Breathable Carbon-Free Electrode: Black TiO\textsubscript{2} with Hierarchically Ordered Porous Structure for Stable Li–O\textsubscript{2} Battery

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This paper introduces oxygen-deficient black TiO\textsubscript{2} with hierarchically ordered porous structure fabricated by a simple hydrogen reduction as a carbon- and binder-free cathode, demonstrating superior energy density and stability. With the high electrical conductivity derived from oxygen vacancies or Ti\textsuperscript{3+} ions, this unique electrode features micrometer-sized voids with mesoporous walls for the effective accommodation of Li\textsubscript{2}O\textsubscript{2} toroid and for the rapid transport of reaction molecules without the electrode being clogged. In the highly ordered architecture, toroidal Li\textsubscript{2}O\textsubscript{2} particles are guided to form with a regular size and separation, which induces the most of Li\textsubscript{2}O\textsubscript{2} external surface to be directly exposed to the electrolyte. Therefore, large Li\textsubscript{2}O\textsubscript{2} toroids (=300 nm) grown from solution can be effectively charged by incorporating a soluble catalyst, resulting in a very small polarization (=0.37 V). Furthermore, disordered nanoshell in black TiO\textsubscript{2} is suggested to protect the oxygen-deficient crystalline core, by which oxidation of Ti\textsuperscript{3+} is kinetically impeded during battery operation, leading to the enhanced electrode stability even in a highly oxidizing environment under high voltage (=4 V).

1. Introduction

With the increase in our society’s demands for energy storage, conventional Li-ion batteries are now reaching the limit in terms of energy density and price.\textsuperscript{[1–3]} In particular, rapid development and commercialization of electric vehicles and energy storage systems need more cost-effective, higher energy-density power sources, which cannot be fully satisfied by current progress of Li-ion batteries.\textsuperscript{[4–10]} As an alternative, Li–O\textsubscript{2} batteries are now attracting tremendous interest due to their extremely high theoretical energy density (=3500 W h kg\textsuperscript{-1}), which is far higher than that of conventional Li-ion batteries (=400 W h kg\textsuperscript{-1}).\textsuperscript{[6–8,11,12]} Unlike Li-ion batteries, which often contain heavy transition metals as redox-active elements in the crystal structure of cathodes, the operation of Li–O\textsubscript{2} system proceeds if charge and mass, i.e., electron, Li\textsuperscript{+}, and oxygen, can be supplied to an adequate substrate. As an aforementioned substrate, carbon has been ubiquitously used with various forms (carbon black, CNT, graphene, etc.), due to such advantages as light weight, large surface area, and high electronic conductivity with relatively low cost from which high energy density can be drawn.\textsuperscript{[13–18]}

However, parasitic reactions originating from complex interactions among battery components such as carbon additives, discharge products, electrolyte, and binder are especially aggravated on carbon, which leads to the premature cell death constraining it from being used for air cathodes.\textsuperscript{[19–21]} In the meantime, Bruce and co-workers suggested titanium carbide (TiC) as an alternative for such carbon cathodes.\textsuperscript{[22]} Compared with carbon, they showed that the TiC greatly reduced side reactions with the electrolyte and electrode degradation, and led to reversible formation/decomposition of Li\textsubscript{2}O\textsubscript{2}, along with their previous work of nanoporous Au.\textsuperscript{[23]} In the circumstances, several researchers continued to work on titanium-based materials (TiSi\textsubscript{2},\textsuperscript{[24]} TiO\textsubscript{2},\textsuperscript{[25–27]} TiN,\textsuperscript{[28,29]} and Ti\textsubscript{4}O\textsubscript{7}\textsuperscript{[30]}) to prove that such materials can be promising substrates in terms of gravimetric energy density, cost, environmental benignity, or so.

A notable feature of TiC is surface-present TiO\textsubscript{2}, which is expected to protect the bulk side of TiC against further oxidation and side reactions, sustaining sufficient activity for discharge/charge reactions.\textsuperscript{[22,31,32]} Considering that the surface reaction of Li–O\textsubscript{2} batteries relies on the surface chemistry of electrode, this observation implies that TiO\textsubscript{2} can operate as a stable cathode for Li–O\textsubscript{2} system, only provided that proper...
electrical conductivity is guaranteed. In case of magnéli Ti_4O_7 cathode, studied by Nazar and co-workers, the surface of Ti_4O_7 was revealed to be oxygen-deficient TiO_{2-x}, and the substoichiometry was maintained even during the exposure to oxygen-rich environment.[10]

This oxygen deficient TiO_{2-x} or so-called black TiO_2 can be synthesized by a simple H_2-thermal treatment on pure TiO_2, which requires milder synthetic condition than TiC or Ti_4O_7 in terms of reductive atmosphere and temperature. The Ti^{4+} ions and oxygen vacancies in TiO_{2-x} are known to trigger various novel properties, including high electrical conductivity[33–35] and catalytic activity.[36,37] Therefore, studies on the air cathode with bulk TiO_{2-x} seem to be necessary to account for the potential applications of titanium-based materials.

