B₄C as a stable non-carbon-based oxygen electrode material for lithium-oxygen batteries

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ABSTRACT

Lithium-oxygen (Li-O₂) 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 (B₄C) as the non-carbon based oxygen electrode material for aprotic Li-O₂ batteries. B₄C 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 B₄C are systematically investigated in an

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aprotic electrolyte. Li-O₂ cells using B₄C based air electrodes exhibit better cycling stability than those using carbon nanotube- and TiC-based air electrodes in 1 M LiTf-Tetraglyme electrolyte. The performance degradation of B₄C based electrode is mainly due to the loss of active sites on B₄C electrode during cycles as identified by the structure and composition characterizations. These results clearly demonstrate that B₄C is a very promising alternative oxygen electrode material for aprotic Li-O₂ batteries. It can also be used as a standard electrode to investigate the stability of electrolytes.

Keywords: boron carbide; non-carbon electrode; oxygen electrode; lithium-oxygen battery; aprotic electrolyte

1. Introduction

Lithium-oxygen (Li-O₂) 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-O₂ 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 reaction of these two components have been regarded as the main degradation mechanisms in these batteries. Li-O₂ batteries using carbon-based oxygen electrodes with high specific capacities (>1000 mAh 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 Equation 1 and 2 [11].

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 Li₂CO₃ 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 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-O₂ batteries will be decreased manifold. Most recently, a stable non-carbonaceous electrolyte has been developed for Li-O₂ batteries, but the use of carbon based cathode still causes the formation of Li₂CO₃ 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-O₂ 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 (Co₃O₄, MnO₂, RuO₂, and Ti₄O₇) [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 density and cost and good catalytic activities for ORR and OER. Titanium carbide (TiC) was reported to show a high performance in a 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 ($\sim 2.5 \text{ g cm}^{-3}$ 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 composite has also been used as the oxygen electrode material for aprotic Li- O_2 batteries, showing a very high capacity ($16,000 \text{ mAh g}^{-1}_{\text{composite}}$), high discharge voltage plateau (2.73 V) and stable cycling performance for 120 cycles under a capacity limited protocol at $1000 \text{ mAh g}^{-1}_{\text{composite}}$ [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 carbon nanotube (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 $0.3\sim 0.8 \Omega \text{ cm}$ [42], corresponding to the electronic conductivities of $1.25\sim 3.33 \text{ S cm}^{-1}$. CNT was purchased from Cheap Tubes Inc. and the electronic conductivity is $>100 \text{ S cm}^{-1}$ [43]. NH_4HCO_3 powders (99% purity) and PTFE suspension (60%) was 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) nano-particles 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 hrs, it was annealed at 300°C for 1 hr 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 cm².

Li-O₂ 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 hrs prior to use. Volume of the electrolyte applied was 100 μL. The assembled cells were loaded into gas-tight Teflon containers (with a volume of about 226 cm³). Then the Teflon containers were transferred out of the glovebox and filled with ultrahigh purity O₂ (1 atm).

2.2 Electrochemical measurements

The cells were equilibrated at open circuit for 3 hrs 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 B₄C, 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 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 ($\lambda = 2.2910 \text{ \AA}$) 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 K α radiation. Phases were identified by comparison with reference data from the International Centre for Diffraction Data using the program JADE (Materials Data Inc., CA). Transmission electron microscopy (TEM) investigation was conducted using a Titan 80-300 microscope operated at 300 kV. The morphologies of the electrodes before and after test were examined by an FEI Helios Nanolab dual-beam focused ion beam scanning electron microscope (FIB/SEM) with an electron beam voltage of 5 kV. X-ray photoelectron spectroscopy (XPS) measurements of the electrodes were performed with a Physical Electronics Quantera scanning X-ray microprobe with a focused monochromatic AlK α X-ray (1486.7 eV) source for excitation and

a spherical section analyzer. The samples were sealed on standard sample holders inside a glovebox filled with argon gas prior to characterization.

