Nanoporous NiO Plates with a Unique Role for Promoted Oxidation of Carbonate and Carboxylate Species in the Li–O2 Battery

Misun Hong,†,*‡ Hee Cheul Choi,†,*‡§ and Hye Ryung Byon*†

†Byon Initiative Research Unit (IRU), RIKEN, Hirosawa 2-1, Wako, Saitama 351-0198, Japan
‡Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science (IBS), 77 Cheongam-Ro, Nam-Gu, Pohang 790-784, South Korea
§Department of Chemistry, Pohang University of Science and Technology (POSTECH), 77 Cheongam-Ro, Nam-Gu, Pohang 790-784, South Korea

Supporting Information

ABSTRACT: We report a novel catalytic reaction to promote oxidation of carbonate and carboxylate species using nanoporous nickel oxide (NiO) in the lithium–oxygen (Li–O2) battery. These nanoporous NiO catalysts in the shape of two-dimensional (2-D) hexagonal plates are incorporated on the carbon nanotube (CNT) electrode, which remarkably enhances oxidation efficiency of carbonate and carboxylate species as representative side products in Li–O2 electrochemistry and greatly improves the cycleability to more than 70 cycles. The oxidation reaction predominantly occurs at the nanoporous NiO toward which the carbonate and carboxylate species may migrate for the complete decomposition. This result is notably distinguished from a NiO-free CNT electrode, where such a passivation layer becomes thicker and precludes electron transfer, thus inducing poor cyclability.

INTRODUCTION

High demand for future energy storage systems has been driving rapid growth of battery research. In particular, since the urgent target for the applications in electric vehicles and grid storage demands great enhancement of energy density, there has been an advent of new battery systems beyond conventional lithium ion, lead–acid, and nickel–metal hydride batteries.1–3 In this context, a nonaqueous Li–O2 battery has been also extensively studied on account of high theoretical energy density (over 3 kWh kg cell−1) through the Li–O2 electrochemical reaction (2Li+ + O2(g) + 2e− ↔ Li2O2(s)).2,4,5 Furthermore, recent studies demonstrate improvements in performance providing an optimistic outlook for the Li–O2 cell. For example, a remarkable and reliable capacity higher than 1000 mAh g−1 has been demonstrated using lightweight carbons as a positive electrode.6 The electrical efficiency could be improved by using oxygen evolution reaction (OER) promoters that eliminate bulk Li2O2 at lower recharge potential.7–9 In addition, development of high-capacity materials for the negative electrode such as nanometer-sized and lithiated Si and SnO210,11 and metallic Li coated with a protective layer12,13 has added the possibility to accomplish a practical Li–O2 battery.

Despite such promising progress, however, the Li–O2 cell reaction still has crucial drawbacks, namely the accompanied parasitic side reactions by superoxide (O2•−, emerging via O2 gas reduction) and Li2O2. These oxide species are highly reactive toward organic components such as the aprotic electrolyte and carbon electrode, thus producing the side products of lithium carbonates (Li4CO3 and lithium alkyl carbonate) and lithium carboxylates (LiCO2R, where R is hydrogen or an alkyl group).14–24 To mitigate these chronic side reactions, the use of superoxide-tolerant electrolytes,25,26–28 carbon-free electrodes,29–33 and cycling with a limited depth of discharge34 have been considered. However, the approach pursuing complete prevention of side reactions is highly challenging, because of inherent electrolyte decomposition that occurs at Li2O2/electrolyte.19,20 As a result, the nonconductive side products passivate the positive electrode, which induces poor cyclability in the Li–O2 cells.22

Hence, a new strategy targeting the decomposition of side products is of great interest. The purpose is to circumvent the decrease of electrical conductivity in the positive electrode by oxidation of side products, mostly consisting of carbonate and carboxylate species. To efficiently oxidize the carbonate/carboxylate species, a proper catalyst is required, which must be stable and capable of functioning at a suitable potential close to that of the active OER of the Li2O2. In addition, low cost and a negligible effect on the electrolyte oxidation are essential.35 Here, for the first time, we report active oxidation of carbonate/
carboxylate species in the Li−O₂ cell, using a catalyst of thin and nanoporous NiO plates that are incorporated with carbon nanotubes (CNTs) (denoted as NiO/CNT electrode). It is noted that, despite some reports presenting NiO additives with carbonaceous electrodes and usage in the Li−O₂ cell,²⁶,²⁷ the new catalytic effect from NiO has not yet been demonstrated, although some computational results have envisioned such a role for NiO.²⁸,²⁹ We reveal that the carbonate/carboxylate species are precipitated over the NiO/CNT electrode then decomposed at the NiO under repeated discharge and recharge, respectively. In particular, migration of carbonate/carboxylate species toward the NiO along the CNT can contribute to its almost-complete decomposition, which results in recovered electrode at the end of recharge. In contrast, thick passivation layers of carbonate/carboxylate are still observed on the NiO-free CNT electrode after recharge, albeit with a higher potential. The nanoporous NiO is stable and has a negligible contribution to the electrolyte oxidation, which eventually improves cycling performance and electrical efficiency of the Li−O₂ cell.