Along with the investigation of material itself, tailoring the electrode architecture is another crucial part of developing an efficient and stable cathode. Recent studies demonstrated that discharge capacity could be dramatically increased up by solvent-mediated growth of Li_2O_2.[38–40] While efficient architectures for the utilization of such solution-growth mechanisms are still in question, introduction of macropores to the electrode can be beneficial, by which large Li_2O_2 up to several hundred nanometers can be efficiently incorporated in the electrode structure without being clogged.

Furthermore, since the emergence of soluble catalysts as alternatives to conventional solid catalysts (Pt, Au, RuO_2, etc.),[41–43] air-permeable architectures containing sufficient and sustainable diffusion paths have been considered as an effective way for enhancing the transport kinetics of soluble catalysts as well as oxygen and other reaction species.[44] Therefore, an air cathode for high-performance Li–O_2 batteries necessarily features the combined characteristics of both proper electrical conductivity and advantageous architecture, available for the use of a soluble catalyst.

In this work, oxygen-deficient black TiO_2 with the ordered macroporous structure is fabricated by a simple hydrogen reduction, and applied to Li–O_2 battery as a carbon- and binder-free electrode. A soluble catalyst, LiI, was also introduced as an enhancer for the operation of the TiO_2 electrode. Together with the high electrical conductivity derived from oxygen vacancies or Ti^{4+} ions, this hierarchical electrode has mesoporous surface beneficial for the oxygen-reduction reaction, as well as interconnected micrometer-sized empty spaces to accommodate discharge products and to facilitate diffusion of the reaction molecules and soluble catalyst without clogging of the electrode. We observed, in this ordered architecture, that toroidal Li_2O_2 particles were grown in a regular size and separation, sustaining large interface with the electrolyte and enabling the soluble catalyst to readily decompose Li_2O_2. Our straightforwardly designed electrode, namely, “breathable” carbon-free electrode exhibited a significantly decreased polarization, hence, an excellent round-trip efficiency over 300 cycles.

2. Results and Discussion


Figure 1 presents the synthetic procedure for preparing the hierarchically ordered porous black TiO_2 (HOP-bTiO_2) on a Ni mesh. Monodisperse polystyrene (PS) latex microsphere with a size of ≈1.5 µm were compactly loaded on/between each strand of Ni mesh, and this PS/Ni was used as a template (Figure S1, Supporting Information) for the fabrication of ordered macroporous structure (with details in the Experimental Section). With titanium precursor solution impregnated into the interspaces between PS spheres, the ordered macroporous TiO_2 (OP-TiO_2) crystals are obtained after calcination. After the hydrogen reduction for 10 h, anatase TiO_2 phase is transformed to rutile, generating mesoporous surface, and finally HOP-bTiO_2 was fabricated on the Ni mesh (Figure S2, Supporting Information).

The H_2 reduction time of the as-prepared macroporous TiO_2 was chosen for such phase transformations to occur, leading to the concomitant volume contraction and morphological evolution. The reduction time of 10 h was a proper duration, in our experiment, for which mesoporosity can be produced without severe coarsening of the TiO_2 nanoparticles, otherwise disturbed by sintering or grain growth of TiO_2. It should be noted that the adequate combinations of annealing temperature, time, and atmosphere were used as a method for the fabrication of...
hierarchically ordered structure as well as PS beads, while other researchers have usually adopted dual-templating method to fabricate such structures.\(^{45-49}\)

X-ray diffraction and photographs of the electrodes before and after H\(_2\) thermal treatment (Figure 2a,b) clearly show the transformation of TiO\(_2\) from anatase to rutile phase, and the color change from white to black is indicative of the modified optical and electronic properties by the partial reduction of Ti\(^{4+}\) to Ti\(^{3+}\).\(^{33}\) The change of electronic structure in black TiO\(_2\) is corroborated by X-ray photoelectron spectroscopy (XPS) in Figure 2c, where the control TiO\(_2\) (rutile phase) is synthesized by post heat-treatment in air after the formation of anatase TiO\(_2\). The binding energy of Ti \(2p\) is slightly lower in black TiO\(_2\), indicating that Ti ions in black TiO\(_2\) surface have lower oxidation state than that of the control TiO\(_2\), consistent with the previous studies on the oxygen-deficient TiO\(_2\).\(^{50-52}\)

The oxygen vacancies (\(V_o\)) created during H\(_2\) reduction in the crystal structure will induce electrons to be transferred to the \(t_2g\) orbitals of Ti, possibly reducing Ti\(^{4+}\) to Ti\(^{3+}\). Ti \(L\)-edge soft X-ray absorption spectroscopy (sXAS) further supports the presence of Ti\(^{3+}\) ions in the black TiO\(_2\) (Figure S3, Supporting Information), where the peak-intensity (X-ray absorption by electron transition from \(2p\) to \(3d\) orbitals) ratio of \(e_g/t_{2g}\) is higher in black TiO\(_2\) than that of the control TiO\(_2\).\(^{53-55}\) In filling \(t_{2g}\) band by electrons, there is higher possibility in excitation of electrons to \(e_g\) band level by absorption of the incident X-rays, and this could be the evidence of reduced status of TiO\(_2\).\(^{53,54}\) In addition, similar absorption features from partial electron yield and total electron yield (TEY) indicate that such reduction of Ti\(^{4+}\) not only occurs in the outermost surface of TiO\(_2\), given that the detection depth in a TEY mode extends to a few nanometers.\(^{56-58}\)

