Hierarchical Porous Carbonized \( \text{Co}_3\text{O}_4 \) Inverse Opals via Combined Block Copolymer and Colloid Templating as Bifunctional Electrocatalysts in Li–O\(_2\) Battery

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Hierarchically organized porous carbonized-\( \text{Co}_3\text{O}_4 \) inverse opal nanostructures (C-\( \text{Co}_3\text{O}_4 \) IO) are synthesized via complementary colloid and block copolymer self-assembly, where the triblock copolymer Pluronic P123 acts as the template and the carbon source. These highly ordered porous inverse opal nanostructures with high surface area display synergistic properties of high energy density and promising bifunctional electrocatalytic activity toward both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). It is found that the as-made C-\( \text{Co}_3\text{O}_4 \) IO/Ketjen Black (KB) composite exhibits remarkably enhanced electrochemical performance, such as increased specific capacity (increase from 3591 to 6959 mA h g\(^{-1}\)), lower charge overpotential (by 284.4 mV), lower discharge overpotential (by 19.0 mV), and enhanced cyclability (about nine times higher than KB in charge cyclability) in Li–O\(_2\) battery. An overall agreement is found with both C-\( \text{Co}_3\text{O}_4 \) IO/KB and \( \text{Co}_3\text{O}_4 \) IO/KB in ORR and OER half-cell tests using a rotating disk electrode. This enhanced catalytic performance is attributed to the porous structure with highly dispersed carbon moiety intact with the host \( \text{Co}_3\text{O}_4 \) catalyst.

1. Introduction

The fast depletion of fossil fuels and extended environmental concerns have inspired active research on the utilization and storage of clean and sustainable energy. Among various energy storage technologies, rechargeable metal–air batteries have the highest potential for next generation electrical vehicles and hybrid electrical vehicles.[11–8] In metal–air batteries, a metal anode such as Li or Zn is coupled with an air breathing cathode that utilizes high purity oxygen as the reactant in electrochemical reactions. Among the emerging metal–air batteries, rechargeable lithium–air batteries (also called Li–O\(_2\) batteries) are considered one of the most attractive high energy storage and conversion electrical energy devices due to their extremely high theoretical energy density.[9–12]

Up to date, however, the successful commercialization of rechargeable Li–O\(_2\) batteries still rely on an improvement of poor safety characteristics as the formation of lithium dendrite, round-trip efficiency, and cycle life.[13–15] Several contributions of prime importance have been reported to enhance the battery performance by improving critical constituents including the Li anode,[16–18] operating atmosphere,[19,20] binders,[21] solvents,[22] and lithium salts.[23,24]

Albeit the extension of the above-mentioned exploratory works, the choice of the air cathode has been often underlined as the dominating issue in the performance of Li–air batteries. Accordingly the bifunctional activity of the cathode in Li–O\(_2\) battery, i.e., oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is the key factor of battery performance.

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Major challenges associated with the commercialization of Li–O2 battery reside in the sluggish kinetics, which require efficient bifunctional catalytic activity, crucial in enhancing the Li–O2 cell performance. Currently, commercial carbon-based electrode support Ketjen Black (KB) has been widely utilized due to its high conductivity, high surface area, and cost effectiveness. It is noted, however, that the overpotential of OER is much higher than that of ORR, thus affecting the overall stability of Li–O2 battery. In addition, the stability of these materials raises concerns regarding the successfulness of an aspired commercialization. Attempts to improve reference C-based materials or to develop alternative C-free cathodes to suppress the formation of carbon-related by-products have emerged as an uprising topic of interest in the past few years.\cite{25,26} Notably, noble metals, carbides and nitrides, and oxides, stable toward nucleophilic attack by O2 and O2^2−, have been highlighted in numerous research studies.\cite{6,27–30}

