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Full paper

B_4C as a stable non-carbon-based oxygen electrode material for lithium-oxygen batteries

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ABSTRACT

Lithium-oxygen ($Li-O_2$) batteries have extremely high theoretical specific capacities and energy densities when compared with Li-ion batteries. However, the instability of both electrolyte and carbon-based oxygen electrode related to the nucleophilic attack of reduced oxygen species during oxygen reduction reaction and the electrochemical oxidation during oxygen evolution reaction are recognized as the major challenges in this field. Here we report the application of boron carbide (B_4C) as the non-carbon based oxygen electrode material for aprotic $Li-O_2$ batteries. B_4C has high resistance to chemical attack, good conductivity, excellent catalytic activity and low density that are suitable for battery applications. The electrochemical activity and chemical stability of B_4C are systematically investigated in an aprotic electrolyte. $Li-O_2$ cells using B_4C-based air electrodes exhibit better cycling stability than those using carbon nanotube- and titanium carbide-based air electrodes in the electrolyte of 1 M lithium trifluoromethanesulfonate in tetraglyme. The performance degradation of B_4C-based electrode is mainly due to the loss of active sites on B_4C electrode during cycles as identified by the structure and composition characterizations. These results clearly demonstrate that B_4C is a very promising alternative oxygen electrode material for aprotic $Li-O_2$ batteries. It can also be used as a standard electrode to investigate the stability of electrolytes.

1. Introduction

Lithium-oxygen ($Li-O_2$) batteries have attracted significant research attention in recent years due to their much higher theoretical energy density than conventional Li-ion batteries [1–5]. However, there are still many important material challenges that need to be addressed before the successful development of aprotic $Li-O_2$ batteries [4–10]. The instability of both electrolyte and carbon-based oxygen electrode caused by the nucleophilic attack of reduced oxygen species during oxygen reduction reaction (ORR) and the electrochemical oxidation during oxygen evolution reaction (OER) have been regarded as the major challenges in this battery system. Unfortunately, the development of stable battery components is relatively hysteretic. Although ether-based electrolytes and carbon-based oxygen electrodes have been widely used by many research groups, the side reactions of these two components have been regarded as the main degradation mechanisms in these batteries. $Li-O_2$ batteries using carbon-based oxygen electrodes with high specific capacities (> 1000 mA h g^{-1}_C) are usually based on low loading of carbon (< 1 mg cm^{-2}), thus the total capacities delivered are still low. The possible parasitic reactions of carbon during ORR are shown in Eqs. (1) and (2) [11].

$$Li_2O_2 + C + 1/2O_2 \rightarrow Li_2CO_3 \quad (1)$$

$$2Li_2O_2 + C \rightarrow Li_2O + Li_2CO_3 \quad (2)$$

In OER, carbon will be oxidized when the voltage exceeds 3.5 V or even throughout the charge process [12,13]. The voltage required for electrochemical decomposition of side reaction products is high, for instance, the voltage for Li_2CO_3 decomposition is predicted to be 4.38–4.61 V and that for LiOH is even higher [14]. Both electrolyte and carbon electrode will be oxidized under such a high voltage and lead to irreversible capacity loss and low Coulombic efficiency (CE) [11,15]. Although many effective OER catalysts, either solid or soluble [16–23], have been developed to reduce the charge voltage in favor of carbon-based oxygen electrodes, the parasitic reactions still exist which raise the charge voltages continuously [23,24]. The surface of solid catalysts

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can be covered by side reaction products and lose active sites during cycling. The soluble catalysts, so-called mediators can chemically decompose the discharge products more effectively since they are able to diffuse through the electrode. However, the oxidized mediators may react and corrode Li metal anode. Furthermore, unlike solid catalysts, the mediators actually partially react with the discharge products. To deliver more capacity requires more mediators. When the mass of the mediator is involved in gravimetric specific capacity, the specific capacity of such Li-O_2 batteries will be decreased manifold. Most recently, a stable non-carbonaceous electrolyte has been developed for Li-O_2 batteries, but the use of carbon based cathode still causes the formation of Li_2CO_3 and cell failure after tens of cycles [25]. Therefore, the development of non-carbon based cathode materials is of great importance for pursuing stable operation of Li-O_2 batteries.

Non-carbon based oxygen electrodes are normally composed of non-carbon based catalysts with or without binder. They have to satisfy several requirements simultaneously, including sufficient electronic conductivity, low density, chemical and electrochemical stability during operation, low cost, etc. A recent review has summarized the advancement in this field during the last a few years [26]. Due to the large difficulties in achieving all the above requirements, only a few materials such as metal oxides (Co_3O_4, MnO_2, RuO_2, and Ti_4O_7) [27–30], precious metals (Au and Ru) and carbides have been reported [31–33]. Metal oxides often have high density and low electronic conductivity and are therefore preferably prepared on conductive substrates. The active sites reside only at the surface of the catalysts. Precious metals and carbides with higher conductivities can be used as oxygen electrode materials alone. However, the high cost and density of precious metals hinder their applications. Carbides possess low cost and good catalytic activities for ORR and OER. Titanium carbide (TiC) was reported to show a high performance in a dimethyl sulfoxide (DMSO)-based electrolyte, owing to its high electronic conductivity and protective oxide surface layer [33]. However, the catalytic activity of TiC strongly depends on the thickness of oxide layers [1,2,25,34], which makes the evaluation of this material obscure and complicated. Additionally, it has been reported that TiC has a lower stability than carbon-based materials in tetraglyme-based electrolytes [24].

