect on the deliverable energy density of a Li–O₂ battery [3,4]. The porous oxygen cathode plays an important role in the oxygen reduction reaction (ORR) during discharge process [5], however the ORR is too sluggish [6], that it usually requires metal oxides or noble metal catalysts to enhance the kinetics. The noble metal catalysts like Pt is confirmed to be effective, however its widespread use is impeded due to its high cost and limited nature resource [7]. Therefore, there is a great incentive to find cheap, stable and more effective metal-free ORR catalysts to retain a high discharge voltage.

To date, various carbon materials have been prepared for air cathodes, including Super P, Ketjen Black (KB), carbon nanotubes and graphene. However, their pristine forms are deficient to satisfy specific demands for lots of different applications [8–10]. It has been

proved that substitutional doping of heteroatoms in the graphitic lattice is an effective way to optimize the material properties [11,12]. Since B and N have small size mismatches, they are the most popular heteroatoms when compared with the other doping elements (P, S, Si) [13]. For instance, N-doped carbon materials have drawn much attention because conjugation between the nitrogen lone-pair electrons and graphene π -systems can significantly enhance the ORR activity [14]. More recently, Zhang and co-workers have successfully prepared B-doped graphene (BG) by a thermal annealing approach [15]. The product BG has been demonstrated to show better ORR electrocatalytic activity than pristine graphene. Furthermore, Zhang and co-workers synthesized B/N co-doping graphene (BCN), which exhibited superior electrocatalytic activities to the commercial Pt/C electrocatalyst [16]. The excellent electrochemical performance of BCN could be attributed to the defects and functional groups as active sites arising from the N and B co-doping doping. Taken together, the above doped materials have been widely used as metal-free catalysts for fuel cells and metal–air batteries. We noticed that there were only a few reports focusing on the performance improvement of B-doped carbon materials as cathode materials for Li–O₂ batteries, such as the discharge platform and rate capability.

Herein, for the first time, we successfully prepared B-doped KB (B-KB) and employed the material as cathode catalyst for Li–O₂ battery. The result showed that the B-KB not only exhibited excellent electrocatalytic activity for ORR but also delivered an extremely high discharge capacity and stable discharge platform.

* Corresponding authors. Tel: +86 10 62794226; Fax: +86 10 89796031.

E-mail addresses: hexm@tsinghua.edu.cn (X. He), jinyunxue@126.com (Y. Jin).

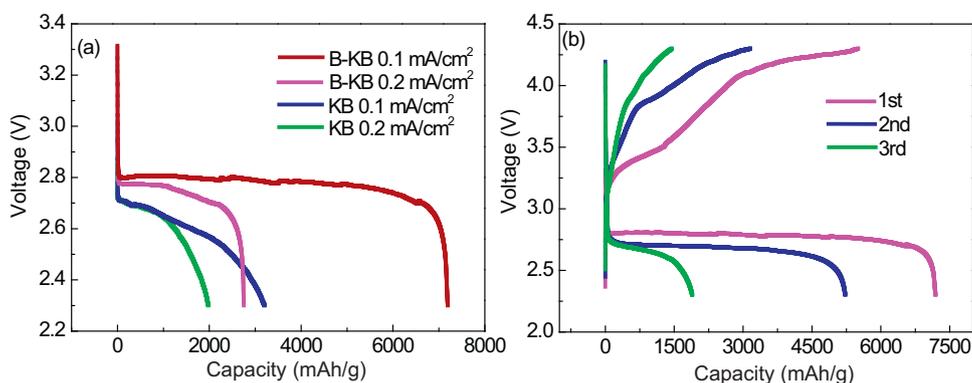


Fig. 1. (a) Initial discharge curves of the KB and B-KB cathodes between 2.3 and 4.3 V at various current densities, (b) full discharge/charge curves of B-KB between 2.0 and 4.3 V at 0.1 mA/cm².

2. Experimental

2.1. Materials

Initially, commercial Ketjenblack (KB) EC600JD was washed with 6 mol/L HCl solution for the removal of metal impurities. Then, the carbon materials were oxidized with 70 wt% HNO₃ for 6 h and then re-washed and filtered, followed by drying in an oven at 80 °C.

To prepare B-KB, the oxidized KB and boric acid (H₃BO₃) in a weight ratio of 1:5 were mixed and ground in a mortar, and the mixture was then placed in the center and heated at 900 °C for 4 h. After being cooled down to room temperature in Ar atmosphere, the products were refluxed in deionized water at 85 °C for 6 h to extensively remove excessive boric oxides and were then filtered and finally dried in vacuum.

