Co₃O₄ nanocrystals coupled with O- and N-doped carbon nanoweb as a synergistic catalyst for hybrid Li-air batteries

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Abstract

Expensive Pt-based catalysts are usually required to achieve a high discharge voltage and long operation life for hybrid Li-air batteries. However, the cost of the catalysts needs to be lowered by either reducing the Pt loading in the catalysts or replacing Pt with less expensive catalysts. Here, we report the strong coupling of Co₃O₄ nanocrystals with an O- and N-doped carbon nanoweb (ON-CNW) as a low-cost, highly-efficient catalyst for hybrid Li-air batteries **with an alkaline catholyte**. Co₃O₄/ON-CNW greatly reduces the discharge overpotential compared to ON-CNW and exhibits longer cycle life, which is even better than that of the best reported N-doped mesoporous carbon (0.016% decrease in efficiency per cycle for 130 cycles compared to 0.017% decrease per cycle for 100 cycles obtained with N-doped mesoporous carbon). Although Pt/C exhibits a slightly higher initial discharge voltage (3.02 V compared to 3.00 V for Co₃O₄/ON-CNW), the cycle life of Pt/C is < 50 cycles, making Co₃O₄/ON-CNW as a viable, stable cathode for hybrid Li-air batteries.

Keywords: hybrid Li-air batteries; carbon nanoweb; nitrogen-doping; Co₃O₄ nanocrystals; synergistic activity

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1. Introduction

Li-air batteries hold promise to replace traditional Li-ion batteries in the areas of electric vehicles (EVs) and renewable energy storage due to their advantages in energy density and low-cost active materials. The extremely high theoretical energy density of Li-air batteries is due to the large capacities of the lithium metal anode, inexhaustible oxygen from air, and the high voltage of the Li-O₂ couple [1]. There are four different kinds of Li-air batteries described in the literature: aprotic, hybrid, aqueous, and solid-state [2]. Among these, the aprotic Li-air batteries have been the most widely studied. However, these batteries exhibit formidable challenges: decomposition of the aprotic electrolytes, corrosion of the lithium metal anode, and serious degradation of the air cathode, especially when carbon-based catalysts or supports are employed [3-7]. Even if all of the problems associated with the battery chemistry are solved, the system-level energy density of aprotic Li-air batteries will be low due to the need for additional device components to keep the whole cell in a dry oxygen atmosphere [8, 9]. This is because H₂O and CO₂ have detrimental effects on the cell reversibility and stability.

Hybrid Li-air batteries possess the highest theoretical energy density due to the four-electron transfer per oxygen molecule [10]. The concept is enabled by a solid electrolyte to separate the lithium-metal anode in an aprotic anode electrolyte from the air electrode in an aqueous catholyte. One of the main challenges with hybrid Li-air batteries is the poor efficiency and cycling stability of the bifunctional catalysts [11]. Noble-metal catalysts have shown certain improvements in cell performance [12, 13], but the high cost and scarcity of noble metals hamper the practical applications of these bifunctional air electrodes [14]. To

lower the catalyst cost, we reported a metal-free O- and N- doped carbon nanoweb (ON-CNW) as the ORR catalyst [15]. The metal-free ON-CNW showed better catalytic activity and durability than a N-doped carbon nanoweb (N-CNW) and a N-doped carbon nanosphere (N-CNS), which emphasized the effects of morphology and surface functional groups on catalytic performance. However, the catalytic performance of ON-CNW was lower than that of commercial Pt/C.

A possible approach to develop a catalyst that outperforms Pt/C is to couple cobalt oxide (CoO or Co₃O₄) nanocrystals with O- and N-doped carbon materials to realize synergistic catalytic activity [16]. There are many advantages with this type of composite catalysts that can enable superior ORR performance. First, the carbon substrate helps with the homogeneous dispersion of cobalt oxide nanoparticles, increasing the number of catalytically active sites. Second, the carbon support improves the electrical conductivity and mass transport to the catalytically active sites through the porous carbon structure. Third, the cobalt oxide nanoparticles decompose HO₂⁻ and suppress carbon corrosion, increasing the stability of the carbon substrate [17, 18]. Fourth, cobalt oxide nanocrystals form intimate bonds with oxygen and nitrogen functional groups on the carbon surface, which substantially improves the catalytic activity of the composite catalyst compared to the metal-free catalysts or the physical mixture of cobalt oxide with metal-free catalysts [16, 19]. O- and N-doped carbon nanotubes (CNT), graphene (GN), or normal carbon materials have been combined with cobalt oxide to form highly active catalysts for ORR [19, 20]. However, most of them have been limited to one- or two-dimensional structures with limited oxygen and electrolyte diffusion.