3. Results and Discussion

According to the characterization data given by the manufacturer (see Fig. S1 in the Supplementary Information), the B₄C nanoparticles used in this work have a high purity of 99+%, hexagonal crystalline structure and average particle size 45~55 nm. Fig. 1 shows the morphologies of the as-purchased B₄C and TiC particles. Both carbide particles are well crystallized as revealed by HRTEM images. B₄C particles have an average size of ~50 nm, and shows graphite-like structure (*d* space: ~3.6Å), as seen in Fig. 1a as well as Fig. S2 in the Supplementary Information. It is noted that the surface of B₄C particle is free of any other amorphous phase (Fig. 1b). TiC particles show a slightly smaller average size of 30~40 nm (Fig. 1c) and have an amorphous layer on the surface as seen in the HRTEM image in Fig. 1d. The multi-walled CNTs have a diameter of ~20 nm and exhibit the layered structure of the wall and corrugated morphology with many defects on the surface (Fig. 1e, f) [44].

Fig. 1. TEM images of B₄C (a, b), TiC (c, d) and CNT (e, f) nanoparticles under different magnification.

3.1 Stability studies

To investigate the chemical stability of B₄C and TiC against attacks from the superoxide and peroxide, micro-XRD was used as a probing technique to check their reactivity toward Li₂O₂ and superoxide in the form of KO₂. B₄C and TiC powders are separately hand-milled with commercial Li₂O₂ or KO₂ in a weight ratio of 1:1 in a glovebox under Ar for 1 hr. A simple assessment can be determined regarding chemical stability by monitoring changes in XRD patterns of the mixtures compared with those of pure substances. The XRD pattern of the as-purchased B₄C powders shows graphite-like structure as shown in Fig. 2a. There are small amounts of LiOH and Li₂CO₃ present in the XRD pattern of the Li₂O₂ sample, and KOH in the KO₂ sample, due to the relatively low purity of those commercial oxide powders. The XRD patterns of B₄C mixtures show no other obvious diffraction peaks besides those of pure substances within the detection limit of the instrument, indicating the good chemical stability of B₄C against Li₂O₂ and KO₂. In the XRD pattern of TiC (Fig. 2b), although no other peaks except those of TiC appears in the spectra, we cannot exclude the presence of TiN and TiO₂ because they both have very similar diffraction patterns as those of TiC and a surface layer of TiN and TiO₂ cannot be easily identified through XRD patterns. The XRD patterns of TiC mixtures show no other obvious diffraction peaks either. Both carbides demonstrate good chemical stabilities against Li₂O₂ and KO₂. Further investigation on the chemical stability of B₄C in KO₂-DMSO solution reveals that B₄C will be slightly oxidized by O₂⁻ to a little extent, as shown in Fig. S3(a-c). However, the oxidation reaction can reach to a steady-state and does not further deteriorates, probably due to the protection of B-suboxides surface layer.

Cyclic voltammetric (CV) scanning at 100 mV s⁻¹ within 2.0~4.7 V under Ar indicates that B₄C electrode has a higher electrochemical stability than TiC electrode during both anodic and cathodic polarization process in 1 M LiTf/Tetraglyme electrolyte (see Fig. S3d in the supplemental information). A similar measurement has been reported that TiC electrode is

less inert than carbon-based materials (SP carbon and reduced graphene oxide) in a DME-based electrolyte [24].

Fig. 2. Micro-XRD patterns of B₄C (a) and TiC (b) particles and their mixture with Li₂O₂ and KO₂, respectively.

3.2 Cell performance

Due to the relatively low electronic conductivity ($\sim 1 \text{ S cm}^{-1}$) and specific surface area ($\sim 12.5 \text{ m}^2 \text{ g}^{-1}$ measured by BET method) of B₄C powders, the content of non-conductive PTFE binder may play an important role in the electrode performance. Thus, the composition ratio of PTFE is firstly optimized for the B₄C electrodes. Fig. 3 shows the discharge/charge profiles of Li-O₂ cells using B₄C/PTFE electrodes with various PTFE contents. All the cells were tested under the same limited capacity of $100 \text{ mAh g}^{-1}_{\text{B}_4\text{C}}$ ($0.3\sim 0.5 \text{ mAh cm}^{-2}$) at 0.1 mA cm^{-2} within the voltage range of 2.0~4.6 V. Extra parallel cells for each PTFE content electrode and the results are reproducible. All B₄C cells show a similar high discharge voltage plateau at 2.7 V and a charge voltage plateau at 4.1~4.2 V in the first cycle. The cell with 10% PTFE in the oxygen electrode can only be cycled for 25 times under the limited capacity before the cycle voltage exceed the pre-set limit (Fig. 3a), possibly due to the poor conductivity and relatively less active sites on the surface of B₄C electrode. The over-potential between OER and ORR is about 1.4 V in the first cycle and reduces to 1.2 V in the

5th cycle. The discharge voltage decays much faster than the charge voltage and ends at 2.0 V before achieving the controlled capacity after 25 cycles. The charge voltage profiles show a slow change, indicating the good stability of B₄C material during charging.