Recently, many efforts have been particularly devoted to the development of porous materials for highly active cathode catalysts, with high surface area and stable architecture.\cite{6,26,31–33} 3D ordered macroporous (3DOM) materials, in particular inverse opal structures, have attracted increasing interest due to their promising features, e.g., facile charge transport via interconnected nanoframework, appropriate oxygen transport via porous structure, and high surface area for accommodation of discharge products. Olivares-Marín et al. proposed binder-free carbon inverse opal with controlled macropore size as Li–O2 cathode in which the dual porosity enabled the best performance. However, the discharge/charge capacity was low even at a low current density.\cite{34} Xu et al. suggested 3DOM LaFeO3 perovskites as a catalyst of cathode with a ratio of KB and catalyst being 2 to 1. It is noted that the conventional KB might exhibit a dominant catalytic activity in this system and the Brunauer–Emmett–Teller (BET) surface area of prepared catalyst was at a lower level (~30 m^2 g^-1) than other porous materials.\cite{35} Park et al. demonstrated that the 3DOM Co3O4 catalysts were capable of exhibiting higher electrochemical performance than Co3O4 nanoparticle in half-cell tests and Zn–air battery, although the work merely focused on a structural comparison between the samples.\cite{36} Li et al. demonstrated the development of pomegranate-like bifunctional electrocatalyst incorporating Co3O4 nanocrystals embedded in a nitrogen-doped partially graphitized carbon framework for Zn–air batteries. Nevertheless, this work did not show any reasonable capacity or energy density values.\cite{37}

Herein, we developed hierarchically organized nanoporous hybrid carbon-Co3O4 inverse opal nanostructures via complementary colloid templating and direct carbonization of block copolymer (BCP) scaffolds, and systematically demonstrated their enhanced electrochemical activity in half-cell and Li–O2 battery tests. The key of the fabrication route proposed in this study includes facile preparation of carbonaceous nanohybrids via direct conversion of BCPs into graphitic carbons and incorporation of multiple length scale nanopores in the inverse opals, based on the protocol established in our previous works.\cite{38–45} To demonstrate the design concept, cobalt oxide (Co3O4) was chosen as a model material owing to its abundance and theoretically high electrocatalytic activity.\cite{46} Comprehensive characterization of Co3O4 nanoparticle (Co3O4 NP), Co3O4 inverse opal (Co3O4 IO), and carbonized Co3O4 inverse opal (C-Co3O4 IO) was obtained. To the best of our knowledge, this is therefore the first 3DOM-based C-Co3O4 nanocomposite utilized for a Li–O2 battery so far. The incorporation of the prepared Co3O4-based materials was therefore intended in commercial conductive carbons such as KB or Vulcan XC72, representative of cathodes of choice with application in Li–O2 cells. Herein, mechanical mixtures of KB and Co3O4 were evaluated in both OER and ORR half-cells, and in Li–O2 battery. The enhanced oxygen electrocatalysis is systematically investigated based on the new class of hierarchical mesoporous carbon–Co3O4 nanostructures by optimizing the composition and morphology in terms of improved specific capacity, cycle stability, overpotential, etc.

## 2. Results and Discussion

### 2.1. Structure and Morphology Analysis

**Figure 1** shows the schematic diagram for the fabrication of Co3O4 inverse opal (Co3O4 IO) and mesoporous carbonized Co3O4 inverse opal (C-Co3O4 IO) nanostructures by complementary colloid and BCP self-assembly processes. Sol–gel precursors of Co3O4 are infiltrated into the interstitial sites of self-assembled colloidal polystyrene (PS) beads array. Subsequent calcination at ~400 °C induces simultaneous gelation of the precursors and removal of PS templates, leading to the formation of Co3O4 IO nanostructure. To generate C-Co3O4 IO, poly(ethylene oxide-block-propylene oxide-block-ethylene oxide) triblock copolymers (P123) were infiltrated together with Co3O4 precursors. P123 simultaneously acts as a structure directing agent\cite{47,48} and a carbon precursors, whereas the
Co3O4 precursors are selectively combined with the hydrophilic domains of P123. Importantly, periodically arranged mesopores are generated in the resultant C-Co3O4 IO driven by the phase separation of BCPs and the removal of hydrophobic domains of P123. Thus, hierarchically organized C-Co3O4 IOs retaining multiple length scale nanopores are obtained by simple yet unique strategy developed in this study. It is noted that in the case of C-Co3O4 IO synthesis, an additional oxidation step by calcination in air is needed to convert CoO to Co3O4. The above-mentioned samples were therefore physically mixed with KB in a weight proportion of 50:50%. Characterization of the prepared Co3O4-based catalysts is detailed below.