The three-dimensional (3D) carbon nanoweb (CNW) serves as an ideal backbone support for catalytically active sites, showing considerable improvement compared with the nanosphere counterpart [15]. Herein, we present for the first time, strongly coupled Co_3O_4 nanoparticles with O- and N-doped carbon nanoweb ($\text{Co}_3\text{O}_4/\text{ON-CNW}$) as a highly active ORR catalyst for hybrid Li-air batteries. The catalytically active sites are composed of strongly coupled Co_3O_4 and O/N-functional groups. Co_3O_4 nanoparticles possess little ORR activity by themselves, but exhibit high catalytic activity, close to that of commercial Pt/C catalyst, when grown onto ON-CNW. When applied in hybrid Li-air batteries, $\text{Co}_3\text{O}_4/\text{ON-CNW}$ shows a much better cycling stability than both ON-CNW and commercial Pt/C catalysts.

2. Experimental

2.1 Synthesis

ON-CNW was prepared by a two-step carbonization and KOH-activation of a polypyrrole (PPy) nanoweb [15]. The PPy nanoweb was synthesized by the polymerization of pyrrole with cetrimonium bromide (CTAB) as a surfactant. Cetrimonium bromide (CTAB, 0.6 mmol) and 1 M HCl (60 mL) were added into a 250 mL round-bottom flask and stirred in an ice bath for 10 min. Meanwhile, a solution containing 1.8 mmol ammonium peroxydisulfate (APS) dissolved in 10 mL of water was added into the flask. A white precipitate was immediately formed upon the addition of the above solution. After stirring for 0.5 h in an ice bath, 200 μL of pyrrole was injected into the above solution drop by drop. The solution slowly became dark and a black reaction product (PPy nanoweb) was collected after 4 h of reaction in the ice bath. After washing with 1 M HCl and DI water and drying overnight, the PPy nanoweb was

carbonized at 900 °C for 3 h under nitrogen atmosphere. ON-CNW was finally obtained by activation with KOH powder in a mass ratio of 1:2 at 600 °C for 0.5 h and washed afterwards.

To synthesize $\text{Co}_3\text{O}_4/\text{ON-CNW}$, 180 mg ON-CNW was dispersed in a mixture of 240 mL of ethanol, 5 mL of de-ionized (DI) water, and 5 mL of ammonium hydroxide solution (32 wt.%). After that, 6.0 mL of 0.6 M $\text{Co}(\text{Ac})_2$ solution was added into the above solution. The solution was refluxed at 80 °C for 10 h. A black powder was collected by centrifugation and washed several times with DI water and ethanol. $\text{Co}_3\text{O}_4/\text{ON-CNW}$ was finally obtained by heat treating the black powder at 550 °C for 3 h in nitrogen and 200 °C for 20 h in air.

2.2 Characterizations

The X-ray diffraction (XRD) data were obtained with a Philips X-ray diffractometer equipped with $\text{CuK}\alpha$ radiation from 10 to 90 ° at a scan rate of $0.02^\circ \text{ s}^{-1}$. The morphology and elemental distribution were observed with scanning transmission electron microscopy (STEM, Hitachi S-5500) at 30 keV. The microstructure was characterized with a transmission electron microscope (TEM, JEOL 2010F) at 200 keV. X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Kratos Analytical spectrometer using monochromatic Al $\text{K}\alpha$ X-ray source. The XPS spectra were deconvoluted and analyzed with CasaXPS software with Lorentzian functions and a Shirley background. The Co_3O_4 content in the composite was determined by thermogravimetric analysis (TGA, Perkin-Elmer TGA 7 Thermogravimetric Analyzer) with a heating rate of $5^\circ \text{ C min}^{-1}$ from 30 to 800 °C.

2.3 Electrochemical measurements

The intrinsic catalytic activity of the catalysts was measured with an Autolab PGSTAT302N potentiostat (Eco Chemie B.V.) with a standard rotating disk electrode (RDE) setup. A saturated calomel electrode (SCE) was used as the reference electrode and platinum mesh as the counter electrode. For the electrode preparation, Co_3O_4 , ON-CNW, the mixture of Co_3O_4 (48 wt.%) + ON-CNW, $\text{Co}_3\text{O}_4/\text{ON-CNW}$, or Pt/C (20 wt.%) powder were suspended in ethanol (5 mg mL^{-1}). Then, $5 \text{ }\mu\text{L}$ of the catalyst was dropped onto the glassy carbon RDE with a diameter of 5 mm. After drying in air, $5 \text{ }\mu\text{L}$ of 0.5 wt.% Nafion solution was loaded onto top of the electrode as a binder. The linear sweep voltammetry (LSV) was obtained by sweeping the potential from 0.0 to -1.0 V vs. SCE at a scan rate of 10 mV s^{-1} under various rotation speeds, from 1600 to 400 rpm. Cyclic voltammetry (CV) plots were recorded by sweeping the potential between 0.0 and -1.0 V vs. SCE at a scan rate of 10 mV s^{-1} . Chronoamperometry curves were recorded at -0.28 V with a rotation speed of 1000 rpm. All experiments were carried out at room temperature.