The scanning electron microscopy (SEM) images of Figure 2e,f exhibit that the electrode consists of mesoporous frameworks or layers which provide reaction site for oxygen reduction. The close-packed anatase TiO\(_2\) grains become loosely aggregated with the concurrent volume contraction (\(\Delta V_{\text{anatase - rutile}} \approx 8%\))\(^{64}\) during the H\(_2\) reduction, which gives rise to the mesoporous surface in HOP-bTiO\(_2\). As a result, HOP-bTiO\(_2\) is an aggregate of regularly arranged TiO\(_2\) nanoparticles with the size of 12.3 ± 4.1 nm (Figure S6, Supporting Information). The mesoporous nature of HOP-bTiO\(_2\) is also confirmed by Figure S7 (Supporting Information), where the pore-size distributions based upon the methods of nonlocalized density functional theory and Barrett–Joyner–Halenda are displayed.
along with N₂ adsorption/desorption isotherms. A discrete micropore size of ≈1.9 nm is observed whereas the mesopores are distributed in a broad sense. Meanwhile, the micrometer-sized regular empty spaces, surrounded by the mesoporous walls, are interconnected by the voids where the removed PS spheres have resided in contact with each other. The interconnected voids can act as diffusion channels, and hence, reduce the tortuosity of the electrode. This ordered-macroporous architecture, so-called inverse-opal structure, was already proven beneficial for the fuel cell in which the enhanced mass-transfer or effective diffusivity of reaction molecules (methanol, oxygen, etc.) were demonstrated by the increased current density in the mass-transfer controlled regime.

2.2. Electrochemical Properties of HOP-bTiO₂ Electrode

The electrochemical performances of HOP-bTiO₂ as an Li–O₂ cathode are assessed in Figure 3, exhibiting one of the highest performances of noncarbonaceous electrodes. The first discharge curve (Figure 3a) is observed within the range of 2.2–4.5 V at 500 mA g⁻¹, and shows a high capacity of

![Figure 3](image-url)

Figure 3. a) Discharge/charge profile of the HOP-bTiO₂ electrode, b) discharge/charge profile with the capacity limited to 1000 mA h g⁻¹, and c) cyclability and terminal voltage of the HOP-bTiO₂ (at a rate of 500 mA g⁻¹). The SEM images of the HOP-bTiO₂ electrode: d) after first discharge to 1000 mA h g⁻¹, e) after fully discharged, and f) after fully recharged (marked by (d), (e), and (f) in the voltage profile in (a)). g) Schematic representation of the growing tendency of Li₂O₂ that is guided by the ordered electrode architecture. h) STEM image of the stacked Li₂O₂ toroids in a fully discharged state.
≈7500 mA h g⁻¹ by virtue of the enhanced electrical conductivity as well as the low mass of TiO₂. The Fourier-transformed infrared spectroscopy of the HOP-b-TiO₂ after the 1st discharge and charge confirms that the dominant discharge product is Li₂O₂ which is completely decomposed during subsequent charging (Figure S8, Supporting Information). In terms of the discharge product, it is reported that LiO₂ species begins to form either by a film or solution-mediated growth,[27] with oxygen dissolved in the electrolyte near the electrode surface. Then, a thermodynamic equilibrium is established by the compromise between the solubility of LiO₂ (dissolved in the electrolyte), and the adsorption energy of LiO₂* where * refers to a surface-adsorbed species. The Li₂O₂ occurs through either disproportionation or electrochemical reduction of the LiO₂ species.[71,74]

Compared to the relatively small overpotential during discharge (with respect to the equilibrium potential of Li₂O₂ formation/decomposition, 2.96 V vs Li/Li¹), large overpotential is observed during the charge process, indicative of the sluggish kinetics of Li₂O₂ decomposition. Typical voltage profiles with the capacity limited to 1000 mA h g⁻¹ are presented in Figure 3b (1st and 260th cycles). Decrease in the terminal charging potential (=4.0 V) is observed, compared to the fully charged state in Figure 3a (=4.5 V), which is attributed to the limited capacity by which electrolyte decomposition can be alleviated. The cyclability and terminal voltage of the HOP-b-TiO₂ with the capacity limited to 1000 mA h g⁻¹ are summarized in Figure 3c. Despite the abrupt increase in the cell polarization and decay of capacity from the last few cycles, the carbon-free HOP-b-TiO₂ can operate for ≈260 cycles without premature cell death. Such an abrupt increase in the polarization and deterioration of cell performance can originate from the electrolyte decomposition or from the degradation of other cell components.[19–21] Obviously, the long-term cyclability of HOP-b-TiO₂ for ≈260 cycles is much greater than that of the conventional carbonaceous electrodes, and one of the highest values of noncarbonaceous electrodes.