The field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were represented to investigate the morphology of the nanostructures involved in each step of the entire fabrication process in Figure 1. Co3O4 nanoparticles (NPs) with a diameter in the 20–60 nm range (Figure S1a,b, Supporting Information) were also prepared for further comparison of the performance of the IO-based electrocatalysts. Well-defined, ordered, and periodic arrays of self-assembled PS beads were obtained (Figure S1c, Supporting Information). The inset in panel (a) is the magnified FE-SEM image. c) FE-SEM and d) TEM images of C-Co3O4 IO. The inset in panel (c) is the magnified FE-SEM image.

The crystal structure of both Co3O4 nanostructures was examined by X-ray diffraction (XRD) (Figure 3b). The XRD patterns of all samples were confirmed to agree with reported spinel cobalt oxide (JCPDS No. 42-1467). The Co3O4 NP shows much higher crystallinity than other inverse opal structures according to the highly compact nature without pore formation. On the other hand, C-Co3O4 shows the lowest crystallinity because of the oxidation step to induce Co3O4 from CoO. The coherent crystal size of C-Co3O4 IO was confirmed to be around 17.51 nm based on the Scherrer’s equation, which is in good agreement with the size of Co3O4 crystallites as shown in TEM image (Figure 2d). To confirm the presence of carbon moieties, Raman spectroscopy was performed (Figure 3c). With C-Co3O4 IO characteristic G and D bands were observed around 1600 and 1350 cm−1, respectively. The G band indicates nanocrystalline sp2 hybridized carbon and D band corresponds to disordered carbon, which correlate with P123 template conversion into partially graphite carbon. The peaks observed at lower range between 100 and 700 cm−1 were ascribed to the Co3O4 structure.

2.2. Electrochemical Performance in Half-Cell Tests

The electrochemical activity of the as-prepared Co3O4-based catalysts and mixtures of...
KB with Co$_3$O$_4$ (catalyst/KB) was systemically investigated and compared with a commercial KB reference, which was believed critical in the evaluation of the performance of the hybrid catalysts in both ORR and OER activities to utilize in Li–O$_2$ battery. Figure 4 depicts ORR and OER activities of the aforementioned samples supported on a rotational glass-carbon electrode. The electrocatalytic activities were investigated by linear sweep voltammetry (LSV) in O$_2$-saturated 0.1 m KOH electrolyte at a scan rate of 5 mV s$^{-1}$ using a three electrode system. Catalytic parameters were in each case conveniently summarized in Table 1. Cyclic voltammetry (CV) of the evaluated samples in N$_2$-saturated 0.1 m KOH solution at a scan rate of 20 mV s$^{-1}$ have been included in the Supporting Information of this work (Figure S3, Supporting Information). KB leads to higher current density in CV.