**RESULTS AND DISCUSSION**

**Preparation of Nanoporous NiO/CNT Electrode.** The nanoporous NiO/CNT powder was synthesized via hydrothermal reaction and calcination (see Experimental Section in the Supporting Information). For the hydrothermal reaction, nickel(II) hydroxide (Ni(OH)₂) precipitates on the CNT and grows in the shape of a two-dimensional hexagonal plate via edge-sharing Ni−OH chains.⁴⁰−⁴² In the subsequent calcination process, the Ni(OH)₂ converts to NiO where hydroxyl ions are released as water molecules leaving behind small pores, forming the nanoporous NiO hexagonal plates.⁴² Transmission electron microscopy (TEM) images in Figures 1a and 1b display homogeneous distribution of resultant nanoporous NiO plates with a lateral size of 210 ± 33 nm on the CNT. A small pore size of <2 nm and a high BET surface area of 63 m² g⁻¹ are estimated for nanoporous NiO sheets, which were synthesized in the absence of CNT, using N₂ adsorption−desorption isotherm (see Figure S1 in the Supporting Information). The nanoporous NiO has the rock-salt crystal structure (Fm̅3m, a = 4.177 Å, JCPDS Card No. 47-1049). A high-resolution TEM image of an individual NiO nanoplate in Figure 1c reveals lattice fringes with a spacing of d₁ = 2.08 Å for the {200} crystallographic plane and d₂ = 2.42 Å and d₃ = 2.33 Å for the {111} plane. The selected-area electron diffraction (SAED) pattern of NiO/CNT (Figure 1c, inset) corroborates the 111, 200, and 220 planes of rock-salt crystalline NiO in addition to the graphite 002 plane of CNT, which is in good agreement with the XRD pattern (Figure 1d). A mass ratio of NiO is optimized to ~40 wt % in the NiO/CNT powder (see Figure S2 in the Supporting Information). The CNT mostly consisting of sp² bonding of carbon provides exclusive mechanical strength and chemical inertness. Even after the hydrothermal reaction, the graphitic layer of CNT in the as-prepared NiO/CNT has almost comparable quality to that of pristine CNT, as evidenced by a similar D-band to G-band intensity ratio (I_D/G = 1.0−1.1) in the Raman spectra (see Figure S3a in the Supporting Information) and a minor oxygen-associated peak in the C 1s X-ray photoelectron spectroscopy (XPS) result (see Figures S3b and S3c in the Supporting Information).

**Electrocatalytic Activity of NiO for Carbonate and Carboxylate Species.** To investigate the electrocatalytic activity of nanoporous NiO for the side products, we first conducted deposition of carbonate/carboxylate species, followed by anodic linear sweep voltammetry (LSV) in three-electrode cells. The carbonate/carboxylate species were deposited on NiO/CNT- and NiO-free CNT-loaded glassy carbon (GC) electrodes using galvanostatic reduction where O₂ gas-saturated propylene carbonate (PC) containing Li salt was used for the electrolyte with two metallic Li foils for the counter and reference electrodes (see inset in Figure 2). The PC

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**Figure 1.** Morphology and structure of NiO/CNT: (a) low-magnification and (b) high-magnification TEM images with size distribution of nanoporous NiO (see inset in panel (a)). (c) A high resolution TEM image of NiO nanoplate with SAED (inset) and (d) XRD pattern of NiO/CNT. The d-spacings d₁, d₂, and d₃ in panel (c) indicate lattice fringes of the crystallographic NiO plane {200} (d₁ = 2.08 Å) and {111} (d₂ = 2.42 Å and d₃ = 2.33 Å).