The full-cell tests were conducted with a layered-structure cell reported before [21]. The anode side, containing lithium metal in an organic carbonate electrolyte (1 M LiPF_6 in ethylene carbonate (EC) / diethylcarbonate (DEC) (1:1 v/v)) and a piece of solid electrolyte ($\text{Li}_{1+x+y}\text{Ti}_{2-x}\text{Al}_x\text{P}_{3-y}\text{Si}_y\text{O}_{12}$ or LTAP, 0.15 mm thick, $1 \times 10^{-4} \text{ S cm}^{-1}$, $0.76 \text{ cm} \times 0.76 \text{ cm}$, OHARA Inc., Japan), was assembled in an argon-filled glove box. The lithium metal was separated from the solid electrolyte by two layers of Celgard® polypropylene separator. The cathode side, containing the bifunctional air electrodes and an aqueous catholyte (2 mL of 0.5 M LiOH + 1 M LiNO_3 solution), was then attached to the anode in air. The air electrodes

contained a decoupled ORR air electrode containing 80 wt.% catalyst (carbon black, ON-CNW, $\text{Co}_3\text{O}_4/\text{ON-CNW}$, or Pt/C) and 20 wt.% LITHion binder (Ion Power, USA). The air electrode also consisted of an OER air electrode containing 1.0 mg cm^{-2} of NiCo_2O_4 nanoflakes grown onto Ni foam (NCONF@Ni) [22]. The discharge-charge tests were carried out with two independent channels on an Arbin 2000 battery cycler.

3. Results and discussion

3.1 Structure and morphology characterizations

$\text{Co}_3\text{O}_4/\text{ON-CNW}$ was synthesized by a solution-based method [16]. In the first step, N-doped carbon nanoweb with rich O-functional groups was synthesized according to our previous report [15]. Subsequent deposition of Co_3O_4 nanoparticles was achieved by the hydrolysis of cobalt acetate ($\text{Co}(\text{OAc})_2$) under reflux in a mixture of ethanol and water at 80°C . The obtained black powder was collected by centrifugation and washed with deionized (DI) water. The $\text{Co}_3\text{O}_4/\text{ON-CNW}$ composite was finally obtained by a two-step calcination of the black powder at 550°C for 3 h in a nitrogen atmosphere and 200°C for 20 h in air. A low temperature of 200°C was chosen because pure Co_3O_4 could be obtained at this temperature without oxidizing the carbon support and a lower calcination temperature resulted in CoO impurity.

The assembly of Co_3O_4 nanocrystals on ON-CNW ($\text{Co}_3\text{O}_4/\text{ON-CNW}$) was confirmed by the X-ray diffraction (XRD) pattern shown in Figure 1. As shown in Figure 1a, the pure ON-CNW possesses a broad peak around 24° due to the presence of a disordered carbon phase. The small peak around 44° represents graphitic planes with small size and low three-dimensional order on the ON-CNW surface formed during the high-temperature

carbonization process [23]. After refluxing with $\text{Co}(\text{OAc})_2$ and heat treatment in a nitrogen atmosphere, the XRD pattern (Figure 1b) exhibits CoO peaks together with the carbon peaks. There are also two minor peaks associated with Co, indicating that some Co^{2+} was reduced to metallic Co during the high-temperature calcination in nitrogen. Both the CoO and Co phase could be easily transformed into Co_3O_4 by calcination of the composite at 200 °C for 20 h in air. As can be seen in Figure 1c, pure spinel-phase Co_3O_4 was observed in the XRD pattern together with the broad carbon peak around 24 °. The heat-treatment temperature in air was so low that neither apparent weight loss nor change of the morphology was observed with the carbon nanoweb.

Figure 2a is a typical scanning electron microscope (SEM) image of the synthesized $\text{Co}_3\text{O}_4/\text{ON-CNW}$. It has the typical nanoweb morphology as shown in our previous report [15]. The bright-field scanning transmission electron microscope (STEM) image in Figure 2b shows that the surface of the nanoweb is decorated with a uniform layer of nanoparticles, which were shown to be Co_3O_4 by XRD in Figure 1c. The energy dispersive X-ray (EDX) elemental mappings and corresponding morphology are shown in Figure 2c-f. The nitrogen and cobalt signals are uniformly distributed over the nanoweb surface due to the nitrogen doping in the polypyrrole-derived carbon and the evenly distributed Co_3O_4 nanoparticles on the carbon surface. Defects and functional groups are needed on the carbon surface to provide sites for the nucleation and anchoring of oxide nanocrystals. ON-CNW possesses a large amount of defects and functional groups on the surface which stem from the KOH activation process. Thus, unlike most of other carbon supports [19], no extra oxidation step was needed for the ON-CNW. During the reflux process, the nucleation of Co-containing precursor on

the ON-CNW surface was realized by the hydrolysis of $\text{Co}(\text{OAc})_2$, which was then converted to crystalline Co_3O_4 during the two-step calcination process.