Figure 4a shows the ORR activity of KB, catalysts, and mixtures of KB with catalyst (catalyst/KB) by monitoring voltammograms in O$_2$, at a rotation speed of 1600 rpm. The catalytic activities of the samples were assessed by corresponding onset and half-wave potentials.$^{[52]}$ It is clearly observed that the polarization curves obtained with all catalyst/KB and KB exhibit positively shifted onset potentials, compared with the individually tested Co$_3$O$_4$ catalysts. The incorporation of KB is concluded to lead to an increase in the ORR onset and half-wave potential. Among the Co$_3$O$_4$-based samples, the Co$_3$O$_4$ NP (light blue line) reveals the lowest ORR activity and limiting current density. The result seems to highlight the fact that high surface area of the 3D IO hierarchical architecture notably contributes to boost the electrochemical ORR activity of these materials. Kinetic current densities at 0.7 V in the kinetic and diffusion-controlled region (0.8–0.5 V vs reversible hydrogen electrode; RHE) are further compared in Table 1. In ORR half-wave potential and kinetic current at 0.7 V, it is followed to order Co$_3$O$_4$ NP < Co$_3$O$_4$ IO < C-Co$_3$O$_4$ IO. Among the investigated samples, C-Co$_3$O$_4$ IO/KB shows the highest kinetic current density at 0.7 V. Similar trends were witnessed upon comparison of the half-wave values for each evaluated electrocatalyst. Co$_3$O$_4$ IO/KB and C-Co$_3$O$_4$ IO/KB revealed the highest $V_{\text{half}}$ (0.66 V), which is in line with the corresponding onset potential of both electrocatalysts. KB was shown to display a maximal oxidation current as low as 8.88 mA cm$^{-2}$ in the evaluated potential range. Contrarily to ORR, KB exhibits herein a poor performance as an OER electrocatalyst. Mixtures of catalyst with KB unveiled improved catalytic activity compared to Co$_3$O$_4$-based electrocatalysts. As observed in the case of ORR, IO-based catalysts showed notably higher activity than Co$_3$O$_4$ NP, implying an impact of the high surface area of the 3D hierarchical architecture to enhance the electrochemical reaction.
C-Co$_3$O$_4$ IO/KB offers the highest current density, with a value of 44.02 mA cm$^{-2}$ and an OER potential at 10 mA cm$^{-2}$ of 1.71 V vs RHE, highlighting the potential interest of this material in Li–O$_2$ batteries. Surprisingly, however, the incorporation of KB seems to only slightly improve the performance of the hybrid electrocatalyst. In the absence of KB, for instance, C-Co$_3$O$_4$ IO attains an equally remarkably high density of 41.76 mA cm$^{-2}$. This can be rationalized based on the poor performance displayed by the individually tested KB sample. On the contrary, Co$_3$O$_4$ has been previously reported as a catalyst of choice in OER. [53,54] Similarly, the incorporation of a carbon moiety during the carbonization of Co$_3$O$_4$ in presence of P123 appears to merely result in a slight improvement of the performance of the electrocatalyst, as underlined by the performance of both C-Co$_3$O$_4$ IO/KB and Co$_3$O$_4$ IO/KB.

The electrochemical performance in OER and ORR half-cell tests supports the impact of the IO structure in both reactions, whereas the incorporation of KB seems to be of major interest during the ORR evaluation. These results seem to hint the interest of C-Co$_3$O$_4$ IO/KB as a bifunctional catalyst in Li–O$_2$ battery.

### 2.3. Electrochemical Performance in Li–O$_2$ Battery

The electrocatalytic activity of C-Co$_3$O$_4$ IO catalyst for ORR and OER was examined in Li–O$_2$ cells and compared to Co$_3$O$_4$ IO, Co$_3$O$_4$ NP, and bare KB. The first discharge/charge curves of Li–O$_2$ cells, with the four different cathodes in an O$_2$-saturated electrolyte (1.0 m lithium bis(trifluoromethylsulphonyl) imide; LiTFSI in tetraethylene glycol dimethyl ether; TEGDME), were displayed in Figure 5a. Reported capacities are normalized by the mass of KB used in the cathodes operated at 100 mA g$^{-1}$ within 2.0–4.5 V. [55,56] Both the discharge and, particularly, the charge overpotentials of Li–O$_2$ cells are improved in the presence of C-Co$_3$O$_4$ IO. Notably, the discharge capacity could be increased up to 6959 mA h g$^{-1}$ with C-Co$_3$O$_4$ IO/KB when compared with the KB reference sample (3591 mA h g$^{-1}$), reflecting a nearly twofold capacity increase. The evaluated Li–O$_2$ cells using Co$_3$O$_4$ NP/KB, Co$_3$O$_4$ IO/KB, and C-Co$_3$O$_4$ IO/KB as cathodes revealed an increase in their corresponding discharge overpotential by 16.3, 6.5, and 19.0 mV, respectively, in comparison with KB-based devices (Figure S4, Supporting Information). More importantly, while the difference in values of overpotentials was rather negligible on discharge, corresponding charge overpotentials were remarkably decreased by 82.3, 166.3, and 284.4 mV, respectively, when compared with the aforementioned counterparts. The drawbacks associated with the application of carbon-based cathodes in Li–air batteries have been extensively detailed in many researches. The decomposition of Li$_2$O$_2$ at lower charge may in this context be of interest as promising sidesteps in the bottlenecks associated with the well-established application of carbon materials in Li–O$_2$ batteries.