The origin of the enhanced electrochemical properties of HOP-b-TiO₂ electrode was identified with SEM images. Figure 3d is taken after discharged to 1000 mA h g⁻¹, and shows that the discharge product, Li₂O₂, is formed in toroidal shape with a diameter of ≈300 nm. Therefore, it is highly likely that such toroidal Li₂O₂ is a result of solution-mediated growth, as opposed to the Li₂O₂ film that, otherwise, is limited to only a few nanometers.[7,36] It is known that ether-based electrolytes lead to both solution/surface Li₂O₂ growth, depending on the discharge potential (overpotential), electrode material, and additives.[7,18–40]

Interestingly, the toroidal-shaped Li₂O₂ particles are suspended on the wall of mesoporous TiO₂ framework. At fully discharged state (Figure 3e), all of the TiO₂ arrays are covered uniformly by the Li₂O₂ particles, and the thickness of the ordered macrowalls increases to the size of individual toroid (≈300 nm) as seen in Figure 3d, compared to the pristine electrode with the wall size of several tens of nanometers (Figure 2b). The morphologies of the discharged electrode are also represented in Figures S9 and S10 (Supporting Information). As a result, Li₂O₂ toroids are regularly stacked on the TiO₂ nanoparticles guided by highly ordered architecture, as the scheme of Figure 3g. The stacked toroidal Li₂O₂ particles are also confirmed by a scanning transmission electron microscopy (STEM) image at the fully discharged state (Figure 3h). The morphology of the Li₂O₂ at 4000 mA h g⁻¹, which corresponds to ≈50% depth of discharge (DOD), is quite indistinguishable from that at 100% DOD, as seen in Figure S11 (Supporting Information). Meanwhile, the images of fully charged state clearly exhibit that the electrode recovers its pristine morphology (Figure 3f), and diffusion channels are maintained during cycling. It is believed that the Li₂O₂ particles can efficiently be grown from solvent, and high specific capacity (>7500 mA h g⁻¹) is the result of the efficient utilization of the electrode materials.

By virtue of regular empty spaces separated by ≈1 μm, solvated lithium ions and oxygen molecules can be effectively transported into deep inside of the electrode without it being clogged by Li₂O₂, rendering all the black TiO₂ materials to be utilized during the cell operation. We believe that these observations are distinguishable from those of conventional nanoparticle-based electrodes where the Li₂O₂ particles are formed at the interspaces or surfaces of aggregated nanoparticles.[38,39] Since the spaces between nanoparticles are irregular and insufficient for the accommodation of large toroids, full-utilization of the possible discharge capacity from solvent-mediated growth can hardly be achieved. However, our HOP-b-TiO₂ electrode deliberately includes large and regular empty spaces so that large size of Li₂O₂ particles can be afforded without being restricted from the interparticle spaces, and is clearly reflected as high specific capacity of HOP-b-TiO₂ electrode.

These morphological features, along with the carbon-free composition, also assure the high cyclability of HOP-b-TiO₂ electrode. As confirmed from SEM images in Figure 3d,e, the diffusion channels and empty spaces are preserved after the formation of discharge products (≈300 nm), and the electrode can sustain the open structures even when the hardly removable side products, e.g., Li₂CO₃ are formed from the electrolyte decomposition.[20–23] Although electrolyte decomposition occurring at the interfaces between electrolyte and Li₂O₂ can be adequately alleviated by the carbon-free electrode, it still could degrade the electrode stability by clogging pores during repeated cycles. HOP-b-TiO₂ after the cell death (Figure S12, Supporting Information), however, still maintains the open structures even when side products cover all of the electrode surfaces. The unique architecture of HOP-b-TiO₂ is obviously more advantageous than the conventional electrodes bearing intrinsic nanopores. In short, HOP-b-TiO₂ not only has merits in the diffusion kinetics and full utilization of electrode surfaces, but also is less susceptible to the side reactions by the retention of breathable open structures during long-term cycles.

Although our HOP-b-TiO₂ is beneficial for the Li₂O₂ formation, diffusion kinetics and electrode stability, this architecture, at least, is not most favorable for the decomposition of Li₂O₂ due to its toroidal morphology. Namely, the Li₂O₂ toroids, that enclose the HOP-b-TiO₂, have limited interfaces with the electrode most of which are exposed to the liquid electrolyte. Different from the conventional nanoparticle-based electrodes which include conductive additives (e.g., carbon black) in the vicinity of the insulating Li₂O₂ particles, electron extraction from the Li₂O₂ to HOP-b-TiO₂ would be challenged by the
limited interfacial area between them. Relatively large overpotential on charge (Figure 3a), compared to the previous literatures on Ti-based nanoparticles (TiC, Ti₃O₇) with TiO₂ surface that have similar discharge potentials, may originate from this different morphological features by which the electron paths are confined to one direction of the electrode. It should be noted that, however, vast majority of Li₂O₂ toroid on HOP-bTiO₂ is directly exposed to the electrolyte, which can provide suitable environments for the employment of soluble catalysts.

