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Abstract

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Keywords

foam, like, nico₂o₄, efficient, 3d, catalyst, self, lithium, oxygen, batteries, assembled

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Liu, L., Wang, J., Hou, Y., Chen, J., Liu, H., Wang, J. & Wu, Y. (2016). Self-assembled 3D foam-like NiCo₂O₄ as efficient catalyst for lithium oxygen batteries. *Small*, 12 (5), 602-611.

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Self-assembled 3D foam-like NiCo₂O₄ as Efficient Catalyst for Lithium Oxygen Batteries

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Keywords: 3D foam-like, ORR, OER, overpotential, Li₂O₂

A self-assembled three-dimensional (3D) foam-like NiCo₂O₄ catalyst has been synthesized via a simple and environmental friendly approach, wherein starch acts as the template to form the unique 3D architecture. Interestingly, when employed as cathode for lithium oxygen batteries, it demonstrated superior bi-functional electrocatalytic activities towards both the oxygen reduction reaction and the oxygen evolution reaction, with a relatively high round-trip efficiency of 70% and high discharge capacity of 10137 mAh g⁻¹ at a current density of 200 mA g⁻¹, which is much higher than those in previously reported results. Meanwhile, rotating disk electrode measurements in both aqueous and non-aqueous electrolyte were also employed to confirm the electrocatalytic activity for the first time. This excellent performance is attributed to the synergistic benefits of the unique 3D foam-like structure and the intrinsically high catalytic activity of NiCo₂O₄.

1. Introduction

Intensive research efforts worldwide are being devoted to the realization of a new generation of lithium oxygen batteries, as a result of their high theoretical specific energy, which is

almost ten times that of Li-ion batteries.^[1,2] Such batteries are the technology of choice for the electrification of transport and are expected to find application in static electricity storage, especially in grid distribution networks.^[3] Although the reaction mechanism of lithium oxygen batteries is simple and straightforward, the practical use of lithium oxygen batteries has been restricted by numerous scientific challenges, including high discharge-charge overpotential, low energy efficiency, poor rate capability, and especially short cycle life, which are caused by the sluggish kinetics of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER).^[4] It has been demonstrated that the performance of Li-O₂ batteries is strongly determined by both the materials and the architecture of the oxygen electrodes, which contribute most of the voltage gap and cyclic capability of such batteries.^[5]

Various catalysts have been studied for Li-O₂ batteries to overcome these challenges.^[3, 4, 6-15] Among them, NiCo₂O₄, a typical ternary spinel nickel cobalt oxide with the advantages of low cost, natural abundance, higher electronic conductivity than those of Co₃O₄ and NiO, and especially good bi-functional catalytic activity towards the ORR and OER, has aroused much interest for use as an electrocatalyst for Li-O₂ batteries.^[16-20] A NiCo₂O₄ nanowire array grown on carbon cloth was reported as cathode for Li-O₂ batteries, but only a capacity of approximately 1000 mAh g⁻¹ was delivered, which was because the active sites only exist on the tips of the NiCo₂O₄ nanowires.^[21] To achieve a higher capacity, Wang et al. synthesized mesoporous NiCo₂O₄ nanosheets via a hydrothermal method, and higher reversible capacity was demonstrated, as well as good cycling stability.^[18] Although enhanced electrocatalytical performances of NiCo₂O₄ have been reported, they are far from satisfactory, either due to low capacity or to high discharge-charge overpotential,^[22] which may be largely due to their unfavourable cathode structure.

Generally speaking, an ideal oxygen electrode requires a highly conductive and porous structure to facilitate both electron and oxygen transportation.^[23-25] Typically, in a lithium oxygen battery, the formation of Li₂O₂ only occurs on the triple junctions where electrolyte,

catalytic active sites, and oxygen coexist. The more tri-phase regions, the more Li_2O_2 will be produced, and therefore, higher capacity can be delivered from the battery.^[21] The three-dimensional (3D) skeleton structure has drawn much attention for the design of the oxygen electrode, according to previous reports, due to the following advantages:^[27, 28] a) it can provide suitable tunnels to supply continuous pathways for oxygen and meanwhile provide sufficient space for Li_2O_2 formation according to the triple-junction oxygen reduction process, b) it can increase the electrical conductivity of the electrode and facilitate the charge transfer and electrochemical kinetics, c) it can enlarge the contact area between the electrolyte and the electrode to deliver high capacity and rate capability. Inspired by the 3D architecture, nickel foam has been widely employed by researchers as a porous catalyst support for Li-O₂ batteries.^[29] Porous carbon derived from a graphene oxide gel in nickel foam was directly used as an O₂ cathode, which facilitated a continuous O₂ flow.^[30] Liu et al. reported Co_3O_4 grown on nickel foam with a 3D network structure as a cathode material for Li-O₂ batteries, and a voltage gap of no more than 0.5 V was achieved, which can be ascribed to the Ni foam skeleton, which provided continuous pathways for O₂.^[29] Although deposition of catalyst on nickel foam can form an interconnected porous structure, contact resistance still exists between the catalyst and the nickel foam, which inevitably causes overpotential during charge and discharge processes.^[30, 31] Moreover, the pores and tunnels of the commercial nickel foam are large (usually 200 μm in diameter), which correspondingly decreases the surface area of the catalyst loaded on it. Meanwhile, these too large pores are usually flooded by the electrolyte, forming two-phase instead of three-phase regions.^[26] Therefore, the development of a well-designed 3D foam-like cathode architecture by integrating small porous channels in it will be a good choice for enhanced Li-O₂ batteries.^[33]