The electrochemical reaction of oxygen in the Li–O$_2$ cell was also probed using CV. Figure 5b depicts the representative CV response of the cells at a scan rate of 0.1 mV s$^{-1}$ between 2.0 and 4.5 V, obtained during the fifth cycle after stabilization. The C-Co$_3$O$_4$ IO/KB cathode exhibits higher ORR and OER current density compared with Co$_3$O$_4$ IO/KB, Co$_3$O$_4$ NP/KB, and KB. The results transpire a superior electrochemical activity toward both the formation and decomposition of the discharge products.
The demonstrated superior battery capacity, lower overpotential, and improved OER and ORR performances reflect the potential interest of our novel material in Li–O₂ battery applications. The incorporation of a hierarchical 3D mesoporous structure with a carbon moiety as a catalyst in a KB-based cathode appears to facilitate the continuous flow of the species involved during both discharge and recharge processes.\cite{12,57,58} Whereas literature reports may remain controversial, previous work citations seem to suggest that in the presence of hybrid electrocatalysts comprising Co₃O₄ and a carbon-based counterpart, the deposition of Li₂O₂ may occur preferentially in the surface of carbon.\cite{59,60} The presence of Co₃O₄ remains however critical in the decomposition of Li₂O₂ during the charge process.\cite{61,62} It is believed that the presence of Co₃O₄ with extended BET surface area (Figure 3a) may present a higher number of active sites assumed crucial in the O₂-Li₂O₂ conversion. Accordingly, Co₃O₄ can take full advantage of its intrinsic activity, leading to an improved OER performance.\cite{52} The assumption is in good agreement with the results obtained in both OER half-cell and Li–air cell performances. The dispersion of Co₃O₄ in the KB evidenced in representative SEM image in Figure S5 (Supporting Information) is therefore of prime interest for a faster decomposition of Li₂O₂. Conversely, the incorporation of carbon moieties in the IO structure using P123 augments the number of active sites where the formation of Li₂O₂ is expected to be preferred. The assumption may shed additional light to the higher battery capacity when KB is alternatively mixed with Co₃O₄ IO (4910 mA h g⁻¹) or C-Co₃O₄ IO (6959 mA h g⁻¹). The extended BET surface area and generated mesoporosity of the carbon moieties may provide enough void volume for a gradual deposition of formed discharge products in the introduced carbon moieties of C-Co₃O₄ IO. The sample additionally evidences an improved electrocatalytic activity by effective transportation of electrons due to the presence of the carbon species in the IO structure.