2.3. Combination of Electrode Architecture and Redox Mediator

Since the architecture of HOP-bTiO₂ electrode provokes the use of soluble catalysts for the decomposition of Li₂O₂, lithium iodide (LiI) as a redox mediator (RM) is introduced to our electrolyte. LiI is known to have various oxidation voltages, depending on the type of electrolyte solvent and electrode surface/morphology.[75] As shown in the voltage profiles in Figure 4a, charging potential is dramatically reduced by LiI, compared to the electrode without redox mediator, resulting in a very small polarization of ~0.37 V. Also, this charge potential is relatively low, and kept constant up to the capacity of 1000 mA h g⁻¹. As shown in Figure 4b, the polarization increases from the 1st to the 340th cycle (0.37 to 0.95 V at 500 mA h g⁻¹). However, it should be noted that the polarization is still less than 1 V, and is even lower than that of the 1st cycle of HOP-bTiO₂ without LiI (1.1 V at 500 mA h g⁻¹ in Figure 3b). Meanwhile, the discharge voltage with the addition of LiI is still found to be Li₂O₂, as seen in Figure S13 (Supporting Information).

The degree of enhancement in HOP-bTiO₂ though the application of LiI catalyst is more notable (Figure S14, Supporting Information), compared to the nanoporous black TiO₂ electrode. The HOP-bTiO₂ also proves its superiority, when compared with OP-TiO₂ (Figure S15, Supporting Information). The unique architecture of HOP-bTiO₂ is clearly beneficial as to the application of LiI for the Li₂O₂ decomposition, which may be attributed to the enhanced catalyst transport through the connected diffusion channels (Figure 2f) and large interfaces between Li₂O₂ and electrolyte. Since the breathable open structure is robust even at the full-discharged state (~7500 mA h g⁻¹ in Figure 3e), and still provides diffusion channels, LiI as a redox mediator can effectively be transported to deep inside of the electrode during charge. A conceptual scheme is represented in Figure 4c for better perception. With decreased charging potential, the HOP-bTiO₂ electrode shows extremely high stability up to ~340th cycles (Figure 4d), indicative of a synergistic effect of both the electrode architecture and soluble catalyst. Since electrochemical decomposition of oxygen-dissolved tetraethylene glycol dimethyl ether (TEGDME) dramatically occurs from ~4.3 V,[76] the extreme-high stability of HOP-bTiO₂ with LiI resulted from the decreased charging potential (less than 4.0 V for 340 cycles), while the HOP-bTiO₂ without LiI rapidly decays after ~230th cycle with its charging potential reaching the voltage range of TEGDME decomposition (~4.3 V).

It is generally reported that the charging process of Li₂O₂ battery with a redox mediator proceeds through two steps.[61,43,75]

In the first step, RM is electrochemically oxidized to RM⁺ on the cathode, in our case, on mesoporous TiO₂ surface. In the following second step, oxidized RM⁺ ions react chemically with Li₂O₂ particles. As mentioned earlier, in our ordered electrode architecture, Li₂O₂ toroids have grown, and enclosed the regularly separated TiO₂ nanoparticles, with a vast majority of Li₂O₂ surface exposed to the electrolyte, without possible impediment from TiO₂ nanoparticle arrays or pore walls (Figure 3d). Therefore, the unique morphology of HOP-bTiO₂ along with the growing aspects of Li₂O₂ is featured by large reactive interfaces between Li₂O₂ and electrolyte with RM⁺ dissolved, as well as the effective transport of RM⁺ molecules to the Li₂O₂ surface, which contributes to the small polarization over 300 cycles, as exhibited in Figure 4d. To the best of knowledge, it is such an outstanding result that the polarization even after 340 cycles was kept less than ~1 V at the capacity of 500 mA h g⁻¹, if the comparison is limited to the studies in which carbon-free electrodes are of interest.[77,78]

Despite intensive studies on generating huge Li₂O₂ toroidal particles through solvent-mediated growth,[38–40] decomposition of such large particles still has been challenging. As for the reversible decomposition of such large Li₂O₂, our study combines soluble catalysts with the properly-designed architecture, as a result of which provides two types of interfaces for RM to function. First, the mesoporous surface (interface 1) of HOP-bTiO₂ is associated with the electrochemical reaction sites for the oxidation of redox mediators (RM → RM⁺ + e⁻). Second, the Li₂O₂ surface is structurally induced to have large exposure to RM⁺, and the interface between them (interface 2) is related to the chemical decomposition of Li₂O₂ by RM⁺. We believe that the enlargement of these two types of interfaces, as featured by our HOP-bTiO₂, can be a key to the design of advanced air cathode, especially for the electrodes utilizing solvent-mediated growth of Li₂O₂.