In this work, we used environmentally friendly starch as a template, and a self-assembled 3D foam-like NiCo_2O_4 framework with mesopores inside was obtained. It is expected that during discharge, the large macro-tunnels can function as “highways” to supply oxygen to the

interior parts of the cathode, while the mesopores on nanowalls are the “exits” to provide the triple junctions (solid-liquid-gas) required for the oxygen reduction reaction and act as centres for Li_2O_2 crystallization.^[30] Rotating disk electrode (RDE) measurements both in aqueous and non-aqueous electrolytes were employed to explore the electrocatalytical properties of the as prepared 3D foam-like NiCo_2O_4 . Remarkably, the as-prepared hierarchically self-assembled 3D-structured NiCo_2O_4 manifested improved catalytic performance, with a high round-trip efficiency of 70% and a stable lifespan of 80 cycles for lithium oxygen batteries.

2. Results and Discussion

Soluble starch was used as the template for the fabrication of 3D foam-like NiCo_2O_4 , and the process is schematically shown in **Figure 1**. It was reported that starch is a natural polysaccharide polymer with abundant hydroxyl groups, which can facilitate supramolecular associations by inter- and intramolecular hydrogen bonding.^[35] Co^{2+} and Ni^{2+} cations, formed by the dissolution of nickel acetate and cobalt acetate in water, can thus favourably bind with the -OH containing groups on starch molecules when they are mixed together.^[36] Upon heating to 90 °C, the aqueous dispersion of starch in a complex with Co^{2+} and Ni^{2+} became gel-like as a result of swelling and disruption of the starch granules. The resulting sponge-like pink gel consisted of a hydrated 3D porous network of predominantly amylose molecules. The as-prepared gel was directly dehydrated via a freeze-drying process to maintain the 3D architecture and then heated at 380 °C for 5 h in air atmosphere. The final product from this process shows a black loose appearance with the same shape as the former gel. According to a previous report,^[37] the starch template can be completely removed at 380 °C in air.

In the process, the starch template plays two main roles in the formation of the 3D foam-like porous structure: Firstly, it prevents small NiCo_2O_4 units from growing into large particles before the decomposition of starch; secondly, the release of CO_2 produced by the decomposition of the starch results in a large number of mesopores in the NiCo_2O_4 nanoparticles. Starch acts as not only as a template, but also as a passivated reagent. So, the

resultant NiCo_2O_4 possesses a 3D foam-like framework with continuous walls that consist of closely packed nanoparticles.

The structure of the as-prepared 3D foam-like NiCo_2O_4 was confirmed by X-ray diffraction (XRD), as shown in **Figure 2**. Remarkably, the peaks (2θ values) at 31.1, 36.5, 44.6, 59.1, and 64.9 ° correspond to the diffractions from the (220), (311), (400), (511), and (440) planes of spinel phase NiCo_2O_4 (JCPDS card no.73-1702).^[15]

SEM images of the calcined NiCo_2O_4 reveal a 3D foam-like framework with continuous pores and walls that consist of closely packed nanoparticles (**Figure 3a** and **3b**). X-ray spectroscopy (EDS) pattern conducted from the 3D foam-like NiCo_2O_4 is shown in **Table S1** and **Figure S1**. Besides the Al and C peaks coming from the SEM holder and conductive adhesive tape, respectively, only the elements Ni, Co and O are detected in the EDS spectrum. The composition analysis reveals that the stoichiometry elemental ratio of Ni: Co: O in the sample is nearly 1: 2: 4, which proves that the whole 3D foam-like NiCo_2O_4 structure consists of NiCo_2O_4 . The TEM image (**Figure 3c**) also proves that the sample has obvious nano-/mesoporous structure with interconnected nanoparticles. Nanowalls could also be observed in **Figure 3c** which are well consistent with the SEM images. It is noteworthy that besides the macro-sized foam-like structure, mesopores with a size of less than 8 nm can also be observed between the nanoparticles, and such mesopores have been reported to offer more diffusion pathways for oxygen and permit the electrolyte to easily penetrate, forming more of the triple-phase (solid-liquid-gas phases) regions required for efficient ORR and OER reactions.^[30-38] The high-resolution TEM (HRTEM) image (**Figure 3d**) indicates that the particles possess a typical crystalline texture, with space between lattice planes of 0.242 nm, which corresponds to the d value of the (311) planes of spinel phase NiCo_2O_4 .