**Figure 2.** Oxidation potentials of carbonate/carboxylate species on NiO/CNT and CNT using anodic linear sweep voltammetry (LSV) on the basis of three-electrode electrochemical cells in O₂-saturated tetraglyme electrolyte with 0.5 M LiTFSI at a sweep rate of 1 mV s⁻¹. The dotted curves are blank electrodes. The galvanostatic depositions of carbonate/carboxylate species (inset) were conducted prior to the anodic LSV in O₂-saturated PC electrolyte with 0.5 M LiTFSI at a limited capacity of 100 mAh g⁻¹CNT and a current rate of 0.1 mA cm⁻²PC.
A solvent, having poor $\text{O}_2^{2-}$ tolerance, is severely decomposed under this condition and forms various carbonate/carboxylate species as the predominant products (see Figure S4 in the Supporting Information). The subsequent anodic LSV was conducted in fresh tetraglyme electrolyte instead of the PC, which is a widely used medium for the Li$^-$/O$_2$ cell, because of the higher $\text{O}_2^{2-}$ tolerance. The anodic LSV profiles in Figure 2 show the active oxidation potential, with respect to the decomposition of carbonate/carboxylate species. Notably, the NiO/CNT exhibits a low onset potential of 3.9 V and a ~400 mV lower peak potential than the NiO-free CNT. In addition, the NiO is negligibly involved in the oxidation of tetraglyme electrolyte. The oxidation curves with blank NiO/CNT and CNT (i.e., bare electrodes in the absence of reduction product) demonstrate comparable onset potentials at ~4.85 V (see Figure S5 in the Supporting Information). Therefore, the results on the basis of three-electrode system demonstrate the catalytic activity of NiO for the oxidation of carbonate/carboxylate species without any adverse effect on electrolyte oxidation.

**The Role of NiO in Discharge–Recharge Cycled Li–O$_2$ Cells.** The role of nanoporous NiO catalyst in the Li–O$_2$ cell is further studied through galvanostatic discharge (DC for the oxygen reduction reaction (ORR)) and recharge (RC for the OER) measurements. A binder-free NiO/CNT or CNT film with a CNT mass of 1.2–2.2 mg$_{\text{CNT}}$ cm$^{-2}$ was simply made via vacuum filtration for the positive electrode in the Li–O$_2$ cell (see the Experimental Section in the Supporting Information). Scanning electron microscopy (SEM) images in Figure S6 in the Supporting Information show a three-dimensional (3D) frame of entangled CNTs with a void space size of ~200 nm, which can offer facile O$_2$ gas transport. Furthermore, this CNT provides superior mechanical strength, electrical conductivity, and appropriate surface area (a BET surface area of ~100 m$^2$ g$^{-1}$), which can accordingly act as a sturdy electrode framework.

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**Figure 3.** Galvanostatic cycling characteristics and IR spectra of deep discharged (2.0 V) and recharged NiO/CNT and CNT electrodes. (a, b) The first, fifth, and tenth discharge–recharge cycling (DC-RC) curves of NiO/CNT (panel (a)) and CNT (panel (b)) in 0.5 M LiTFSI in tetraglyme at a current rate of 0.1 mA cm$^{-2}$. (c) Corresponding discharge capacity retention. (d, e) IR spectra of cycled NiO/CNT electrodes (panel (d)) and CNT electrodes (panel (e)) in wavenumbers of 400–2000 cm$^{-1}$ (left panel) and 200–600 cm$^{-1}$ (right panel). The as-prepared electrodes were soaked in the electrolyte, followed by washing and drying. The small IR peaks for the as-prepared electrodes in 500–1600 cm$^{-1}$ arise from impurities in CsI powder used for the preparation of IR transparent pallets. The terms “$n$DC” and “$n$RC” indicate electrodes cycled $n$ times at the end of discharge and recharge, respectively.
The galvanostatic examinations were conducted under the condition of deep depth of DC and at a cutoff potential of 2.0 V, followed by RC to either the equivalent capacity of the DC or a cutoff potential of 4.5 V at a constant current rate of 0.1 mA cm$^{-2}$. This full DC-RC cycling condition is well-known to intensively induce side reactions and swift termination of cycle life\textsuperscript{15,16,18} which accordingly enables a prompt and reliable evaluation of the oxidation efficiency associated with the cycling performance. Figures 3a–c exhibit representative potential curves of first, fifth, and tenth cycles and capacity-retention profiles for the NiO/CNT and CNT electrodes. Upon the first DC (1DC), the NiO/CNT and CNT electrodes deliver a gravimetric capacity of \(-1250\) and \(1450\) mAh g\textsubscript{CNT}\textsuperscript{-1} with a CNT mass of 1.3 and 1.5 mg\textsubscript{CNT} (equivalent to a capacity of \(~1.6\) and \(~2.2\) mAh), respectively, and a comparable potential of \(~2.55\) V, for which predominantly Li$_2$O$_2$ is formed. The infrared (IR) spectra in Figures 3d and 3e and Figure S7 in the Supporting Information exhibit the absorption peaks for the peroxide at 330, 420, and 530 cm$^{-1}$ (denoted by solid diamond symbols, ◆\textsuperscript{15} but also additional small peaks of trace of the TFSI ion ($\nu$(CF$_3$) at \(~1200\) cm$^{-1}$, denoted by a hashtag symbol, #)\textsuperscript{43} and carbonate species (denoted by open squares and circles, □ and ○, respectively). The peroxide peaks disappear after RC with a lower potential for the NiO/CNT (a plateau of \(~4.0\) V) compared to that of the CNT (4.3–4.4 V, Figures 3a and 3b). This result demonstrates an additional advantage of NiO promoting the peroxide oxidation, which is confirmed by LSV evaluation for the Li$_2$O$_2$ oxidation in the three-electrode cell (Figure S8 in the Supporting Information).