The promising fingerprints of our novel material are further reflected in the outstanding improvement in its cycle stability for Li–O₂ cells. Figure 6 and Figure S6 (Supporting Information) depict typical cycle stability profiles for Li–O₂ cells with all evaluated cathodes at a rate of 100 mA g⁻¹, using a 1000 mA h g⁻¹ capacity-limited cycle method. In agreement with the above-mentioned results, the stability of the Li–O₂ cells could be extended following the order C-Co₃O₄ IO/KB > Co₃O₄ IO/KB > Co₃O₄ NP/KB > KB. Both the discharge and, particularly, the charge cycle stability were notably improved in the presence of C-Co₃O₄ IO, leading to an enhancement of the round-trip efficiency. The discharge profile from the 23th cycle for the C-Co₃O₄ IO/KB cathode reaches 1000 mA h g⁻¹, with an end voltage of 2.58 V compared with KB (12th cycle with 2.3 V). Strikingly, the charge profile from the 19th cycle for the C-Co₃O₄ IO/KB cathode reaches 1000 mA h g⁻¹, with an end voltage of 4.21 V. On the other hand, the discharge profile for KB (12th cycle with 2.3 V) reaches 1000 mA h g⁻¹, with an end voltage of 2.58 V. The sample evidences an improved electrocatalytic activity by effective transportation of electrons due to the presence of the carbon species in the IO structure.
hand, the terminal voltage for the KB cathode merely exhibits 2nd cycle with 4.41 V. Although the cyclability comparison clearly shows the increased catalytic activity of C-Co$_3$O$_4$ IO, we believe that the cyclability of C-Co$_3$O$_4$ IO/KB electrode should be further enhanced to practically utilize it.

Based on the half-cell and full battery tests, the C-Co$_3$O$_4$ IO/KB system provided the best overall electrocatalytic activity and battery performance, notwithstanding a slightly better activity achieved with C-Co$_3$O$_4$ IO/KB for the ORR activity in half-cell test. This minor inconsistency was tentatively attributed to the operating conditions selected in each case. Indeed the half-cell test was performed in KOH medium and ambient condition, while the battery performance was measured in TEGDME electrolyte containing 1 M LiTFSI and inert atmosphere.

The discharge and recharge states of KB, Co$_3$O$_4$ NP/KB, Co$_3$O$_4$ IO/KB, and C-Co$_3$O$_4$ IO/KB cathodes are compared by FE-SEM in Figure S7 in the Supporting Information. The discharge products, Li$_2$O$_2$ with typically toroid-shaped structure, are homogeneously deposited on the KB. After recharging, the undecomposed toroid-shaped Li$_2$O$_2$ is still remained in KB. Co$_3$O$_4$ NP/KB in Figure S5a (Supporting Information) indicates the initial state that Co$_3$O$_4$ NPs (white one) are aggregated on KB (black one). As a result, NPs could not offer sufficient voids for Li$_2$O$_2$ deposition as similarly as KB. This is the reason why discharge products does not fully decompose with remaining in Co$_3$O$_4$ NP/KB after recharge state. While discharging, the fog-like shaped Li$_2$O$_2$ is covered on the inverse opal voids from Co$_3$O$_4$ IO/KB-based cathode. It can be more easily decomposed compared to toroid-shaped Li$_2$O$_2$. With our new system of C-Co$_3$O$_4$ IO/KB, the thin plate-like Li$_2$O$_2$ is deposited on inverse opal voids which the size of the plate-shaped Li$_2$O$_2$ particles is around 300 nm, and therefore similar in size with inverse opal voids. The nature of the discharge products was further confirmed by XRD measurement. The characteristic peaks observed at 32.7°, 34.8°, and 58.5° clearly show the formation of Li$_2$O$_2$ on discharged C-Co$_3$O$_4$ IO/KB cathode, as shown in Figure S8 in the Supporting Information. After recharging to 4.5 V, the deposited Li$_2$O$_2$ in both Co$_3$O$_4$ IO/KB and C-Co$_3$O$_4$ IO/KB is largely reversibly decomposed.