2.2. Physical characterizations

Morphologies of the KB and the B-KB were examined using scanning electron microscopy (SEM, JSM-6701F, JEOL, Japan). The X-ray diffraction (XRD) spectra were recorded using Rigaku D/MAX2400 diffractometer (Japan, Cu K α radiation). The X-ray photoelectron spectroscopy (XPS, PHI-5702, Physical Electronics, USA) was used to confirm the composition and the state of boron and carbon in the samples. The Fourier transform infrared spectroscopy (FTIR) spectra were collected on NicoletMAGNA-560, using KBr pellets. The defects, ordered and disordered structures were characterized by Raman spectroscopy (Jobin Yvon LabRam HR800, excited by 632.8 nm He–Ne red laser).

2.3. Electrochemical measurements

A catalyst paste was prepared by casting a slurry mixture of B-KB, KB and polytetrafluoroethylene (PTFE) in a ratio of 8:1:1, and the mixture was roller-pressed into a stainless steel sheet. Comparative electrodes made with KB and PTFE in a weight ratio of 9:1 were also prepared in a similar way. Swagelok type cells were employed for charge/discharge tests. The electrolyte was 1 mol/L LiTFSI (99.995% pure) in TEGDME (Triethylene glycol dimethyl ether, Aldrich). The cells were cycled using LAND-CT2001A testers in a voltage range of 2.3–4.3 V at different current densities. All the electrochemical measurements were carried out in a dry and pure oxygen atmosphere at 25 °C.

3. Results and discussion

The discharge and charge measurements of KB and B-KB electrodes were performed in the voltage range of 2.3–4.3 V. As shown

in Fig. 1(a), the initial discharge capacity and average operating voltage at the current density of 0.1 mA/cm² were 7193 mAh/g and 2.8 V for B-KB cathode, while 3202 mAh/g and 2.6 V for the pristine KB. With the current density increasing, the achieved capacities dropped significantly. The discharge capacities of both samples decreased to 2752 and 1979 mAh/g for B-KB and KB at the current density of 0.2 mA/cm², respectively. B-KB electrodes not only delivered higher discharge capacity but also exhibited higher average discharge plateau than KB electrodes at different discharge current densities, demonstrating a superior ORR activity. Fig. 1(b) shows the cycling performance of Li–O₂ battery at a current density of 0.1 mA/cm² using B-KB as the cathode supporting material. The cathode delivered an initial discharge capacity of 7193 mAh/g, and then the capacity rapidly decayed to 1894 mAh/g within three cycles. The electrode exhibited unsatisfactory cycleability under this condition, which could be attributed to the accumulation of the discharge products and instability of the electrolyte in the deep discharge process.

In order to avoid the over-growth of discharging products, the batteries were tested with a limited capacity at the current density of 0.1 mA/cm². The KB cathodes were tested for comparison, and it showed only 9 cycles with a cycling capacity of 600 mAh/g (Fig. 2a). The discharge platform and cutoff voltage of the cell at the discharge state obviously dropped in every cycle, as shown in Fig. 2(b). When cycled with different limited capacities (600 mAh/g, 1000 mAh/g and 2000 mAh/g) at a current density of 0.1 mA/cm², as shown in Fig. 3, the cells exhibited more excellent cycle ability than those of KB cathodes. In detail, the reversible capacity kept well for 23 cycles with 600 mAh/g capacity limitation, 14 cycles with 1000 mAh/g capacity limitation and 7 cycles with 2000 mAh/g capacity limitation. Moreover, B-KB cathodes also showed higher average operating voltage and lower overpotential than KB. The discharge platform and cutoff voltage of the B-KB cathode based cells at the discharge state showed a similar trend to those of KB, although the voltage still decreased, the decreasing rate was slower. This phenomenon also suggested that by limiting the depth of discharge, the cycle ability of the Li–O₂ battery could be improved. The main reason is that the increasing rate of the electrode resistance is slower by restricting discharge capacity, and which means the charge process could overcome the partially choked air cathode and the decomposition of Li₂O₂ and Li₂O recovers the porosity and makes the subsequent cycle possible [3].

To further confirm the superior catalytic activity of B-KB to KB, ORR in aqueous solution is investigated. Cyclic voltammograms of the electrochemical reduction of O₂ at KB/GCE and B-KB/GCE in O₂ saturated 0.1 mol/L KOH aqueous solution were collected in a three-electrode system (GCE or modified GCE as the working electrode, a Pt wire as counter electrode, and an Ag/AgCl as the reference). As

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