For further cycling, both electrodes are acutely subjected to the side reactions, providing extensive deposition of side products after DCs. The IR spectra reveal pronounced carbonate, carboxylate, and tetraglyme-associated peaks: the CO$_3^{2-}$ deformation and $\nu$(CO$_3^{2-}$) at 865, 1440, and 1500 cm$^{-1}$ assigned to lithium carbonate (Li$_2$CO$_3$, denoted by open inverted triangles, ▼\textsuperscript{44} the $\nu$(CO$_3^{2-}$) peaks at 1370–1615 cm$^{-1}$ for lithium formate (denoted by open squares, □ and carbonate species (denoted by open squares and circles, □ and ○, respectively). The peroxide peaks disappear after RC with a lower potential for the NiO/CNT (a plateau of \(~4.0\) V) compared to that of the CNT (4.3–4.4 V, Figures 3a and 3b). (Figure S7 in the Supporting Information). This result is very distinct from the pronounced IR peaks on the NiO-free CNT, demonstrating the existence of considerable carbonate/carboxylate species after the 5RC and 10RC (see Figures 3d and 3e)\textsuperscript{20} The efficient oxidation of carbonate/carboxylate species using the nanoporous NiO is further corroborated by XPS surface analysis and SEM observation. The wide-range X-ray photoelectron spectra of NiO/CNT electrodes show almost comparable peak intensity of sp$^3$-hybridized carbon, arising from the CNT at 284.5 eV, after the 5RC. Although a gradual increase of O 1s, F 1s, and S 2s and 2p peaks (Figure 4a) and new appearance of ∆3CO$_2$ + 4Li$^+$ + 4e$^-$ $\rightarrow$ 2Li$_2$CO$_3$ + C  
$E^0 = 2.8$ V