The N_2 adsorption-desorption isotherms collected at 77 K and the pore-size distribution are shown in **Figure S2** in the Supporting Information. The nitrogen sorption curves of the as-prepared NiCo_2O_4 exhibit the combined characteristics of type II/IV according to the IUPAC

classification,^[30-39] with a specific surface area of $46.4 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $0.26 \text{ cm}^3 \text{ g}^{-1}$. The H1 hysteresis loop in the P/P^0 range of 0.6-1.0 is indicative of mesoporosity.^[39] The pore-size distribution of the as-prepared NiCo_2O_4 calculated by the Barrett-Joyner-Halenda (BJH) method (Figure S2b) shows a large distribution of mesopores at sizes less than 10 nm and at 50 nm, respectively. These mesopores refer to the interspace voids between the aggregated nanoparticles, which can also be observed from the TEM results (Figure 3b and 3c). This unique porous structure combined with the 3D foam-like tunnels could be an ideal design for an O_2 electrode:^[30] during the discharge, the large tunnels can function as “highways” to supply oxygen to the interior parts of the cathode, while the mesopores on nanowalls are the “exits” that provide the triple junctions (solid-liquid-gas) required for the ORR reaction.

X-ray photoelectron spectroscopy (XPS) measurements were performed on the as-prepared NiCo_2O_4 , and the corresponding results are presented in **Figure 4**. The XPS spectra indicate the presence of Ni, Co, and O, as well as C from the graphite reference, and no other element peaks are detected (Figure 4a). By using a component fitting method, the Ni 2p emission spectrum (Figure 4b) is reasonably deconvoluted into four peaks, with two spin-orbit doublets characteristic of Ni^{2+} and Ni^{3+} , and one shake-up satellite (indicated as “Sat.”). The binding energy peak at 855.6 eV and its satellite peak at 872.5 eV correspond to Ni^{2+} while the binding energy peak at 861.4 eV and its satellite peak at 879.1 eV correspond to the Ni^{3+} . Similar to Ni 2p, the Co 2p (Figure 4c) was also fitted with two spin-orbit doublets and one shake-up satellite. Specifically, the fitting peaks at binding energies of 778.4 and 794.0 eV are attributed to Co^{3+} , whereas other fitting peaks sitting at 780.0 and 795.1 eV are ascribed to Co^{2+} .^[13, 40] The high resolution spectrum of the O 1s region (Figure 4d) shows three oxygen contributions, which can be denoted as O1, O2, and O3, respectively. Usually, the O1 peak at 529.1 eV is typical of metal-oxygen bonds,^[13, 40] while the O2 peak located at 530.7 eV is assigned to the OH^- groups. The presence of this component in the O 1s spectrum indicates

that the surface of the NiCo_2O_4 is hydroxylated to some extent due to either surface oxyhydroxide or the substitution for oxygen atoms at the surface by hydroxyl groups.^[13, 33]

The O3 contribution at 532.7 eV is usually associated with defects, contaminants, and a number of surface species, including chemisorbed oxygen, under-coordinated lattice oxygen, or species intrinsic to the surface of the spinel.^[13, 41, 42] These above data show that the surface of the as-prepared 3D foam-like NiCo_2O_4 has a composition including Co^{2+} , Co^{3+} , Ni^{2+} , and Ni^{3+} , which may provide good electrocatalytic activity toward ORR/OER reactions.