When the PTFE content in B₄C electrode is reduced to 7% the cell shows an outstanding stability with cycles (Fig. 3b). The discharge voltage plateau is 2.7 V in the first cycle and subsequently maintains at around 2.6 V. It is really impressive that the discharge profiles nearly overlap from the 50th to the 172th cycle, which indicates that the B₄C cell with 7% PTFE in oxygen electrode can maintain a stable and high catalytic activity to ORR during cycles. It also confirms that the content of PTFE does play an important role in cell performance. Less PTFE coverage can significantly enhance the cell cyclability. The charge voltage plateau is about 4.1 V in the first cycle and reduces to 3.9 V in the 50th cycle. The charge profile in the 50th cycle shows two plateaus—one is around 4.0 V and another around 4.5 V. The lower plateau is mainly corresponding to the decomposition of Li₂O₂ and the higher one can be attributed to the decomposition of side reaction products, such as lithium alkyl carbonates, Li₂CO₃ and LiOH, which requires a higher charge voltage [14]. During cycling, the lower plateaus in the charge voltage profiles become shorter and incline upwards gradually, which indicates the increase of accumulated side reaction products in discharge/charge processes. The drop in discharge voltages from the first cycle to the 50th cycle may come from passivation caused by the accumulation of incompletely decomposed side reaction products and the loss of active surface. However, the reproducible discharge performance from the 50th cycle to the 172th cycle implies the latter reason may dominate the electrochemical processes during these cycles. The active sites could be released and maintained at a stable quantity to afford the controlled discharge capacity after charging in each cycle, but the cell resistance will increase eventually.

With the further reduction of the PTFE content to 5% in the oxygen electrode, the B₄C cell shows a faster decaying in discharge performance than that with 7% PTFE under the

same test condition (Fig. 3c). The discharge voltage plateau starts to decrease from the 100th cycle although the discharge capacity can still reach 100 mAh g⁻¹. After 185 cycles, the cell fails in achieving the controlled discharge capacity though its charge performance still stable. The decreased discharge stability of the 5% PTFE-based cell may indicate the reduced bonding strength among B₄C particles and between particles and the current collector. Further decreasing the PTFE composition to 3% in the oxygen electrode leads to shorter cycling stability of the Li-O₂ cell (Fig. 3d). The cell degrades quickly and fails to reach the controlled capacity within the pre-set voltage range for both discharge and charge process in the 100th cycle.

Fig. 3. Discharge/charge profiles of B₄C cells with different PTFE content in oxygen electrode: (a) 10%, (b) 7%, (c) 5% and (d) 3% at 0.1 mA/cm² within the voltage range of 2.0~4.6 V.

The data shown in Fig. 3 indicates that too much PTFE binder in the oxygen electrode leads to high polarization of the cell as a result of high contact resistance and less active sites due to the PTFE coverage. However, if the PTFE content is too small, B₄C particles may not be bonded strongly among themselves and onto the current collector, so the B₄C particles easily fall off the electrode and lose active sites mechanically. At the surface of oxygen electrode, the deposition/decomposition of solid discharge products occurs periodically during discharge/charge cycles. As a result, the oxygen electrodes of Li-O₂ batteries experience volume expansion and contraction as well as change in volume and structure. This will lead to electrodes cracking and pores collapse. Among various PTFE contents, 7% PTFE seems to be the optimal binder content in the B₄C oxygen electrodes. Under the full discharge/charge mode between 2.0 and 4.6 V at 0.1 mA cm⁻², the B₄C cell with 7% PTFE can achieve a stable operation with a constant Coulombic efficiency of ~96% under 100~120 mAh g⁻¹_{B₄C}, as shown in Fig. S4, which is in agreement with results of discharge/charge cycling under limited capacity. Due to the excellent discharge performance for B₄C cell with 7% PTFE, the cut-off charge voltage is adjusted from 4.6 V to 4.7 V after 172 cycles to further investigate the cycle performance of B₄C oxygen electrode. The B₄C cell delivers both controlled discharge and charge capacity for 230 cycles with minor decay in discharge voltage within cut-off voltage window (Fig. 4a). After that, the cell can still achieve stable discharge performance until the cell is voluntarily terminated after 250 cycles. The total cycle time is about 1600 hrs (Fig. S5a). However, increasing the capacity limitation to 200 and 300 mAh g⁻¹_{B₄C} in the cycling significantly reduces the cycle life (Fig. S6a, c).