2CO$_2$ + O$_2$ + 4Li$^+$ + 4e$^-$ $\rightarrow$ 2Li$_2$CO$_3$  
$E^0 = 3.82$ V

Most importantly, these carbonate/carboxylate species are almost completely decomposed from the NiO/CNT electrode. The IR spectra for the fifth and tenth RC (denoted as 5RC and 10RC, respectively) show the disappearance of carbonate/carboxylate peaks on the NiO/CNT, which is in a good agreement with the $^1$H NMR spectra (see Figure S11 in the Supporting Information). This result is very distinct from the pronounced IR peaks on the NiO-free CNT, demonstrating the existence of considerable carbonate/carboxylate species after the 5RC and 10RC (see Figures 3d and 3e)\textsuperscript{20} The efficient oxidation of carbonate/carboxylate species using the nanoporous NiO is further corroborated by XPS surface analysis and SEM observation. The wide-range X-ray photoelectron spectra of NiO/CNT electrodes show almost comparable peak intensity of sp$^3$-hybridized carbon, arising from the CNT at 284.5 eV, after the 5RC. Although a gradual increase of O 1s, F 1s, and S 2s and 2p peaks (Figure 4a) and new appearance of small peak at 286–288 eV correlated with the C–O, C≡O, and C–OH\textsuperscript{53} in the C 1s binding-energy region (Figure 4b) account for minor residue of LiTFSI and tetraglyme solvent in the electrolyte and occurrence of oxidation of CNT surface, there is no evidence of significant carbonate/carboxylate species. In contrast, the CNT electrodes reveal a considerably smaller peak intensity of sp$^3$-hybridized carbon after the 5RC (Figure 4c), which indicates the presence of thick passivation layer covering the CNT. The chemical composites of this layer can be demonstrated from the normalized C 1s spectrum in Figure 4d, where a carbonate/carboxylate species-related peak
is obvious at 288−291 eV, in addition to a tetraglyme-related species at 286−288 eV and a sp³-hybridized diamond-like carbon shoulder at 285.2 eV. The presence of side-product layer can be also visibly confirmed from the SEM observation (Figure 5). The NiO/CNT electrodes exhibit thin passivation layers on both CNTs (a total diameter ($d \leq 100$ nm including the CNT ($d = 10−40$ nm)) and NiO nanoplates after DC, and their complete disappearance after RC for fifth and tenth cycles (see Figures 5a−e). On the other hand, thick and dense layers with a total $d$ of 300−500 nm are observed for the 5DC CNT electrode, which still remain thick ($d = 200−300$ nm) after the subsequent RC (Figures 5f−h).

All these results support the almost complete decomposition of predominant carbonate/carboxylate species in the presence of the NiO while the thick and dense passivation layer is accumulated on the NiO-free CNT after cycling. This result demonstrates that the nanoporous NiO catalyst notably enhances the efficiency for the oxidation of carbonate/carboxylate species during cycling. It is noteworthy that any additional role of NiO for the transformation of discharge products morphology and crystallinity, thus contributing to improve its decomposition efficiency during cycled RC, is negligible (see Figure S12 in the Supporting Information). The cycling product is mostly amorphous, which covers the electrode without any notable distinct feature for both CNT and NiO/CNT electrodes. In addition, it should be noted that the RC potential does not fully represent the catalyst efficiency. The potential profiles show only 100 mV difference between the 10-cycled NiO/CNT (~4.1 V on average) and CNT (~4.2 V) (Figures 3a and 3b), albeit with clear differences in the decomposition of side products. Instead, the effect of NiO role is apparent when cycling performance is evaluated. Notably, a rapid capacity drop to ~17% is observed for the CNT (Figure 3c). This is due to the hindrance of charge transfer from the cumulative passivation layers of carbonate/carboxylate species. In contrast, the revitalized electrode with high conductivity by the NiO catalyst can serve as a suitable ORR platform for every cycle. It is noted that the thick passivation layer may be decomposed with increasing RC potential on the CNT electrode, which, however can eventually compromise cyclability due to the rapid consumption of electrolyte and considerable damage to the CNT electrode.

Stability of Nanoporous NiO. The nanoporous NiO structure is stable for the deep depth of cycles. The Ni K-edge X-ray absorption near-edge structure (XANES) spectra with the fluorescence yield (FY) mode exhibit an intense white line at a photon energy of ~8346 eV with a half-height energy of ~8340 eV for as-prepared and cycled NiO/CNT electrodes (see Figure S13 in the Supporting Information). These resultant spectra demonstrate neither reduction nor oxidation of NiO.

Figure 5. SEM images of deep depth of DC and RC electrodes: (a−e) NiO/CNT electrodes of (a) the as-prepared sample, and at the end of (b) 5DC, (c) 5RC, (d) 10DC, and (e) 10RC. (f−h) CNT electrodes of (f) the as-prepared, and at the end of (g) 5DC and (h) 5RC.
Furthermore, TEM images and the correlated SAED obtained at 0, 50%, and 100% of the 5RC show the retaining rock-salt crystal structure of nanoporous NiO (Figure S14 in the Supporting Information). These results highlight the stability of nanoporous NiO without either chemical or structural transformation, thus accounting for stable RC potential, linked with the fully decomposed carbonate/carboxylates, during cycling.