The new 3D foam-like NiCo_2O_4 was subjected to linear sweep voltammetry (LSV) measurements on a rotating disk electrode (RDE) in O_2 -saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} in the potential range of -0.9-0.1 V (vs. AgCl/Ag). Super P and standard commercial Pt/C (10 wt% Pt on Vulcan XC-72 carbon) were tested as control samples. Compared with standard commercial Pt/C (**Figure S3a**) and Super P (**Figure S3c**), our as-prepared 3D foam-like NiCo_2O_4 gives more defined diffusion-controlled LSV waves (**Figure 5a**). With increasing rotation speed, the limiting current density also increases. Furthermore, the limiting current density of the ORR on the 3D foam-like NiCo_2O_4 electrode is always higher than that of the Super P electrode and much more stable than that of standard commercial Pt/C at each rotation rate, suggesting better ORR activity on the 3D foam-like NiCo_2O_4 electrode.^[30] The linearity of the Koutecky-Levich plots and the near parallelism of the fitting lines for the 3D foam-like NiCo_2O_4 electrode (inset of **Figure 5a**) suggest first order reaction kinetics toward the concentration of dissolved oxygen and similar electron transfer numbers for the ORR at different potentials.^[43, 44] The electron transfer number (n) was calculated to be 4.0 at 0.45-0.75 V from the slopes of the Koutecky-Levich plots,^[36] suggesting that the 3D foam-like NiCo_2O_4 favours a $4e^-$ oxygen reduction reaction, as in the ORR catalysed by commercial Pt/C catalyst measured in the same 0.1 M KOH electrolyte ($n = 4$ for Pt/C, see Supplementary Figure S3a and S3b), while Super P could only catalyse a $2e^-$ oxygen reduction reaction (see Supplementary Figure S3c and S3d). **Figure 5b** indicates

that the catalytic activity of the as-prepared 3D foam-like NiCo_2O_4 significantly outperforms that of Super P at a rotation speed of 1600 rpm, as evidenced by the positive shifts of the onset potential and the half-wave potential ($E_{1/2}$) to -0.15 and -0.34 V (vs. AgCl/Ag), respectively. In contrast, the values for the Super P are -0.3 V and -0.43 V, respectively. Also, the diffusion current density of the 3D foam-like NiCo_2O_4 is notably stronger than that of Super P, suggesting synergistic effects on the ORR catalytic activity of 3D foam-like NiCo_2O_4 .

We also extended the potential of the as-prepared 3D foam-like NiCo_2O_4 electrode and the control samples to 0.9 V (vs. AgCl/Ag) to the water oxidation regime and evaluated the electrocatalytic oxygen evolution reaction (OER) (Figure 5c). In 0.1 M KOH, the 3D foam-like NiCo_2O_4 electrode offers a rather higher current density than Super P, with a value of 24 mA cm^{-2} and an onset potential of 0.6 V. The above results show that the 3D foam-like NiCo_2O_4 is a powerful bi-functional catalyst for both oxygen reduction and oxygen evolution.^[46] Since the primary goal of this work is to develop an efficient ORR/OER catalyst for non-aqueous lithium oxygen batteries, the ORR activity of the 3D foam-like NiCo_2O_4 catalyst in O_2 -saturated 1 M LiCF_3SO_3 in tetraethylene glycol dimethyl ether (TEGDME) was also studied using RDE with a rotation speed of 1600 rpm (Figure 5d). With a similar trend to the ORR activity measured in aqueous electrolyte, a significant improvement in the ORR activity was observed on the 3D foam-like NiCo_2O_4 catalyst compared to the Super P catalyst in terms of more positive onset and half-wave potential. These direct ORR and OER assessments indicate that the as-prepared 3D foam-like NiCo_2O_4 is a promising catalyst for Li- O_2 batteries.

The cathode performance using an electrolyte containing O_2 -saturated 1.0 M LiCF_3SO_3 in TEGDME for the Li- O_2 battery is shown in **Figure 6**. All the capacities reported in this work are normalized by the mass of carbon used in the cathodes. Cyclic voltammetry (CV) curves of the as-prepared 3D foam-like NiCo_2O_4 and Super P control sample (Figure 6a) show that