2.4. Origin of High Stability of Black TiO₂ Electrodes

Although rapid increase of polarization was observed in HOP-bTiO₂ from the last few cycles, both the terminal discharge and charge potentials (at 1000 mA g⁻¹) are not significantly changed up to ~230th cycle (Figure 3c). Considering that the abrupt decay originates mainly from the electrolyte decomposition (Figure S10, Supporting Information), this relatively constant polarization implies that the electrode material itself is stable during the battery operation. Photographs of the pristine HOP-bTiO₂ and cycled HOP-bTiO₂ (Figure S16, Supporting Information) reveal that the black color, indicative of the modified electronic structure, is retained in both electrodes. Meanwhile, XPS analyses of Ti 2p show slight peak shifts to higher binding energy after discharge (Figure 5a), while that of Li is clearly shows the formation of Li₂O₂ (Figure 5b). From the Ti XPS spectra of Figure 5a, the oxidation states of Ti were estimated with the control TiO₂ as a standard for Ti⁴⁺. Binding energy difference between Ti⁴⁺ and Ti⁴⁺ was based on several literatures[79–80] assuming that oxidation of Ti accompanies a linear shift of binding energy from Ti⁴⁺ to Ti⁴⁺.[10] The oxidation states of Ti were calculated to be +3.54, +3.69, +3.63 for the pristine, discharged, and charged electrodes, respectively.
Figure 4. a) First discharge/charge profile of the HOP-bTiO$_2$ without and with LiI catalyst. b) First- and 340th-cycle voltage profiles of the HOP-bTiO$_2$ with LiI. c) Schemes comparing the effect of electrode architecture, HOP-bTiO$_2$ versus nanoporous electrode, on the activity of a redox mediator. d) Cyclability and terminal voltage of the HOP-bTiO$_2$ without and with LiI catalyst (at a rate of 500 mA g$^{-1}$ and capacity limited to 1000 mA h g$^{-1}$).
(Figure S17, Supporting Information). As for the increased oxidation state after discharge, we believe that Li$_2$O$_2$, in contact with the TiO$_{2-x}$ surface, may have induced slight oxidation. Nonetheless, it is quite surprising that further shift or oxidation is not observed in Ti 2p after subsequent charges, in spite of rather high potential (≈4 V) at which the TiO$_{2-x}$ is prone to be oxidized to TiO$_2$. The HOP-bTiO$_2$ electrode is still stable even at a fully charged state (charged up to ≈4.5 V vs Li$^+$/Li) where oxidation of the HOP-bTiO$_2$ would be more driven, due to the highly oxidizing environment (Figure S18, Supporting Information). The observed stability can be associated with the amorphous nanoshell around crystalline core, as often reported in the case of black TiO$_2$.[60,81]

Likewise, the outermost layer of our HOP-bTiO$_2$ consists of disordered nanoshell of ≈1 nm, with the crystalline phase present as the core (Figure 5c). Such disordered nanolayer is generated during the H$_2$ reduction, which is proved by the extended reduction time, as shown in Figure S19 (Supporting Information). The TiO$_2$ nanocrystals display relatively clean surfaces before the hydrogenation, while that of the reduced TiO$_2$ exhibits thicker nanoshell with the increased reduction time. With 40 h H$_2$ reduction, the amorphous coating grows to be ≈5 nm in thickness.

As seen through TEM after discharge (Figure 5d), a thick layer is observed around the crystalline core, where the layer consists of the discharge product Li$_2$O$_2$ and the disordered nanoshell that are quite indistinguishable. This disordered nanoshell seems to react with the oxygen species created during discharge, and therefore, the outermost disordered layer, in close proximity with Li$_2$O$_2$, could have changed into stoichiometric TiO$_2$, as confirmed from the shift of XPS spectra. The surface TiO$_2$ was also observed in TiC[22,31,32] and Ti$_4$O$_7$[30] after the 1st discharge by XPS in Ti, and remained relatively constant after repeated cycles, without severe bulk oxidation. A. Naldoni et al. claimed that highly disordered and reactive phase of black TiO$_2$ surface becomes nearly stoichiometric TiO$_2$ upon exposed to air, and preserves bulk defect from further oxidation.[81]

In a similar way, the slightly oxidized nanoshell could play an important role in our HOP-bTiO$_2$ retaining its black TiO$_2$ characteristics. As a proof, the pristine HOP-bTiO$_2$ electrode shows no color changes when exposed to air for ≈1 year (our empirical observation). Although slight oxidation occurs on
the surface of HOP-bTiO$_2$ during discharge, this oxidized layer can prevent the remaining Ti$^{3+}$ ions from further oxidation, as reflected in the high cyclability of HOP-bTiO$_2$ electrode. Meanwhile, the thick layer of Li$_2$O$_2$ is taken away in the charged TiO$_2$ (Figure 5e), similar to the pristine TiO$_2$ (Figure 5c).

In the earlier work of black TiO$_2$, Tian et al. identified chemical composition of the nanoshell to be amorphous Ti$_2$O$_3$ in which a typical TiO$_6$ octahedron is distorted with Ti interstitial diffusion.\cite{82} However, the Ti 2p$_{3/2}$ binding energy of Ti$_2$O$_3$ is $\approx$458 eV, which does not match our Ti 2p XPS results. Indeed, it is still controversial how and why the oxygen-deficient TiO$_2$ is stable in either air-exposed or electrochemically charged state, despite of various applications of black TiO$_2$ to photocatalysis, fuel cells, Li-ion batteries, etc. In our case, we conclude that the amorphous layer oxidized during the first discharge guarantees the high stability of black TiO$_2$ during extended cycles.