On the basis of highly stable NiO, striking cycling performance of the NiO/CNT can be demonstrated under a limited capacity of 1000 mAh g\textsubscript{CNT} \textsuperscript{−1}. The capacity retention sustains over 70 cycles with very stable DC potential and RC potential (Figures 6a, c). This cycling stability is notably greater than that of the NiO-free CNT electrode delivering total ∼50 cycles with a gradual decrease of DC potential (Figures 6b, d). The enhanced capacity retention (Figure 6e) is therefore attributed to the role of NiO contributing to efficient elimination of side products. The termination of long cycling may result from the degradation of metallic Li as the negative electrode and depletion of electrolyte while we cannot fully rule out inactivation of NiO catalyst working after 600 h.

Proposed Mechanism for Decomposition of Carbonate and Carboxylate Species on NiO/CNT. Along with catalytic performance, understanding the oxidation mechanism of the carbonate/carboxylate species using solid catalyst is vital. It was expected that the decomposition only occurred with products that either covered the nanoporous NiO or were in close proximity to the NiO/CNT interface. However, unlike this hypothesis, the entire passivation layer on the electrode disappeared after RC. In light of the SEM images of NiO/CNTs (Figures 5b–e), the entire product, even the portion passivating the CNT part, is decomposed after the subsequent RC. The detailed process is not very clear, while we propose that the carbonate/carboxylate species migrate along the CNT toward the nanoporous NiO where the oxidation is vigorously performed. TEM images at 0, 50%, and 100% depth of the SRC show that the products homogeneously passivated on the NiO/CNT appear to form agglomerates next to the NiO in the interim, then disappear at the completion (see Figure 7 and Figures S15a–f in the Supporting Information). Namely, the bare CNT in the NiO/CNT electrode is exposed during the RC as the products are concentrated on the NiO, which is distinguished from the existence of passivation layer on the NiO-free CNT electrodes, even after the 100% SRC (see Figures S15g and S15h in the Supporting Information). The reason and driving force for such migration in the presence of NiO is currently unknown and accordingly further detailed study is under investigation on the basis of an in situ visualization system.

Figure 6. Long-term cycling performance of NiO/CNT and CNT electrodes. Time-potential profile of the galvanostatic discharge–recharge cycles for (a) NiO/CNT and (b) CNT electrodes in 0.5 M LiTFSI in tetraglyme at either a limited capacity of 1000 mAh g\textsubscript{CNT} \textsuperscript{−1} or cutoff potentials of 2.0 and 4.5 V vs Li/Li+. The arrows indicate the number of cycles. Discharge–charge potential profiles of the 1st, 20th, and 55th cycles for (c) NiO/CNT and (d) CNT. (e) Corresponding discharge capacity retention of NiO/CNT (blue) and CNT (red).

Figure 7. Decomposition process of passivation layer of carbonate/carboxylate species on NiO/CNT. (a–c) TEM images at (a) 0, (b) 50%, and (c) 100% accomplished SRC. The yellow arrows indicate nanoporous NiO plates. The scale bars are 100 nm. (d) Schematic illustration of carbonate/carboxylate decomposition.
CONCLUSION

In summary, we demonstrated promoted decomposition of carbonate/carboxylate species and peroxide in Li–O₂ cells. The nanoporous NiO/CNT successfully oxidized the poorly conductive carbonate/carboxylate layer, which resulted in improved cyclability. In addition, the low-cost nanoporous NiO had negligible effect on the electro-oxidation of tetraglyme, which could make the NiO/CNT a feasible catalyst for the practical Li–O₂ cell. We believe that this strategy can significantly improve Li–O₂ cell performance in combination with other components that have been strategically suggested to alleviate the parasitic side reactions. That is, design of a carbon-free electrode in conjunction with the nanoporous NiO promoter and the utilization of stable electrolyte under the operation of an adequate depth of discharge is a good example. In such a cell, a relatively small amount of side products may be formed, which can be decomposed by the nanoporous NiO/In nanoporous NiO/CNT success fully oxidized the poorly tetraglyme, which could make the NiO/CNT a feasible catalyst for the practical Li–O₂ cells. The suppressed side reactions and prolonged active electrode surface can enhance cycle life and limitation of aging of the Li–O₂ cell for use as a promising future battery.

ASSOCIATED CONTENT

Supporting Information
Experimental procedure, additional electrochemical analyses and characterizations using TEM, SEM, XRD, BET, TGA, Raman spectroscopy, XPS, NMR, XANES. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: choihc@postech.edu (H. C. Choi).
*E-mail: hrbyon@riken.jp (H. R. Byon).

Author Contributions
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Notes
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