no redox phenomenon can be observed for the 3D foam-like NiCo₂O₄-based electrode in argon-saturated electrolyte, demonstrating the lack of any electrochemical reaction in such an atmosphere. Besides the more positive ORR peak potential, however, the as-prepared 3D foam-like NiCo₂O₄ exhibits an oxidation (OER) peak at 3.7 V (*vs.* Li⁺/Li), corresponding to the decomposition of discharge products, while there is no oxidation peak for Super P electrode below 4 V (*vs.* Li⁺/Li) in O₂-saturated electrolyte. The first discharge and charge curves of a lithium oxygen battery with the 3D foam-like NiCo₂O₄-based electrode are compared with those of the pure Super P electrode at the same current density (200 mA g⁻¹) in Figure 6b to enable an understanding of the excellence of the 3D foam-like NiCo₂O₄ in terms of its ORR and OER kinetics. The lithium oxygen battery with the pure Super P sample exhibits a discharge and charge overpotential of 0.31 and 1.18 V, respectively, with a low round-trip efficiency of 64%. In contrast, the battery with the as-prepared 3D foam-like NiCo₂O₄ presents discharge-charge overpotentials of 0.2 and 0.97 V, respectively, which results in a higher round-trip efficiency of 70%. Additionally, the initial discharge capacity of the 3D foam-like NiCo₂O₄ electrode is 101376 mAh g⁻¹, which is significantly higher than that of the Super P electrode (5928 mAh g⁻¹). To the best of our knowledge, this is the first report that a lithium oxygen battery with NiCo₂O₄-based catalyst shows such low discharge-charge overpotential with such a high specific capacity based on the mass of carbon. Also, in order to make sure that all the capacity has resulted from the oxygen reduction reaction instead of from lithium insertion into the NiCo₂O₄ electrode, discharge curves in traditional R2032 cells without O₂ atmosphere were collected (See Supporting Information, **Figure S4**). A negligible capacity of 2 mAh g⁻¹ could be delivered when the discharge potential was cut to 2.35 V, suggesting that NiCo₂O₄ only functions as an oxygen reduction reaction catalyst. Additionally, the rate performance of the 3D foam-like NiCo₂O₄ in comparison with Super P was further investigated at higher discharge current densities of 500 and 1000 mA g⁻¹, respectively, when the discharge potential was cut to 2.35 V (Figure 6c and Supplementary

Figure S5a). A specific capacity of 8202 mAh g⁻¹ was found for the 3D foam-like NiCo₂O₄-based electrode, while 4070 mAh g⁻¹ can be delivered by the Super P electrode at a current density of 500 mA g⁻¹. Even when the current density was increased to 1000 mA g⁻¹, the capacity of the 3D foam-like NiCo₂O₄ still remained as high as 5598 mAh g⁻¹, while the discharge plateau remained above 2.5 V. The good rate capability is likely to have benefited from its unique structure: during the discharge, large amounts of oxygen can be supplied by the “highways” of the macro-tunnels and stored in the interior parts of the cathode, facilitating the rapid oxygen reduction reaction at high current densities.^[30, 38]

Figure 6d shows the typical initial discharge and charge profiles of the 3D foam-like NiCo₂O₄-based electrode and the Super P electrode with a fixed capacity of 1000 mAh g⁻¹ and a current density of 200 mA g⁻¹, from which a much lower discharge and charge overpotential can be observed for the 3D foam-like NiCo₂O₄-based electrode. Remarkably, the discharge-charge curves from the 5th to the 30th cycles even overlap (Figure 6e), and the specific capacity suffers no loss up to 80 cycles (Figure S5b) for the 3D foam-like NiCo₂O₄-based electrode, suggesting its good stability and reversibility. The stable cycling performance of the as-prepared 3D foam-like NiCo₂O₄-based electrode in comparison with the Super P electrode is also manifested by the terminal discharge-charge potential with a fixed capacity of 1000 mAh g⁻¹ at a current density of 200 mA g⁻¹. As shown in Figure 6f, after 80 cycles, the terminal discharge and charge potentials of the NiCo₂O₄-based electrode are 2.47 V and 4.35 V (vs. Li⁺/Li), respectively, whereas, Super P electrode could only maintain such performance for less than 15 cycles. The better cycling stability of the 3D foam-like NiCo₂O₄-based electrode than that of the Super P electrode demonstrates its promising application as an effective ORR and OER catalyst for lithium oxygen batteries.

To further understand the reaction mechanism of the 3D foam-like NiCo₂O₄, XRD measurements on the electrode at different discharge-charge stages of lithium oxygen batteries and examination of the morphologies of the electrode at corresponding stages were

also conducted. XRD patterns of the NiCo_2O_4 electrodes at different stages for the first cycle at a current density of 100 mA g^{-1} are shown in **Figure 7a**. Compared with the XRD pattern of the fresh electrode, new diffraction peaks could be observed for the discharged electrode. They can be assigned to the (100), (101), and (110) peaks of Li_2O_2 (as highlighted in Figure 7a). These peaks indicate that Li_2O_2 is a major crystalline discharge product.^[47, 48] The three diffraction peaks disappeared when the battery was recharged, however, which suggests that the discharge product Li_2O_2 is decomposed during the charging process. Meanwhile, before the discharge, the fresh NiCo_2O_4 -based electrode shows a rather loose morphology with macro-tunnels (Figure 7b) that can permit oxygen flow and Li_2O_2 deposition. During the 1st discharge, the insoluble species precipitate on the surface of the cathode, and a less porous morphology was obtained compared to the pristine porous electrode before the discharge. Moreover, the band at approximately 800 cm^{-1} in the Raman spectrum of the electrode after discharge (**Figure S6**) is ascribed to O–O stretching vibrations of lithium peroxide, further confirming the presence of lithium peroxide.^[49] After the 1st charge, the porous structure is essentially regained for the NiCo_2O_4 -based electrode, indicating a reversible reaction (Figure 7d). Since the fundamental features of the ORR and OER processes in aqueous and non-aqueous electrolytes share similarities,^[50] catalysts that can favour a 4e^- electron reaction in aqueous media have been reported to easily facilitate a 2e^- reaction in non-aqueous electrolyte.^[51] Thus, it is not surprising that we acquired satisfactory electrocatalytical results for our as-prepared 3D foam-like NiCo_2O_4 in terms of reversible Li_2O_2 formation and decomposition, as well as reduced discharge-charge overpotential, based on the former RDE results involving a 4e^- ORR reaction and excellent OER performance. Moreover, the 3D foam-like structure not only provides more contact sites and larger space for Li_2O_2 deposition, it also simultaneously improves the transport of oxygen and electrolyte, which underpin enhanced discharge-charge capacity, as well as stable cycling capability.