Due to the high loading of B₄C (3~5 mg cm⁻²) in oxygen electrodes, the actual total capacity delivered by B₄C cells under 100 mAh g⁻¹_{B₄C} is comparable to those for the carbon based cells with low loading of carbon (0.3~0.5 mg cm⁻²) in oxygen electrodes that give a specific capacity of 1000 mAh g⁻¹_{carbon}. The reasons for the low specific capacity of B₄C cells compared with carbon-based cells can be attributed to the low surface area of B₄C particles

which cannot provide a large amount of active sites for Li-O₂ reactions and the low pore volume to store a large number of discharge product (Li₂O₂). Carbon-based materials have been extensively developed for centuries and a large number of carbon materials with very low tap density and large specific surface area have been developed and widely applied, such as Ketjen black carbon, CNT, carbon nano-fiber (CNF), graphene, etc. Larger surface area provides more active sites and higher pore volume gives more space to store the discharge products, which allows to obtain higher capacities. Even though some active sites on the surface of carbon are irreversibly covered by side reaction products or lost in corrosion, there are still abundant active sites to support the electrochemical reactions to a certain capacity for certain period of operations. In fact, some preparation techniques of B₄C material with large specific surface area have been developed for the application in the fields like microelectronics, nuclear, space and medical applications [45-47]. The advancement in this area will encourage and promote the development of B₄C-based Li-O₂ batteries.

Fig. 4. (a-c) Discharge/charge profiles of Li-O₂ cells with different catalyst in oxygen electrode: (a) B₄C, (b) TiC, (c) CNT; and (d) discharge capacity with cycles for the three cells.

To date, TiC has been reported to show the best performance among non-carbon based cathode materials [33]. Owing to the high electronic conductivity of TiC and good stability of TiO₂ surface layer, TiC cells showed very good cycling stability, even better than Li-O₂ cells using nano-porous gold oxygen electrode [31]. A capacity retention of 98% was achieved in 0.5 M LiClO₄/DMSO electrolyte and little Li₂CO₃ formed after 100 cycles. However, when tested in 0.5 M LiPF₆/tetraglyme electrolyte, TiC cell did not show a performance as stable as that in DMSO-based electrolyte probably because of the instability of LiPF₆ against reduced oxygen species [48]. Since tetraglyme with a low donor number is more stable than DMSO when in contact with Li metal and the former is also probably the most widely used solvent in electrolytes for Li-O₂ battery studies at present, TiC oxygen electrode prepared by a similar

method with TiC powders purchased from the same supplier was evaluated in a similar cell with Li metal as the anode, 1 M LiTf/Tetraglyme as the electrolyte, under limited capacity of 100 mAh g⁻¹_{TiC} (i.e. 0.3~0.5 mAh cm⁻² depending on electrode loading) within 2.0~4.7 V [33]. In this case, the TiC cell shows a fast capacity-decay after 8 cycles (Fig. 4b, d).