The importance of protecting layers in titanium-based materials is already dealt with a number of studies, including TiC and Ti$_4$O$_7$, as mentioned earlier.\cite{22,30–32} Anyhow, our results highlight again that the materials even vulnerable to the oxygen or high voltage can be used as stable air cathodes with the presence of protective layers. The detailed mechanisms of interplay between electrode surface and discharge products, and its role in the electrode stability needs to be further understood to develop a more advanced Ti-based cathode for stable Li–O$_2$ batteries. Suggested mechanisms regarding the high efficiency and stability of HOP-bTiO$_2$ are illustrated in Figure 6.

3. Conclusions

In this work, we have designed a highly stable and efficient air cathode of oxygen-deficient TiO$_2$ for Li–O$_2$ batteries, as a carbon- and binder-free electrode. Tailoring the offstoichiozymetry of oxygen and inverse-opal structure from the sacrificial templates enhanced the electrical conductivity, and rendered the architecture of electrode to be favorable for the reversible formation/decomposition of Li$_2$O$_2$, respectively, during discharge/charge processes. From the electrode architecture, the Li$_2$O$_2$ grew into a toroidal shape, and was suspended on the HOP-bTiO$_2$ framework, being separated by the dimension of macropores ($\approx$1 µm). The growing tendency of Li$_2$O$_2$ provoked the use of the soluble catalyst, and the HOP-bTiO$_2$ electrode with LiI showed extremely-high stability up to $\approx$340th cycle at a current density of 500 mA g$^{-1}$. This high performance of HOP-bTiO$_2$ electrode is attributed to the large exposed surface of Li$_2$O$_2$ to the electrolyte and enhanced mass transport of soluble catalyst to the Li$_2$O$_2$ surfaces due to the small tortuosity. The breathable carbon-free electrode with soluble catalysts was found to be effective for the reversible formation/decomposition of large toroidal Li$_2$O$_2$. Disordered nanoshell observed on the crystalline surfaces contributed to the stability of black TiO$_{2-x}$ electrode even in an oxidative environment under high-charging potential, highlighting the importance of the protection layer on the stability of titanium-based electrodes.

4. Experimental Section

Materials Preparation: Ni mesh was ultrasonically cleaned for 30 min in anhydrous ethanol (EtOH) and for 3 min in a 0.5 M hydrochloric acid (HCl) to remove any contaminants and amorphous surface oxides, and was dried in vacuum chamber overnight. Then, Ni mesh was vertically immersed into 30 mL of 0.3 wt% polystyrene-microbead solution, which was prepared by diluting PS-microbead solution (2.5 wt% in water, Alfa Aesar) with anhydrous ethanol. By keeping the Ni mesh in the PS solution at 60 °C overnight, PS microbeads were uniformly coated on the Ni mesh. As a titanium source, 1 mL of titanium chloride (TiCl$_4$, Sigma-Aldrich) was slowly added into 50 mL of anhydrous ethanol, and stirred at ambient condition for 1 h. After stirring, 3 µL of TiCl$_4$ solution was dropped on PS/Ni mesh (0.79 cm$^2$) by micropipette, and infiltrated into interspaces between beads using vacuum-filtration method. After dried, this TiCl$_4$-treated PS/Ni mesh was transferred to box furnace, and annealed at 400 °C for 3 h (ramping rate of 5 °C min$^{-1}$) in air to form TiO$_2$ with a removal of PS template. For the synthesis of oxygen-deficient
The authors declare no conflict of interest.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This research was supported by the National Research Foundation of Korea (NRF-2014R1A2A1A01003542) and by the Office of Naval Research Global (ONRC: N62909-16-1-2083). Y.P. acknowledges the financial support from the NRF grant (2014R1A2A1A01003542). S.H. and S.N. acknowledge the support from NST grant by the Korea government (MSIP) (No. CAP-15-D4-KITECH).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
black TiO$_2$, hierarchically ordered structures, Li-O$_2$ batteries, Li$_2$O$_2$
toroid, stability
Supporting Information


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Supporting Information

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Figure S1. SEM images of polystyrene-filled Ni mesh (PS/Ni mesh) used as a template for the fabrication of ordered porous TiO$_2$. 
Figure S2. SEM images of the HOP-βTiO$_2$ with different magnification.
Figure S3. Ti $L$-edge soft x-ray absorption spectroscopy (sXAS). Total electron yield (TEY) and partial electron yield (PEY) spectra for both the black TiO$_2$ and control TiO$_2$ are displayed with the fitted lines. The area ratios for $e_g$ to $t_{2g}$ from fitting are also present in the table.

<table>
<thead>
<tr>
<th>Area ($e_g$/$t_{2g}$)</th>
<th>Control TiO$_2$</th>
<th>Black TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEY $L_3$</td>
<td>2.24 ± 0.29</td>
<td>2.63 ± 0.26</td>
</tr>
<tr>
<td>TEY $L_2$</td>
<td>2.30 ± 0.34</td>
<td>2.56 ± 0.32</td>
</tr>
<tr>
<td>PEY $L_3$</td>
<td>2.21 ± 0.36</td>
<td>2.62 ± 0.35</td>
</tr>
<tr>
<td>PEY $L_2$</td>
<td>2.33 ± 0.35</td>
<td>2.54 ± 0.36</td>
</tr>
</tbody>
</table>
Figure S4. XPS spectra in the O 1s region for the black and control TiO$_2$. A shoulder peak of the black TiO$_2$ (marked by a circle) corresponds to the OH species, indicating that the relatively larger amount of OH species are incorporated to the black TiO$_2$ surface than that of the control TiO$_2$. 
Figure S5. Measurement of bulk electrical conductivities. (a) Pellets of TiO$_2$ and black TiO$_2$ for the 4-point-probe method and (b) experimental setup for the method proposed in B. Dunn’s work. The ITO electrode was deposited with a mask by RF sputtering, and the TiO$_2$ films were cast by a doctor-blade method.