To better elucidate the performance of the Li–air cell during cycling, electrochemical impedance spectroscopic analysis (EIS) is measured on Li–O$_2$ cells at the initial stage, and at the end of the first discharge and recharge processes for each evaluated cathode (Figure 7). Anodic contribution in Li–O$_2$ cell was considered negligible. All EIS curves after the discharge/charge process exhibited expected profiles. The diameter of the semicircle represents the charge-transfer resistance during the ORR. This charge transfer resistance significantly increased with discharge from about 100 to 500 Ω for KB, 110 to 400 Ω for Co$_3$O$_4$ NP/KB, 130 to 350 Ω for Co$_3$O$_4$ IO/KB, and from about 120 to 800 Ω for C-Co$_3$O$_4$ IO/KB, respectively. The high charge-transfer resistance for both electrodes is attributed to the accumulation of highly resistive reaction product on the surface. In particular, poor electronic conductive precipitates mostly ascribed to Li$_2$O$_2$ are distinctly observed at large extent at the electrode/electrolyte interface after the first discharge, leading to a significant increase in the interfacial resistance. After charging, a more significant decrease in C-Co$_3$O$_4$ IO/KB electrode is noted compared to KB, due to the decomposition of formed discharge Li$_2$O$_2$ products. It suggests that the electric charge transport was improved by the incorporation of carbon moieties in Co$_3$O$_4$ and consequently a narrow charge...

Figure 7. EIS results of Li–O$_2$ cells. a) KB, b) Co$_3$O$_4$ NP/KB, c) Co$_3$O$_4$ IO/KB, and d) C-Co$_3$O$_4$ IO/KB at different discharge/charge stages (current density: 100 mA g$^{-1}$).
potential gap was induced for the C-Co$_3$O$_4$ IO/KB-based battery.[8] The EIS analysis further underlines the superiority of C-Co$_3$O$_4$ IO/KB with high electrochemical activity and charge efficiency.

3. Conclusion

This contribution suggests a simple procedure for the fabrication of hierarchically organized mesoporous carbon–Co$_3$O$_4$ inverse opal nanostructures using P123 and PS beads as templates. The resulting 3D hierarchical macro-mesoporous structure incorporating carbon moieties was mechanically mixed with commercial KB and employed as electrocatalysts in half-cell tests and Li–O$_2$ cells. The 3D highly ordered mesomacroporous architecture well-dispersed on KB is believed to facilitate the transport of both Li species, O$_2$, and electron transfer. This work reflects the previously reported outstanding character of Co$_3$O$_4$ as an OER catalyst, particularly advantageous in the decomposition of formed discharge Li$_2$O$_2$ species. Conversely, the mesoporous carbon moieties incorporated into the Co$_3$O$_4$ lattice may contribute to an extended cell capacity. This contribution suggests a simple procedure for the fabrication of Li–O$_2$ batteries using a wide range of metal oxides, e.g., Mn$_3$O$_4$, ZnO.

4. Experimental Section

**Chemicals and Materials:** Ethyl alcohol anhydrous (C$_2$H$_5$OH, 99.9%) was purchased from DAE JUNG. Cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 98–99%), sodium dodecyl sulfate (SDS), potassium persulfate (PPS), styrene, poly(ethylene oxide-block-propylene oxide-block-ethylene oxide) triblock copolymer (P123) were purchased from Sigma-Aldrich.

**Synthesis of Polystyrene (PS) Beads:** PS spheres were synthesized as a soft-template via emulsion polymerization. SDS surfactants and PPS initiators with deionized water were kept to 70 °C for 2 h under N$_2$. Styrene monomers, which had been filtered with alumina, was quickly injected to the solution. After polymerization at 70 °C for 4 h, PS beads of 270 nm average diameter were obtained.

**Preparation of Co$_3$O$_4$ Nanoparticle, Inverse Opal, and Carbonized Inverse Opal Nanostructure:** In case of Co$_3$O$_4$ nanoparticle (Co$_3$O$_4$ NP) and neat inverse opal structure (Co$_3$O$_4$ IO), precursor solutions were obtained by dissolving Co(NO$_3$)$_2$·6H$_2$O into ethanol as 0.1 M solution. Co$_3$O$_4$ NP was prepared by drying in air at 120 °C and then calcined in flowing air at a temperature of 400 °C for 2 h. The temperature heating rate was 2 °C min$^{-1}$. PS solution and Co$_3$O$_4$ precursor solution mixed under stirring for 1 d for Co$_3$O$_4$ IO. Then, the precursor infiltrated PS spheres were self-assembled on glass substrate after O$_2$ plasma for 30 min and then drying at 60 °C for 1 h. These dried samples were calcined using same heating temperature-like Co$_3$O$_4$ NP.