In the first cycle of the TiC-based Li-O₂ cell, the discharge voltage plateau is 2.65 V and the total over-potential is about 1.55 V. The charge voltage shows a plateau at ~4.2 V and then increases sharply, indicating the decomposition of side reaction products formed during discharge. Subsequently in the 5th cycle, the discharge performance decays and shows an inclined plateau at around 2.5 V. The charge profile shows a plateau around 4.2 V as well, but an earlier sharp increase than that in the first cycle, indicating the decrease of Li₂O₂ formation and increase of side reaction products during the discharge process. The decay in charge capacity is faster than that in discharge capacity, which is opposite to the B₄C cell (Fig. 4a). The Li-O₂ electrochemical reaction is a surface reaction determined by tri-phase boundary which is formed by active sites on catalyst, electrolyte and the soluble oxygen therein. Though the specific surface area (SSA) of TiC powder is low, about 26 m² g⁻¹ measured by BET method, it is still double that of the B₄C powder. The much faster decay in discharge performance for TiC cell than that for B₄C cell indicates a much faster passivation and loss of active sites on TiC surface, which is in agreement with the lower stability in CV measurements (Fig. S3). Adams et al. [34] revealed the charge performance of the TiC-based Li-O₂ cell highly depends on the thickness of TiO₂ surface layer. An oxide layer thicker than 2 nm inhibits the OER during charging process, which will cause the incomplete decomposition and accumulation of side reaction products on TiC surface. It is therefore speculated that the protective surface layer (TiO₂ and TiOC film, revealed in the following XPS analysis, Fig. S7b) which is shown in TEM images (Fig. 1d) may be unstable and easy to be electrochemically reduced in ORR, deduced from the big cathodic current shown in CV curves (Fig. S3). Then the reduced oxygen species (O₂^{•-}, O₂²⁻) can chemically attack the

surface of TiC directly to form uncontrolled oxide surface layer. This will cause both the passivation and the loss of active sites. Considering the relatively larger SSA of TiC than that of B₄C and the faster decay in both discharge and charge processes performed by TiC cells, passivation caused by oxide surface layer may play an important role in the performance degradation for TiC cells.

The CNT-based Li-O₂ cell is tested under the same condition, that is under limited capacity of 100 mAh g⁻¹_{CNT} (i.e. 0.3~0.5 mAh cm⁻² depending on electrode loading) within 2.0~4.7 V. CNT cell shows a reproducible discharge performance for the initial 50 cycles (Fig. 4c), probably ascribed to the larger SSA (157 m² g⁻¹ measured by BET method) of CNTs and pore volume in the CNT oxygen electrode, which provide abundant active sites for ORR. After that, the cell performance decays obviously. The charge profile looks different from that for B₄C cell (Fig. 4a). No obvious charge voltage plateau around 4 V is shown even in the first charge process. The reason might be the charge process of the CNT cell involves a severe electrochemical oxidation of carbon material, which leads to a complicated charge reaction and a resulting monotonically ascending charge voltage. The charge profile shows a dominant plateau above 4.3 V after tens of cycles, indicating the charge process mainly reflects the decomposition of side reaction products and oxidation of CNTs. In the 100th and 125th cycles, the charge voltage looks fluctuant, probably attributed to a much severe oxidation of CNTs after 100 cycles, which may cause a rapid loss of active sites on CNT electrode and an increase in contact resistance within CNT particles and between CNTs and the current collector. After 125 cycles, the CNT cell only delivers tiny capacities of several mAh g⁻¹ until to the end of test. The total cycle time to achieve the controlled capacity is only about 850 hrs, much shorter than that for the B₄C cell (Fig. S6 in the Supplementary Information). The superior cycling performance of B₄C cells, as shown in Fig. 4d, reveals a much better stability of B₄C than TiC and CNT in Li-O₂ batteries with the tetraglyme based electrolyte. Besides the catalytic activity of B₄C towards ORR and OER [41], the lack of surface layer and relative

inertness against chemical and electrochemical oxidations during charge process may benefit the effective decomposition and removal of side reaction products, which in turn release enough active surface to support a stable discharge performance under $100 \text{ mAh g}^{-1}_{\text{B}_4\text{C}}$.

It is worth to note that some highly crystalline graphite may still exist in the B_4C electrode investigated in this work. However, the capacity contribution of the residual graphite in the electrode is very small. The stoichiometric B_4C has a boron content of 78.25 wt%. The B_4C sample used in this work has a boron content of 77.48% as shown in Figure S1 in the Supplemental Information. This is a typical carbon rich B_4C (or B_{12}C_3) compound with a maximum graphite content of 0.77%. In one of our previous work [49], we have shown that the air electrode based on crystalline graphite exhibits a capacity of only $\sim 80 \text{ mAh/g}$ when used in Li-O_2 batteries. The capacity contribution of 0.77% of residual graphite in our B_4C electrode is only $\sim 0.6 \text{ mAh g}^{-1}$. This value is negligible compared to the typical capacity of B_4C reported in this work ($100\text{-}300 \text{ mAh g}^{-1}$).