The bulk conductivity of the black TiO$_2$ was one order of magnitude lower than that measured in the pelletized form. The reduced conductivity is attributed to the particle-to-particle resistance that may occur in the film cast by a doctor-blade method, and such resistance can be minimized in the cold-pressed pellet. The ITO that has been used as one of the terminal electrodes showed a resistance of ~10 ohms, which might disturb the electronic conduction through the setup in Figure S5.
Figure S6. Grain size distribution of black TiO$_2$ in HOP-bTiO$_2$. 
**Figure S7.** (a) N$_2$ adsorption/desorption isotherms for the HOP-bTiO$_2$. Pore size distributions derived from (b) NLDFT and (c) BJH methods.

NLDFT has been developed in recent years as an evaluation method of pore size distribution of porous materials. It is also known that the NLDFT method can analyze from micropores to mesopores as a unified theory, which is one of the advantages, compared to the classical BJH method. Another feature of NLDFT is that it can describe the gradual density change of adsorbate near the pore wall, whereas the classical theory (based on the Kelvin equation) only assumed the density to be the same as the liquid state.
Figure S8. FT-IR spectra for the HOP-bTiO$_2$ at pristine, discharged (1000 mAh g$^{-1}$), and recharged states. Reference materials are also displayed.
Figure S9. SEM images of the HOP-\(b\)TiO\(_2\) (a) at a discharged state to 1000 mAh g\(^{-1}\) and (b) at fully discharged state (~7500 mAh g\(^{-1}\)).
Figure S10. TEM images for the HOP-bTiO$_2$ electrode with the discharge product (a) at a discharged state to 1000 mAh g$^{-1}$ and (b) at fully discharged state.
Figure S11. SEM images for the HOP-bTiO$_2$ electrode with the discharge product at a discharged state to 4000 mAh g$^{-1}$ which corresponds to ~50% depth of discharge. The images are displayed with different magnifications.
Figure S12. (a) SEM image and (b) XPS spectra (Li 1s region) of HOP-bTiO$_2$ electrode when the cell (without LiI catalyst) died after 270 cycles (Figure 3(c)).
Figure S13. (a) SEM image of the HOP-bTiO$_2$ electrode with the discharge product in the presence of LiI redox mediator. (b) FT-IR spectra for the HOP-bTiO$_2$ at pristine and discharged (1000 mAh g$^{-1}$) states.
Figure S14. SEM images of (a) the pristine nanoporous black TiO$_2$ (NP-$b$TiO$_2$) electrode (fabricated with ~100-nm PS sphere) and (b) after discharge to 1000 mAh g$^{-1}$. (c) Voltage profiles showing the effect of electrode architecture on the activity of LiI catalyst (HOP-$b$TiO$_2$ and NP-$b$TiO$_2$).
**Figure S15.** Comparison of cycle-life performance in terms of terminal voltages (a) without and (b) with LiI. The capacities are limited to 1000 mAh g$^{-1}$. 
**Figure S16.** Photographs of (a) the pristine HOP-bTiO$_2$ electrode and (b) the cycled HOP-bTiO$_2$ electrode after the cell death. The retained black color even after long cycles is indicative of the preserved Ti$^{3+}$ ions with oxygen vacancies in the black TiO$_2$ structure.
Peak position
$(2p_{3/2})$  |  Peak position
$(2p_{1/2})$  |  Oxidation state
---|---|---
Control TiO$_2$  |  458.92 ± 0.02  |  464.61 ± 0.07  |  4.00
Pristine HOP-bTiO$_2$  |  458.06 ± 0.01  |  463.63 ± 0.04  |  3.54 ± 0.02
After discharge  |  458.34 ± 0.01  |  464.02 ± 0.05  |  3.69 ± 0.02
After charge  |  458.21 ± 0.02  |  463.96 ± 0.08  |  3.63 ± 0.02

**Figure S17.** The XPS Ti $2p$ spectra of Figure 5 with the fitting curves after background subtraction. The peak positions with the estimated oxidation states are listed in the table.
Figure S18. The XPS Ti $2p$ spectra at a fully-charged (100% SOC) and a fully-discharged state (100% DOD). The peak positions with respect to the states which are discharged and charged to 1000 mAh g$^{-1}$ are listed in the table.
Figure S19. TEM images of the black TiO\(_2\) with various H\(_2\) treatment of 0 h, 10 h, and 40 h. As the H\(_2\) annealing time increases, the amorphous surface layer becomes thick.