Figure 3a is a low-resolution transmission electron microscope (TEM) image of the synthesized $\text{Co}_3\text{O}_4/\text{ON-CNW}$. The dark Co_3O_4 nanoparticles are clearly observed on the ON-CNW surface. A high-resolution TEM image in Figure 3b shows that the Co_3O_4 particle size is around 10-20 nm. From the high-resolution TEM image shown in Figure 3c, two different lattice fringes are visible which can be indexed to the (111) and (220) planes of Co_3O_4 . The loading of Co_3O_4 on the web surface was determined to be 47.9 wt.% by thermogravimetric analysis (TGA). A high loading of cobalt oxide is critical to form adequate intimate bonding between Co_3O_4 and ON-CNW, which facilitates charge transfer between ON-CNW and Co_3O_4 nanoparticles and thereby improves the ORR activity of the composite catalyst [19].

The schematic representation of the oxygen reduction reaction mechanism on $\text{Co}_3\text{O}_4/\text{ON-CNW}$ in a hybrid Li-air battery is shown in Figure 4a. Upon discharge, oxygen is adsorbed and reduced on the surface of $\text{Co}_3\text{O}_4/\text{ON-CNW}$ and combines with H_2O in the catholyte and Li^+ ions from the anode to produce LiOH . Co_3O_4 nanoparticles are represented by the small red balls anchored onto the surface of the nanoweb. The surface composition and oxidation state were investigated with XPS, shown in Figure 4b-d. From the survey spectra shown in Figure 4b, the elements C, N, O, and Co are present in the sample. The detailed N peak is shown in Figure 4c. The deconvoluted peaks contain mainly four peaks: the pyridinic nitrogen, pyridone/pyrrolic nitrogen, quaternary nitrogen, and pyridinic N-O [15]. From a comparison of the nitrogen peak in ON-CNW [15], the content of pyridone/pyrrolic nitrogen

has decreased in the $\text{Co}_3\text{O}_4/\text{ON-CNW}$ due to the loss of oxygen during the calcination step at 550°C in a nitrogen atmosphere. The Co 2p peak is shown in Figure 4d. As determined previously [24, 25], Co_3O_4 exhibits two spin-orbital doublets of Co^{2+} and Co^{3+} and two shakeup satellites.

3.2 Oxygen reduction performances

Figure 5a shows the cyclic voltammetry (CV) curves of $\text{Co}_3\text{O}_4/\text{ON-CNW}$ compared with ON-CNW and Co_3O_4 nanoparticles in both an oxygen- (solid line) or nitrogen- (dashed line) saturated 0.1 M KOH solutions at a scan rate of 30 mV s^{-1} . Co_3O_4 nanoparticles (SEM images shown in Figure S1) were synthesized by the same procedure as $\text{Co}_3\text{O}_4/\text{ON-CNW}$, but without the ON-CNW carbon support. For the ON-CNW sample, the ORR peak potential was -0.27 V vs. SCE , mainly due to the high activity of the pyridone species on the surface. The ORR peak potential of $\text{Co}_3\text{O}_4/\text{ON-CNW}$ was as high as -0.21 V vs. SCE , which represents a lower overpotential for the ORR compared to both Co_3O_4 and ON-CNW. Since Co_3O_4 itself possesses poor ORR activity, the improved activity of the composite indicates that the deposition of Co_3O_4 nanoparticle on ON-CNW forms new catalytic sites with higher ORR activity. Some of the oxygen functional groups on ON-CNW were removed after calcination in nitrogen atmosphere, decreasing the content of pyridone species, as shown in the XPS results in Figure 4c. Thus, the new ORR active sites should be different from those in the metal-free ON-CNW. Recent studies suggest that the junction site at which Co_3O_4 is anchored onto an O- and N-doped carbon surface is responsible for the high ORR catalytic activity [16, 19]. Co from Co_3O_4 nanoparticles forms intimate bonding with O and N in ON-CNW, enhancing the charge transfer from Co_3O_4 to ON-CNW [26]. Such a charge

transfer is believed to be the main reason why the oxide-carbon composite catalysts possess high ORR catalytic activity, *e.g.* Co₃O₄/GN [16, 27], CoO/CNT [19], Co/CoO/GN [20], Fe₃O₄/GN [28], and Co_xS_{1-x}/GN [29].