Carbonized Co$_3$O$_4$ IO (C-Co$_3$O$_4$ IO) were prepared by the dispersion of PS spheres in water mixing with Co(NO$_3$)$_2$·6H$_2$O, P123, and ethanol. The amount of P123 was 1 wt% of total weight. Then, the precursor infiltrated PS spheres were self-assembled on glass substrate by drying at 60 °C for 2 h. After calcination in Ar at 500 °C for 2 h, PS spheres were removed and P123 was converted into carbon moieties. Further calcination in air for 30 min generated Co$_3$O$_4$ framework.

**Electrochemical Performance Measurement:** To evaluate the electrochemical performance, rotating disk electrode experiments were carried out in a three electrode electrochemical cell using potentiostat. Platinum (Pt) foil and saturated calomel electrode (SCE) were used as the counter and reference electrode. The electrolyte was 0.1 M KOH. 3 μL of prepared catalyst ink were drop-casted on glassy carbon working electrode with 3 mm diameter. Seven kinds of samples which are the 2.5 mg of conductive carbon, Ketjen Black (KB, EC 600JD), Ilshin Chemtech, 50 wt%, and 2.5 mg of catalyst (50 wt%) mixture or only 5 mg of catalyst were dispersed in isopropyl alcohol with NaFon. Li–O$_2$ Battery Measurements: All batteries were assembled in a glove box (Mbraun) under an Ar atmosphere. The electrochemical performances of Li–O$_2$ batteries were investigated using Swagelok cells. A Li–O$_2$ cell was composed of a Li foil, a glass fiber separator (Whatman, GF/D), tetraethylene glycol dimethyl ether (TEGDME) electrolyte containing 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and an air electrode. The reference KB electrode was prepared by a mixture of KB and a polyvinylidene difluoride binder (PVDF, Kynar 2801) at a weight ratio of 8:2. The other electrode was prepared by casting slurry, consisting of 40 wt% KB, 40 wt% catalyst (Co$_3$O$_4$ NP, Co$_3$O$_4$ IO, C-Co$_3$O$_4$ IO) and 20 wt% PVDF binder in N-methyl-2-pyrrolidone (NMP) onto stainless steel mesh current collector. The galvanostatic discharge/charge was tested within a voltage window of 2.0–4.5 V (vs Li/Li$^+$). Electrochemical impedance spectroscopy (EIS) of the Li–O$_2$ cells evaluated within the frequency range of 200 kHz to 10 mHz.

**Instruments and Characterization:** The surface morphology was characterized using a JEOI JSM6700-F scanning electron microscope (SEM). For the elemental analysis, energy dispersive X-ray spectroscopy (EDX) was performed on a JEOI JEM-3011 at an accelerating voltage of 200 kV. Transmission electron microscope (TEM) measurements were carried out using a JEOI JSM2100-F microscope operated at 100 kV. The specific surface area and pore diameter distribution of the structures were examined by measuring N$_2$ adsorption-desorption isotherms with an ASAP 2020 adsorption analyzer at 77 K. All the samples present were degassed at 200 °C for 2 h under vacuum before the adsorption measurement. The crystalline Co$_3$O$_4$ NP, neat Co$_3$O$_4$ IO, and mesoporous C-Co$_3$O$_4$ IO were investigated by X-ray diffractometer (XRD) Cu Kα radiation (D/Max RA, Rigaku Co.). Raman scattering spectra were recorded on a T64000 (HORIBA Jobin Yvon, France). The electrochemical study was performed on an Autolab ECO Chemie PGSTAT302N potentiostat at room temperature. Li–O$_2$ cell measurements, CV measurements were cycled on a WonaTech WBCS 3000 multichannel battery testing system.

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.
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