3. Conclusion

In summary, self-assembled 3D foam-like NiCo_2O_4 was fabricated by an environmentally friendly starch template method and demonstrated superior bi-functional electrocatalytic activity towards both the ORR and the OER when employed as the catalyst for non-aqueous lithium oxygen batteries, as compared to traditional Super P catalyst. The assembled battery shows a relatively high round-trip efficiency of 70%, as well as a high discharge capacity of 10137 mAh g^{-1} at a current density of 200 mA g^{-1} and excellent electrochemical performance in such aspects as high rate capability and stable cycling behaviour. The specific discharge capacity at a current density of 1000 mA g^{-1} reaches 5598 mAh g^{-1} , which is about 55% of that at the current density of 200 mA g^{-1} . When discharge-charge capacities are limited to 1000 mAh g^{-1} , the as-prepared 3D foam-like NiCo_2O_4 shows rather stable and reversible discharge-charge potentials and exhibits no capacity loss up to 80 cycles at a current density of 200 mA g^{-1} . These encouraging results are due to the unique, hierarchically self-assembled 3D foam-like structure, which facilitates continuous oxygen flow through the large tunnels to the interior parts of the electrode and provides enough triple junctions (solid-liquid-gas) for Li_2O_2 deposition and decomposition. This study highlights the importance of a novel electrode design and opens up a promising strategy to develop highly efficient oxygen electrodes for lithium oxygen batteries.

4. Experimental Section

4.1. Materials Preparation

One gram of soluble starch was dissolved in 10.0 mL distilled water with stirring. Then, it was mixed with a 10 mL aqueous solution of nickel acetate (0.1 M) and cobalt acetate (0.2 M) to form a uniform suspension. The mixture was then placed in an oil bath preheated to 90°C and maintained for 20 min under vigorous stirring until a pink gel was obtained. The gelatinized paste was kept at 90°C for an additional 10 min without stirring to age. After cooling to room temperature, it was then freeze-dried for 24 h to obtain the light pink nickel

acetate/cobalt acetate/starch precursor. Then, the precursor was calcined at a temperature of 380 °C with a heating rate of 5 °C min⁻¹ to obtain the hierarchically 3D foam-like NiCo₂O₄.

4.2. Physical Characterizations

X-ray diffraction (XRD) (GBC MMA) patterns were collected over a 2θ range of 10 °- 80 ° with a scan rate of 4 ° min⁻¹ and analysed with Traces™ software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files. X-ray photoelectron spectroscopy (XPS) was conducted on a VG Scientific ESCALAB 2201XL instrument using Al Kα X-ray radiation and fixed analyser transmission mode. The XPS data were analysed using CasaXPS software, and all the results were calibrated by C 1s at 284.6 eV for graphite.

The morphologies of the samples were examined by field emission scanning electron microscopy (FE-SEM, JEOL 7500) and transmission electron microscopy (TEM, JEOL ARM-200F). High-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) images and corresponding element mapping images were collected with the same TEM equipped with a Centurio SSD energy-dispersive X-ray spectroscopy (EDS) detector. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution were determined on a Micromeritics ASAP 2010 adsorption analyser at 196 °C (77 K).