Figure 5b shows the linear sweep voltammetry (LSV) of Co₃O₄, ON-CNW, and Co₃O₄/ON-CNW in O₂-saturated 0.1 M KOH at 1600 rpm with a scan rate of 10 mV s⁻¹. The low current density of Co₃O₄ demonstrates its poor ORR activity. The half-wave potential of Co₃O₄/ON-CNW is 40 mV higher than that of ON-CNW, revealing that oxygen could be reduced much more easily on Co₃O₄/ON-CNW than on Co₃O₄ and ON-CNW. In addition, the diffusion limiting current of Co₃O₄/ON-CNW is also larger than that of ON-CNW. These facts suggest that the catalytically active sites on Co₃O₄/ON-CNW are different and much more active than those on ON-CNW. To further confirm the existence of a synergistic effect, the LSVs of Co₃O₄, mixture of Co₃O₄ (48 wt.%) + ON-CNW, and Co₃O₄/ON-CNW at different rotation speeds are shown in Figure S2-4. The LSVs of ON-CNW were given in our previous report [15]. Among them, Co₃O₄/ON-CNW possesses the largest diffusion current density and longest diffusion controlled plateau, representing the highest ORR activity. Based on the LSVs at different rotation speeds, the Koutecky-Levich (K-L) plots of Co₃O₄/ON-CNW and ON-CNW at -1.0 V *vs.* SCE are shown in Figure 5c. These K-L plots reveal a first-order dependence on the diffusion of O₂ to the electrode surface due to the good linear relationship between 1/*j* and $\omega^{-1/2}$, where *j* is the measured current density and ω is the rotation rate. There are mainly two possible pathways for the electrochemical reduction of O₂. One is the two-electron pathway to produce HO₂⁻. Here, the produced HO₂⁻ may damage the catalytic active sites and decrease the catalytic stability. The ideal pathway is the direct

four-electron pathway to produce water, which should cause no chemical harm to the catalysts. The number of electrons transferred during the ORR (in the limiting current **region**) can be calculated by the K-L equation [30, 31]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{0.2nFA(D_{O_2})^{2/3}v^{-1/6}C_{O_2}\omega^{1/2}}$$

where j , j_k , and j_d are, respectively, the measured, kinetic, and diffusion-limiting current; n is the number of electron transferred; F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$); A is the geometric electrode area (0.196 cm^2); D_{O_2} is the diffusion coefficient of oxygen ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); v is the kinetic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$); C_{O_2} is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$); and ω is the rotation rate (rpm). The number of electrons transferred at -1.0 V vs. SCE for ON-CNW and $Co_3O_4/ON-CNW$ are, respectively, 3.7 and 4.0, revealing that $Co_3O_4/ON-CNW$ produced less HO_2^- during the ORR process.

Catalyst stability is another important aspect of ORR catalysts that needs consideration. Chronoamperometric measurement of the $Co_3O_4/ON-CNW$ composite at -0.28 V vs. SCE (Figure 5d) displayed only a $\sim 10.5 \%$ decrease in current density over 30 000 s, while the current of ON-CNW decreased by $\sim 24.3 \%$ during the same period. Thus, the $Co_3O_4/ON-CNW$ exhibited a much slower decrease in current density than ON-CNW, indicating that the composite is more stable. The excellent durability is mainly due to the high stability of the bonding between Co_3O_4 and ON-CNW. Since the $Co_3O_4/ON-CNW$ catalyzes the ORR mostly through the direct four-electron pathway, the corrosion of the active sites by HO_2^- is minimized. Such intrinsic stability is crucial for the long-term operation of hybrid Li-air batteries.

3.3 Application in hybrid Li-air batteries

The electrochemical performances of Pt/C (20 wt.%), Co₃O₄/ON-CNW, ON-CNW, and carbon black were tested in hybrid Li-air batteries. Figure 6a shows the discharge voltage profiles of hybrid Li-air batteries with Pt/C, Co₃O₄/ON-CNW, ON-CNW, and carbon black as the ORR catalysts at a current density of 0.5 mA cm⁻² for 2 h. The discharge voltage plateaus of Pt/C, Co₃O₄/ON-CNW, and ON-CNW were, respectively, at 3.02, 3.00, and 2.96 V. The discharge voltage of carbon black was < 2.8 V, showing the worst catalytic activity. As a comparison, vertically aligned N-doped carbon nanotube arrays displayed a discharge voltage of 2.90 V in hybrid Li-air batteries in a similar catholyte (0.5 M LiOH + 0.5 M LiNO₃) and at the same current density (0.5 mA cm⁻²) [14]. Graphene nanosheets exhibited a discharge voltage of ~ 2.94 V in the same catholyte (0.5 M LiOH + 1.0 M LiNO₃) and at the same current density (0.5 mA cm⁻²) [32]. It should be noted that the above data from the literature is only for an approximate comparison because different groups use different methods to make the air electrodes with different catalyst loadings. The good electrochemical performance of Co₃O₄/ON-CNW in hybrid Li-air batteries highlights the synergistic effect between Co₃O₄ and the oxygen- and nitrogen- dopants. The rich functional groups on the surface of ON-CNW help in the uniform nucleation and growth of Co₃O₄ nanoparticles on the ON-CNW surface, increasing the number of ORR active sites. The strong coupling between Co₃O₄ and ON-CNW enhances the charge transfer from Co₃O₄ to ON-CNW. The 3D nanoweb structure improves the electronic and mass transport to those active sites during the electrocatalytic process. Furthermore, the Co₃O₄/ON-CNW exhibits a discharge voltage

similar to that of the commercial Pt/C catalyst, demonstrating it to be a promising electrocatalyst for the hybrid Li-air battery.