3.3 Degradation mechanism

The EIS measurements were conducted to investigate the degradation mechanism of B_4C , TiC and CNT cells with discharge/charge cycles as shown in Fig. 5. The real (Z_{re}) and the imaginary components (Z_{im}) of the cell impedances relate to the resistive and capacitive (or inductive) properties of the cells, respectively. The left hand (high frequency) intercept of the impedance data with the Z_{re} axis, named as R_{ohm} gives the total ohmic resistance of the electrolyte, electrodes and all the external electronic resistances (the coin cell cases, fixture and cables). The distance between the intercepts at high (left) and low frequency (right), named as R_p , gives the electrode polarisation resistance and thereby an indication of the electro-catalytic activity. Since fixtures, cables, cell cases, anodes and electrolytes for all the cells are the same, the differences in R_{ohm} and R_p are mainly caused by the differences in the resistance and the polarization of the oxygen electrodes.

Fig. 5. Electrochemical impedance spectra of B₄C cell (a), TiC cell (b) and CNT cell (c) after different cycles under 100 mAh g⁻¹ at charged state.

The B₄C cells exhibit a smaller R_p after the first cycle than that before test (see Fig. 5a and the inset Figure), possibly due to the activation of B₄C material and further wetting of oxygen electrode by electrolyte. The original structure of the B₄C electrode may also change after deposition/decomposition of solid discharge products in the first cycle, which may form micro-cracks when comparing with the B₄C electrode before testing and after first discharge/charge cycle, as shown in the SEM images in Fig. 6c and Fig. S8 in the Supplementary Information. The surface area of the oxygen electrode may therefore increase and permit electrolyte to penetrate further, which expands the tri-phase boundary (TPB) and reduces R_p . After the first cycle, R_p increases gradually and then decreases after 20 cycles. The

increase of R_p indicates the continuous passivation and loss of active sites with cycles. The decrease of R_p after 20 cycles could be attributed to the increase in electrode wetting caused by cracks and volume change from periodic deposition/decomposition of solid discharge products. The micro-cracks will be blocked by deposition of discharge products in the discharge process, which disconnects the conductive network in oxygen electrode. It is possible that some cracks may not contribute to the discharge capacity if their sizes are too small. During the subsequent charge process, the discharge products in micro-cracks may be more difficult to be electrochemically decomposed due to the broken conductive network, which in turn increases R_p and R_{ohm} . Additionally, the hydrophobicity of oxygen electrode may decrease by electrolyte penetrating and wetting in the micro-cracks, which will increase the mass transfer resistance of oxygen diffusion from gas phase to electrolyte phase. It can be seen in the inset of Fig. 5a that R_{ohm} increases evidently after the 75th cycle, demonstrating an obvious passivation. Considering the reproducible discharge profiles from the 50th cycle to the 172th cycle, as shown in Fig. 3b, the increase in R_{ohm} may not dominate the decay in discharge performance for these cycles. Though Li_2CO_3 and LiOH can be decomposed by applying high cut-off charge voltage, they will also be produced at the same time by electrochemical oxidation of electrolyte. The use of non-carbon based B_4C oxygen electrode could benefit from reduced side reactions in the charge process. Introducing catalysts to reduce the charge voltage and suppress the decomposition of electrolytes during charging may further improve the cycling performance of B_4C cells.

As a comparison, the impedance result of the TiC cell reveals the large increase in R_p (Fig. 5b). It does not show an obvious decrease in R_p after the first cycle, as for the R_p of B_4C cell, indicating no significant activation effect for TiC material. The R_p continuously increases with cycles, suggesting the increasing polarization in charge transfer process. This increase may be caused by the formation and growth of insulated oxide surface layer on TiC surface, which results in passivation and coverage of active sites. The R_{ohm} does not show an evident

increase during 20 cycles, indicating the oxide surface layer may be relatively thin and mainly impact the charge transfer polarization, rather than the cell resistance within the short cycle time. The CNT cell shows a relatively smaller R_p than B₄C cell (Fig. 5c) due to the higher electronical conductivity and SSA of CNT material. After the first cycle, R_p does not reduce as much as that for B₄C cell, indicating no significant activation effect for CNT material as well. The slight decrease in R_p may be due to the wetting of the CNT electrode. For the initial 50 cycles, the change of R_p is significantly smaller for CNT cell than that for B₄C cell, which is in agreement with the reproducible discharge performance shown in Fig. 4c. After 50 cycles, R_{ohm} increases largely. Though R_p looks smaller for the 75th cycle than that for the 50th cycle, it is most likely caused by the severe wetting of CNT electrode, considering the evident degradation in discharge performance after 50 cycles (Fig. 4c). After 100 cycles, both R_{ohm} and R_p are huge, much higher than those for B₄C cell, which indicates the severe electrical passivation of CNT electrode surface, rapid loss of active sites and increase in contact resistance caused by carbon corrosion and the resulting severe coverage of insulated side reaction products.