4.3. Li-O₂ Battery Measurements

The electrochemical performances of lithium oxygen batteries were investigated using 2032 coin-type cells with air holes on the cathode side. For the preparation of the 3D foam-like NiCo₂O₄ cathode electrode, 50 wt % catalyst, 40 wt % Super P, and 10 wt % poly(1,1,2,2-tetrafluoroethylene) (PTFE) were mixed in an isopropanol solution. The resulting homogeneous slurry was coated onto a gas diffusion layer (GDL). The same procedure was applied to prepare pure Super P electrodes, which consisted of 90 wt. % Super P and 10 wt % poly(1,1,2,2-tetrafluoroethylene) (PTFE). After that, the electrodes were dried at 120 °C in a vacuum oven for 12 h. All the Li-O₂ batteries were assembled in an Ar-filled glove box

(Mbraun, Unilab, Germany) with water and oxygen contents below 0.1 ppm. They consisted of lithium metal foil as the counter electrode, a glass fiber separator (Whatman GF/D), non-carbonate electrolyte containing 1 M LiCF_3SO_3 in tetraethylene glycol dimethyl ether (TEGDME), and the air cathode electrode. All the assembled coin cells were stored in an O_2 -purged chamber which was connected to a LAND CT 2001 A multi-channel battery tester for 2 h before each test. The galvanostatic discharge-charge tests were then conducted on the battery testing system with the voltage between 2.35-4.35 V (vs. Li^+/Li), and the capacity was calculated based on the mass of the carbon in the cathode. Cyclic voltammetry (CV) was conducted in O_2 saturated 1 M lithium trifluoromethanesulfonate (LiCF_3SO_3) in tetraethylene glycol dimethyl ether (TEGDME). The current densities and specific capacities were calculated based on the amount of carbon in the cathodes.

4.4. Rotating Disk Electrode Tests

RDE tests were performed using a computer-controlled potentiostat (Princeton 2273 and 616, Princeton Applied Research) in a conventional three-electrode cell at room temperature. The glassy carbon (GC) working electrode (5 mm in diameter) was first polished with 1.0 and 0.05 μm alumina powder, rinsed with deionized water, and sonicated first in ethanol and then in double-distilled water. A platinum wire and Ag/AgCl (saturated KCl filled) were used as the counter and reference electrodes, respectively. Typically, the NiCo_2O_4 was redispersed in deionized water + isopropanol + 5% Nafion[®] (v/v/v = 4/1/0.05) to form a homogeneous catalyst ink with a concentration of 2 mg mL^{-1} . Then, 30 μL of this dispersion was pipetted onto the surface of the GC working electrode and dried under ambient conditions. For comparison, the control samples were Super P and commercial Pt/C (10 wt.% Pt on Vulcan XC-72), and were also obtained by the same method described above. Cyclic voltammograms (CVs) were collected in O_2 saturated 0.1 M KOH solution from -0.9 V – 0.1 V at a scan rate of 10 mV s^{-1} . Linear sweep voltammograms (LSVs) to measure the ORR performance were collected in O_2 saturated 0.1 M KOH solution with different rotation speeds from 100 to 2500

rpm from - 0.9 -0.1 V with a scan rate of 10 mV s⁻¹, while OER plots were obtained in Ar atmosphere from 0.1 -0.9 V with a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm.

Koutecky-Levich (K-L) plots show the inverse current density (j^{-1}) as a function of the inverse of the square root of the rotation speed ($\omega^{-1/2}$) at different potential values. The number of electrons involved per O₂ in the ORR was determined by the Koutecky-Levich equation:^[34]

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k} \quad (1)$$

where j , j_k , j_d are the measured, the kinetically controlled and the diffusion controlled current densities, respectively, and ω is the electrode rotation rate. B is determined from the slope of the K-L plot based on the Levich equation:

$$B = 0.2nF(D_{O_2})^{2/3} \nu^{-1/6} C_{O_2} \quad (2)$$

where n represents the number of electrons gained per O₂, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), D_{O_2} is the diffusion coefficient of O₂ in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinetic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and C_{O_2} is the bulk concentration of O₂ ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$).

Supporting Information

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

Acknowledgements

Financial support from an Australian Research Council (ARC) Discovery Project (DP140100401) is greatly appreciated. The authors also are grateful for the use of the facilities in the UOW Electron Microscopy Center, with especial thanks to Wenbin Luo. Many thanks also go to Dr. Tania Silver for critical reading of the manuscript.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Figure 1. Schematic illustration of the preparation of the 3D foam-like NiCo_2O_4 . a) Starch/ Co^{2+} / Ni^{2+} aqueous suspension, b) starch/ Co^{2+} / Ni^{2+} gel, c) starch/ Co^{2+} / Ni^{2+} dry gel, d) NiCo_2O_4 calcined at $380\text{ }^\circ\text{C}$ in air and e) high resolution SEM (HRSEM) image of the obtained NiCo_2O_4 .

Figure 2. XRD pattern of the as-prepared 3D foam-like NiCo_2O_4 .

Figure 3. a,b) HRSEM images, c) TEM image, with the dashed lines indicating the nanowalls, and d) HRTEM image of the as-prepared 3D foam-like NiCo_2O_4 .