In order to investigate the stability of $\text{Co}_3\text{O}_4/\text{ON-CNW}$ in hybrid Li-air batteries, its cyclic performance was compared against a commercial Pt/C catalyst at a current density of 0.5 mA cm^{-2} . A decoupled design of the ORR and OER electrodes was used to eliminate the effects of battery charging on the ORR catalysts. The decoupled OER electrode consisted of NiCo_2O_4 nanoflakes grown onto nickel foam (NCONF@Ni) as reported by us before [22]. It enables a low overpotential and long-term stability during charging of the hybrid Li-air battery, regardless of the ORR catalyst utilized. In this way, differences in cell efficiency and cycle life can be attributed directly to the differences in the ORR catalysts.

Discharge-charge experiments were conducted with two independent channels on an Arbin BT 2000 battery cycler. The discharge and charge voltage profiles were collected alternatively with a 5-minute rest time between each two-hour discharge and charge period. Figure 6b shows the cycling performance of a hybrid Li-air battery with Pt/C (20 wt.% Pt/C, 1 mg cm^{-2}) + NCONF@Ni (1 mg cm^{-2}) decoupled air electrode for 51 cycles. The charge performance was very stable due to the decoupled carbon- and binder-free NCONF@Ni OER electrode. The ORR performance was stable for up to about 46 cycles and suffered from fast degradation afterwards. At the 1st cycle, the round-trip overpotential based on the discharge-charge end voltage was 0.87 V. This value increased to 1.25 V after 51 cycles. To exclude the influence of other factors (*i. e.* cell assembly, catalyst coating, etc.) on the cell performance, we replaced the used ORR air electrode with a new Pt/C ORR electrode (in the same hybrid Li-air cell). As shown in Figure S5, the hybrid Li-air cell with the replaced Pt/C

ORR electrode resumed its normal discharge-charge voltage for about 40 cycles and degraded thereafter, indicating that the Pt/C air electrode has a limited service life in hybrid Li-air batteries. This degradation is mainly associated with the intrinsic poor stability of Pt/C catalysts [33, 34] and the deposition of inactive and insulating Li_2CO_3 which blocks the mass transport in the air electrode [35].

Meanwhile, as shown in Figure 6b, the initial round-trip overpotential for the hybrid Li-air battery with $\text{Co}_3\text{O}_4/\text{ON-CNW} + \text{NCONF@Ni}$ decoupled air electrode is 0.89 V, only 0.02 V higher than that of Pt/C + NCONF@Ni, which mainly comes from the difference in the discharge voltage as shown in Figure 6a. After 130 cycles, while the charge voltage remained almost constant, the discharge voltage underwent a minor drop. The round-trip overpotential at the 130th cycle was 0.98 V, which represents an increase of 0.09 V compared to the initial cycle. These results show that the $\text{Co}_3\text{O}_4/\text{ON-CNW}$ possesses much better stability in a hybrid Li-air battery than commercial Pt/C and even better than nitrogen-doped mesoporous carbon (N-MC) reported previously [22].

Since all of the catalysts were tested under the same experimental conditions, this improvement is mainly associated with the intrinsic catalytic stability and surface properties of the $\text{Co}_3\text{O}_4/\text{ON-CNW}$ catalyst. The Pt/C catalyst suffers from the well-known agglomeration, dissolution, and migration problem of Pt nanoparticles [36]. The carbon support is also subjected to corrosion upon long-term operation. The advantage of the N-MC is the large active N-doped surface area ($1520 \text{ m}^2 \text{ g}^{-1}$), which can survive degradation for a long time [22]. However, HO_2^- is inevitably formed during the ORR process on the carbon surface and gradually corrodes the catalytically active sites. In the $\text{Co}_3\text{O}_4/\text{ON-CNW}$

composite catalyst, HO_2^- formation was mostly suppressed due to the dominant four-electron ORR mechanism. The Co_3O_4 nanoparticles are uniformly distributed on the carbon surface, decomposing most HO_2^- formed and protecting the catalytically active sites from corrosion. Another issue is that CO_2 ingress leads to Li_2CO_3 formation on the catalyst/catholyte/air three-phase interface, easily covering the catalyst surface. The structure and surface properties of the ORR catalyst influence the morphology and distribution of Li_2CO_3 crystals [22]. In general, a porous catalyst with a rough texture and many surface functional groups is more tolerant to Li_2CO_3 deposition, which contributes to a higher percentage of exposed catalytically active sites [32]. A detailed study on the influence of composition and morphology of catalysts on Li_2CO_3 deposition is being currently conducted and will be reported in a future publication.