Boron carbide (B_4C) is a lightweight refractory material (~2.5 g cm^{-3} in density, close to that of carbon and nearly the half of that of TiC) with low cost [35,36]. It is highly resistive against chemical attack and can be therefore a good electrode material for batteries and fuel cells [37–39]. In our previous work, B_4C was used to prepare a core-shell structured Si/B_4C composite as a Li-ion battery anode [40]. Recently, a B_4C nanowire and carbon nanotube (CNT) composite has also been used as the oxygen electrode material for aprotic Li-O_2 batteries, showing a very high capacity (16,000 mA h $g^{-1}_{composite}$), high discharge voltage plateau (2.73 V) and stable cycling performance for 120 cycles under a capacity limited protocol at 1000 mA h $g^{-1}_{composite}$ [41]. The excellent performance is attributed to the high catalytic activity of B_4C nanowires towards ORR and OER. Though B_4C has shown promising characters, to the best of our knowledge, the application of this material in Li-O_2 batteries is really rare and so far no investigation on B_4C as non-carbon based cathode material has been reported yet. In this work, the battery performance of non-carbon based B_4C oxygen electrode is systematically investigated for aprotic Li-O_2 batteries and compared with those using CNT and TiC electrodes.

2. Experimental

2.1. Materials

B_4C (45–55 nm particle size, > 99% purity) and TiC (40 nm particle size, 99% purity) were commercial products purchased from US Research Nanomaterials and SkySpring Nanomaterials, respectively. The resistances of B_4C and TiC are about 0.3–0.8 Ω cm [42], corresponding to the electronic conductivities of 1.25–3.33 S cm^{-1}. CNT was purchased from Cheap Tubes Inc. and the electronic conductivity is > 100 S cm^{-1} [43]. NH_4HCO_3 powders (99% purity) and PTFE suspension (60%) were ordered from Sigma-Aldrich and DuPont, respectively. Tetraethylene glycol dimethyl ether (Tetraglyme) and lithium trifluoromethanesulfonate (LiTf) of battery grade were purchased from BASF Corporation. Li chips (0.25 mm thick, 15 mm diameter) were obtained from MTI Corporation.

The oxygen electrode was composed of catalyst (B_4C, TiC or CNT, respectively) and PTFE binder without any other electronically conductive additive or other catalyst. Briefly, B_4C (or TiC, CNT) nanoparticles and NH_4HCO_3 powders were mixed with PTFE in a mixture of isopropanol and deionized water (mass ratio: 2:1) to form a slurry. The weight ratio of catalyst with PTFE is from 90:10 to 97:3. NH_4HCO_3 powders were used as pore formers and their content was 15 wt% of the total weight of catalyst and PTFE. The slurry was stirred vigorously until forming a uniform paste and then coated onto a 316 stainless steel wire cloth (100 mesh, purchased from McMaster-Carr) to form the electrode. After the electrode was dried at 60 °C in a vacuum oven for 12 h, it was annealed at 300 °C for 1 h in argon (Ar) to remove the pore former. Typical loading of B_4C, TiC or CNT in PTFE bound electrodes was 3–5 mg cm^{-2}. The geometric area of oxygen electrode was about 1 cm^2.

Li-O_2 batteries were assembled in coin cells (CR2032) with holes on cathode case in an Ar filled glovebox (MBraun Inc.) using Li metal chip as the anode, B_4C, TiC or CNT electrode as the cathode, 1 M LiTf in Tetraglyme as the electrolyte and one piece of glass fiber (Whatman glass fiber B) as the separator. Glass fiber separators were dried at 300 °C for 24 h prior to use. The volume of the electrolyte applied was 100 μL. The assembled cells were loaded into gas-tight Teflon containers (with a volume of about 226 cm^3). Then the Teflon containers were transferred out of the glovebox and filled with ultrahigh purity O_2 (1 atm).

2.2. Electrochemical measurements

The cells were equilibrated at open circuit for 3 h before testing. The discharge-charge test was typically carried out in capacity-controlled mode at a current density of 0.1 mA cm^{-2} with a cut-off voltage range of 2.0–4.7 V at room temperature on an Arbin BT-2000 battery tester. The specific capacity shown in this article is based on the mass of cathode material which is B_4C, TiC or CNT, respectively. The electrochemical impedance spectra (EIS) were measured using a two-electrode mode on a Solartron 1287 electrochemical workstation coupled with a Solartron 1255B frequency analyzer. All impedance data were collected in the frequency range of 100 kHz to 0.1 Hz at open circuit voltage (OCV). The applied signal was a sinusoidal potential of 10 mV amplitude. After the cycling test, the cells were transferred back into the glovebox and disassembled for the ex-situ analyses. The oxygen electrodes and Li-metal anodes were separately washed with anhydrous 1,2-dimethoxyethane (DME) for several times to remove the residual electrolyte thoroughly, and then dried under vacuum.

2.3. Characterizations

Samples for powder X-ray diffraction (XRD) analysis were sealed in thin-walled glass capillary tubes (500 μm diameter, 10 μm wall thickness, Charles Supper Co., MA) under inert gas. A Rigaku D/Max Rapid II micro-diffraction system with a rotating Cr target (λ = 2.2910 Å) operated at 35 kV and 25 mA was used to collect the diffraction patterns. A parallel X-ray beam collimated to 300 μm diameter was directed onto the specimen and the diffracted intensities were recorded on a large 2D image plate during a 5 min exposure. Electrode samples were mounted on adhesive tape and loaded into a Bruker protective atmosphere holder in an argon glovebox. The sample holder was placed in a PanAlytical X'Pert Bragg-Brentano diffractometer and XRD data collected from 5° to 100° using Cu Kα radiation. Phases were identified