Fig. 6 shows the typical SEM images of B₄C electrodes at different states. The as-prepared B₄C electrode shows porous structure with micro-pores from tens to hundreds of nanometers (Fig. 6a). Fig. 6b shows the dominant discharge product has toroidal shape with a diameter of ~700 nm. The XRD pattern confirms that the main reaction at cathode is Li₂O₂ which is the electrochemical reduction product of O₂ (Fig. 7). This toroidal structured Li₂O₂ is the typical discharge product formed at a low current density. Fig. S8 in the Supplementary Information shows the crack formed during the first discharge process. After recharge, the toroids disappear, as shown in Fig. 6c, demonstrating the complete decomposition of Li₂O₂ which is supported from the XRD result as well (Fig. 7). After 250 discharge/charge cycles, there is no any toroidal Li₂O₂ to be found as shown in Fig. 6d. The B₄C electrode looks more porous than its before-test counterpart, possibly due to the repeated expansion/contraction in

volume of electrode with cycling, which generates more cracks or holes. Furthermore, B_4C particles appear to be less conductive under SEM observation after long-term cycling compared with those in the as-prepared sample, which is in agreement with the results from EIS analysis and indicates the coverage of insulated residuals of side reaction products.

Fig. 6. SEM images of B_4C electrode before test (a), after the first discharge (b), after the first charge (c), and after 250 discharge/charge cycles (d).

Analysis of the XRD patterns of the B_4C electrodes before and after test provides the insights on discharge products. As shown in Fig. 7, the XRD pattern of B_4C electrode after the first discharge clearly shows that Li_2O_2 is the main discharge product. No significant Li_2O

peak and Li_2CO_3 peak are found, which may be of their low content or amorphous phase. After the first charge, the Li_2O_2 peaks disappear and the XRD pattern of B_4C electrode is almost the same as that for uncycled electrode which suggests the near complete decomposition of the Li_2O_2 product. The XRD pattern for B_4C electrode after 250 cycles is also very similar to that for pristine B_4C electrode but the peaks intensity become weaker, probably due to the coverage of side reaction products. There are no obvious Li_2O_2 peaks but several small peaks of Li_2CO_3 (inset of Fig. 7) were identified in the B_4C electrode after long term cycling, indicating the accumulation of undecomposed Li_2CO_3 after continuous cycles.

Fig. 7. XRD of B_4C electrode before test, after the 1st discharge, after the 1st recharge and after 250 cycles.

The surface compositions of B_4C electrodes before and after test were analyzed by XPS and the results are shown in Fig. 8. Spectrum deconvolutions of each species are carried out to show the existence of different chemical states. The $\text{F}1s$ spectra in Fig. 8a show a C-F bond at 689.1 eV from PTFE binder for all the B_4C samples. A small peak at 684.8 eV for the

three samples after test (i.e. after first discharge, after first recharge, and after 250 cycles in the charged state) is from the Li-F bond and reveals the decomposition of LiTf salt with a chemical formula of $\text{CF}_3\text{SO}_3\text{Li}$ started from the first discharge [48,50]. The XPS S2p spectra for all B_4C electrodes after-test show a prominent peak at 169.3 eV (Fig. 8b), corresponding to S-O bond, which also indicates the decomposition of LiTf. The deconvolution for the B1s spectrum (Fig. 8c) shows the existence of the two possible boron chemical states with binding energies centered at 188.4 and 190.5 eV, which correspond to B-B and B-C bonds, respectively [50]. There is no oxide-related B-O surface species observed at around 193 eV in the B1s spectrum for the B_4C electrode before-test [52], which is in agreement with the observation from TEM. It is well known that B_4C can be inert to the oxidation from molecular oxygen. There is also no obvious B-O peak in B1s spectrum for the B_4C electrode after the first discharge. However, a small component at 193 eV [52], assigned to the B-O bond is found for the B_4C electrode after the 1st recharge. This could be ascribed to the oxidation from active oxygen species with high reactivity during OER. After 250 cycles, B1s features of B-B, B-C and B-O bond are not evident, as the surface of B_4C electrode may be covered by non-boron based species, such as Li_2CO_3 or other incompletely decomposed discharge products.