4. Conclusions

In summary, we have successfully synthesized $\text{Co}_3\text{O}_4/\text{ON-CNW}$ nanocomposites as a highly efficient and durable ORR catalyst for hybrid Li-air batteries. The excellent catalytic performance is due to the unique 3D carbon web support and special catalytic active sites comprised of strongly coupled Co_3O_4 nanoparticles with O-/N- functional groups on the carbon web surface. The obtained catalysts enable long life of hybrid Li-air batteries over 130 cycles with only 0.016% decrease in efficiency per cycle. We believe that the extraordinarily high performance of $\text{Co}_3\text{O}_4/\text{ON-CNW}$ provides a practical low-cost alternative to expensive Pt/C catalyst in hybrid Li-air batteries as well as in other metal-air batteries.

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References

- [1] K.M. Abraham, Z. Jiang, *J. Electrochem. Soc.* 143 (1996) 1-5.
- [2] G. Girishkumar, B. McCloskey, A.C. Luntz, S. Swanson, W. Wilcke, *J. Phys. Chem. Lett.* 1 (2010) 2193-2203.
- [3] J. Lu, L. Li, J.-B. Park, Y.-K. Sun, F. Wu, K. Amine, *Chem. Rev.* 114 (2014) 5611-5640.
- [4] D.G. Kwabi, N. Ortiz-Vitoriano, S.A. Freunberger, Y. Chen, N. Imanishi, P.G. Bruce, Y. Shao-Horn, *MRS Bull.* 39 (2014) 443-452.
- [5] D. Sharon, V. Etacheri, A. Garsuch, M. Afri, A.A. Frimer, D. Aurbach, *J. Phys. Chem. Lett.* 4 (2012) 127-131.
- [6] D. Sun, Y. Shen, W. Zhang, L. Yu, Z. Yi, W. Yin, D. Wang, Y. Huang, J. Wang, D. Wang, J.B. Goodenough, *J. Am. Chem. Soc.* 136 (2014) 8941-8946.
- [7] R. Black, B. Adams, L.F. Nazar, *Adv. Energy Mater.* 2 (2012) 801-815.
- [8] K.G. Gallagher, S. Goebel, T. Greszler, M. Mathias, W. Oelerich, D. Eroglu, V. Srinivasan, *Energy Environ. Sci.* 7 (2014) 1555-1563.
- [9] L. Li, Y. Fu, A. Manthiram, *Electrochem. Commun.* 47 (2014) 67-70.
- [10] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, *Nat. Mater.* 11 (2012) 19-29.
- [11] L. Li, A. Manthiram, *Nano Energy* 9 (2014) 94-100.
- [12] K. Huang, Y. Li, Y. Xing, *Electrochim. Acta* 103 (2013) 44-49.
- [13] L. Li, A. Manthiram, *J. Mater. Chem. A* 1 (2013) 5121-5127.
- [14] Y. Li, Z. Huang, K. Huang, D. Carnahan, Y. Xing, *Energy Environ. Sci.* 6 (2013) 3339-3345.
- [15] L. Li, A. Manthiram, *Adv. Energy Mater.* 4 (2014) 1-7, DOI [10.1002/aenm.201301795](https://doi.org/10.1002/aenm.201301795).
- [16] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nat. Mater.* 10 (2011) 780-786.
- [17] T.S. Olson, S. Pylypenko, P. Atanassov, K. Asazawa, K. Yamada, H. Tanaka, *J. Phys. Chem. C* 114 (2010) 5049-5059.
- [18] J.D. Wiggins-Camacho, K.J. Stevenson, *J. Phys. Chem. C* 115 (2011) 20002-20010.
- [19] Y. Liang, H. Wang, P. Diao, W. Chang, G. Hong, Y. Li, M. Gong, L. Xie, J. Zhou, J. Wang, T.Z. Regier, F. Wei, H. Dai, *J. Am. Chem. Soc.* 134 (2012) 15849-15857.
- [20] S. Guo, S. Zhang, L. Wu, S. Sun, *Angew. Chem. Int. Ed.* 51 (2012) 11770-11773.
- [21] L. Li, X. Zhao, Y. Fu, A. Manthiram, *Phys. Chem. Chem. Phys.* 14 (2012) 12737-12740.
- [22] L. Li, S.-H. Chai, S. Dai, A. Manthiram, *Energy Environ. Sci.* 7 (2014) 2630-2636.
- [23] N. Gavrilov, I.A. Pašti, M. Mitrić, J. Travas-Sejdić, G. Ćirić-Marjanović, S.V. Mentus, *J. Power Sources* 220 (2012) 306-316.
- [24] T. He, D. Chen, X. Jiao, Y. Wang, Y. Duan, *Chem. Mater.* 17 (2005) 4023-4030.
- [25] C.-T. Ho, T.-H. Weng, C.-Y. Wang, S.-J. Yen, T.-R. Yew, *RSC Advances* 4 (2014) 20053-20057.
- [26] J.-S. Lee, G.S. Park, H.I. Lee, S.T. Kim, R. Cao, M. Liu, J. Cho, *Nano Lett.* 11 (2011) 5362-5366.