Figure 4. a) XPS survey spectrum of the as-prepared 3D foam-like NiCo₂O₄. High resolution XPS spectra of b) Ni 2p, c) Co 2p, and d) O 1s.

Figure 5. Linear sweep voltammetry (LSV) curves: a) the as-prepared 3D foam-like NiCo_2O_4 in O_2 -saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} in the potential range of -0.9-0.1 V (vs. AgCl/Ag), with the inset showing the corresponding Koutecky-Levich plots (J^{-1} vs. $\omega^{-0.5}$). b) The as-prepared 3D foam-like NiCo_2O_4 and super P at a rotation speed of 1600 rpm. c) Oxygen evolution curves for the 3D foam-like NiCo_2O_4 and Super P electrodes in the potential range of 0.2-0.9 V (vs. AgCl/Ag). d) The as-prepared 3D foam-like NiCo_2O_4 and Super P at a rotation speed of 1600 rpm in O_2 -saturated 0.5 M $\text{LiCF}_3\text{SO}_3/\text{TEGDME}$ at a scan rate of 10 mV s^{-1} in the potential range of 2.0-3.3 V (vs. Li^+/Li).

Figure 6. a) Cyclic voltammograms acquired at a scan rate of 0.2 mV s^{-1} in $1 \text{ M LiCF}_3\text{SO}_3$ in TEGDME of the as-prepared 3D foam-like NiCo_2O_4 and Super P. b) Initial discharge-charge plots of the as-prepared 3D foam-like NiCo_2O_4 and Super P at a current density of 200 mA g^{-1} . c) Rate performances of the as-prepared 3D foam-like NiCo_2O_4 and Super P at current densities of 200 , 500 , and 1000 mA g^{-1} . d) Initial discharge-charge plots of the 3D foam-like NiCo_2O_4 and Super P with a capacity limitation of 1000 mAh g^{-1} at a current density of 200 mA g^{-1} . e) Discharge-charge curves for selected cycles of the 3D foam-like NiCo_2O_4 with a capacity limitation of 1000 mAh g^{-1} . f) Cycling performances of the 3D foam-like NiCo_2O_4 and Super P with the capacity limitation of 1000 mAh g^{-1} at a current density of 200 mA g^{-1} . Voltage window: 2.35 - 4.35 V (vs. Li^+/Li).

Figure 7. a) XRD patterns of the 3D foam-like NiCo_2O_4 cathode before discharge, after discharge, and after recharge. SEM images of b) fresh, c) discharged, and d) recharged 3D foam-like NiCo_2O_4 cathode.

A self-assembled three-dimensional (3D) foam-like NiCo_2O_4 catalyst has been synthesized via a simple and environmentally friendly approach. When employed as cathode for lithium oxygen batteries, it demonstrated superior bi-functional electrocatalytic activities towards both the oxygen reduction reaction and the oxygen evolution reaction, which is attributed to the synergistic benefits of the unique 3D foam-like structure and the intrinsically high catalytic activity of NiCo_2O_4 .

3D foam-like, ORR, OER, overpotential, Li_2O_2

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Self-assembled 3D foam-like NiCo_2O_4 as Efficient Catalyst for Lithium Oxygen Batteries

Supporting Information

Self-assembled 3D foam-like NiCo₂O₄ as Efficient Catalyst for Lithium Oxygen Batteries

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Table S1. Elemental composition of the as-prepared 3D foam-like NiCo₂O₄.

Element	Weight%	Atom%
Oxygen	28.78314	56.04151
Cobalt	45.68487	26.35494
Nickel	23.73095	13.20083
Carbon	1.6404	4.21581
Aluminium	0.16064	0.18691
Total	100	100

Figure S1. SEM-EDS of the as-prepared 3D foam-like NiCo₂O₄. (inset is the corresponding SEM image)

Figure S2. a) N_2 adsorption-desorption isotherms and b) pore size distribution of the as-prepared 3D foam-like NiCo_2O_4 .

Figure S3. Linear sweep voltammetry (LSV) curves at various rotation speeds in O_2 -saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} in the potential range of -0.9-0.1 V (vs. AgCl/Ag) for a) 10% Pt/C and c) Super P; K-L plots of b) 10% Pt/C and d) Super P.

Figure S4. Discharge curve of the as-prepared 3D foam-like NiCo_2O_4 in traditional R2032 cells without O_2 atmosphere at a current density of 200 mA g^{-1} .

Figure S5. a) Initial discharge curves at various current densities, and b) cycling performance with a capacity limitation of 1000 mAh g^{-1} of the as-prepared 3D foam-like NiCo_2O_4 .

Figure S6. Raman spectrum of the discharged 3D foam-like NiCo₂O₄ cathode.