Fig. 8. XPS spectra of B₄C electrodes before test (black), after the first discharge (red), after the first recharge (green) and after 250 cycles in the charge status (blue); (a) F1s, (b) S2p, (c) B1s, (d) C1s, (e) O1s, (f) Li1s.

In Fig. 8d, the C1s spectra show a peak at 291.9 eV for C-F of PTFE binder and a peak at 284.7 eV for the B-C bond. However, there are no other carbon-related peaks shown in the C1s spectrum for the before-test B₄C electrode, except that from PTFE, indicating a pure B₄C surface composition. The peaks at 289.2, 286.8 and 285 eV for the sample after cycling correspond to C=O, C-O and C-C bonds, respectively [51], which are from Li₂CO₃ or other side reaction products. The O1s spectra in Fig. 8e show a small broad peak in the B₄C electrode before-test, which may be related to some oxygen-containing functional groups adsorbed on surface. The dominant discharge product is Li₂O₂ as shown in the spectrum for the B₄C electrode after the first discharge [53]. The spectrum also shows the formation of Li₂O and Li₂CO₃ in discharge products [53]. Li₂O as a discharge product has been observed in Li-O₂ battery using non-carbon based SiC electrode [32], which implies a possibility of 4-electron ORR to form a high-capacity discharge product. The Li₂O peak is disappeared for B₄C electrodes after the first charge and 250 cycles. There is no Li₂O₂ peak found for the

electrode after the first charge, demonstrating a complete decomposition of peroxide. However, Li_2O_2 is found in the spectrum for B_4C electrode after 250 cycles because the 250th charge process was stopped before achieving the controlled capacity due to the cut-off charge voltage limit (Fig. 4a). Additionally, the peak at 533.6 eV related to B-O bond is not shown for B_4C electrodes after the first discharge [51]. After the first recharge, the main peaks correspond to Li_2CO_3 and a small component is from B-O bond. $\text{Li}1\text{s}$ spectra show the presence of Li_2O for the B_4C electrode after the first discharge, which is disappeared for electrodes after recharge, as shown in Fig. 8f. After 250 cycles, Li_2O_2 peak is observed besides Li_2CO_3 due to incomplete charge process, which is in accordance with the analysis of $\text{O}1\text{s}$ spectra (Fig. 8e).

4. Conclusion

Li-O_2 batteries using B_4C as a non-carbon based oxygen electrode material exhibit a good discharge and charge performance in tetraglyme based electrolyte for 250 cycles. The excellent catalytic activity, absence of surface layer and relatively consistent surface composition contributes to the stable cycling. Though limited by the low specific surface area, B_4C based oxygen electrode performs a much longer cycle life than TiC and CNT based oxygen electrodes. The reason that TiC and CNT oxygen electrodes cannot perform well may be the fast passivation caused by oxide surface layer and the electrochemical oxidation of carbon material, respectively. The degradation mechanism of B_4C cells is mainly from the loss of active sites. The speed of passivation is much slower for B_4C cells than that for TiC and CNT cells, which suppresses the impact of passivation on cell performance. The results show that B_4C with comparable density to carbon, high catalytic activity towards ORR and OER, excellent chemical and electrochemical stability can be a very promising alternative oxygen electrode material. It can be applied not only for improving the stability of aprotic Li-O_2 batteries, but also for studying and screening the stable electrolytes.

Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of Energy (DOE) under Contract no. DEAC02-05CH11231 for Pacific Northwest National Laboratory (PNNL) and under DEAC02-98CH10886 under the Advanced Battery Materials Research (BMR) program. S. S. acknowledges the Chinese Scholar Council for the financial support (201409345008). The microscopic and spectroscopic characterizations were conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility located at PNNL which is sponsored by the DOE's Office of Biological and Environmental Research (BER). PNNL is operated by Battelle for the DOE under Contract DE-AC05-76RLO1830.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at

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