- [27] C. Sun, F. Li, C. Ma, Y. Wang, Y. Ren, W. Yang, Z. Ma, J. Li, Y. Chen, Y. Kim, L. Chen, *J. Mater. Chem. A* 2 (2014) 7188-7196.
- [28] Z.-S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng, K. Müllen, *J. Am. Chem. Soc.* 134 (2012) 9082-9085.
- [29] H. Wang, Y. Liang, Y. Li, H. Dai, *Angew. Chem. Int. Ed.* 50 (2011) 10969-10972.
- [30] S. Wang, D. Yu, L. Dai, *J. Am. Chem. Soc.* 133 (2011) 5182-5185.
- [31] W. Xiong, F. Du, Y. Liu, A. Perez, M. Supp, T.S. Ramakrishnan, L. Dai, L. Jiang, *J. Am. Chem. Soc.* 132 (2010) 15839-15841.
- [32] E. Yoo, H. Zhou, *RSC Advances* 4 (2014) 11798-11801.
- [33] P.J. Ferreira, G.J. la O', Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, H.A. Gasteiger, *J. Electrochem. Soc.* 152 (2005) A2256-A2271.
- [34] L. Li, X. Zhao, A. Manthiram, *Electrochem. Commun.* 14 (2012) 78-81.
- [35] P. Stevens, G. Toussaint, G. Caillon, P. Viaud, P. Vinatier, C. Cantau, O. Fichet, C. Sarrazin, M. Mallouki, *ECS Trans.* 28 (2010) 1-12.
- [36] S. Zhang, X.-Z. Yuan, J.N.C. Hin, H. Wang, K.A. Friedrich, M. Schulze, *J. Power Sources* 194 (2009) 588-600.

Figure Captions

- Figure 1.** XRD patterns of (a) ON-CNW, (b) $\text{CoO}_x/\text{ON-CNW}$ compared with the standard patterns of CoO (JCPDS No. 43-1004) and Co (JCPDS No. 15-0806), and (c) $\text{Co}_3\text{O}_4/\text{ON-CNW}$ compared with the standard pattern of Co_3O_4 (JCPDS No. 43-1003).
- Figure 2.** Morphological and elemental analysis of $\text{Co}_3\text{O}_4/\text{ON-CNW}$: (a) SEM, (b) STEM, and (c-f) EDX mappings of a bunch of $\text{Co}_3\text{O}_4/\text{ON-CNW}$ and corresponding SEM image.
- Figure 3.** (a-c) TEM images showing the morphology and microstructure of the synthesized $\text{Co}_3\text{O}_4/\text{ON-CNW}$ and (d) TGA plot of the composite.
- Figure 4.** (a) Schematic illustration of ORR on the surface of $\text{Co}_3\text{O}_4/\text{ON-CNW}$. Red dots and black mesh represent Co_3O_4 and ON-CNW respectively. (b) XPS survey spectrum of the synthesized $\text{Co}_3\text{O}_4/\text{ON-CNW}$, (c) N 1s XPS spectrum, and (d) Co 2p XPS spectrum.
- Figure 5.** (a) Cyclic voltammograms in O_2 (solid line) or N_2 (dashed line) saturated 0.1 M KOH at 30 mV s^{-1} , (b) linear sweep voltammograms of different catalysts at 10 mV s^{-1} and 1600 rpm, (c) Koutecky-Levich plots at -1.0 V vs. SCE, and (d) chronoamperometry plots at -0.28 V and 1000 rpm.
- Figure 6.** (a) Discharge voltage profiles of different ORR catalysts in hybrid Li-air batteries at a current density of 0.5 mA cm^{-2} . Cycling performance of hybrid Li-air batteries with (b) Pt/C + NCONF@Ni and (c) $\text{Co}_3\text{O}_4/\text{ON-CNW}$ + NCONF@Ni air electrodes.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Vitae

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Graphical Abstract

Co_3O_4 nanocrystals strongly coupled with O- and N-doped carbon nanoweb ($\text{Co}_3\text{O}_4/\text{ON-CNW}$) have been developed as an efficient, non-noble-metal oxygen reduction reaction (ORR) catalyst for hybrid Li-air batteries.