



Metal-organic framework-derived ZrO₂/NiCo₂O₄/graphene mesoporous cake-like structure as enhanced bifunctional electrocatalytic cathodes for long life Li-O₂ batteries

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ABSTRACT

Metal-organic frameworks (2D MOFs) have great potential to improve the electrochemical performance of Li-O₂ batteries with high O₂ accessibility, the catalytic activity of the open active metal sites, and large specific surface areas. Herein, we prepared a 3D hierarchical ZrO₂@NiCo₂O₄/GNS (ZNCO) framework as cathode catalysts in Li-O₂ batteries that have been developed to synthesize with Zr/Ni to Co molar ratio of 0.1:1:2 by a facile hydrothermal method. The coating of foreign Zr⁴⁺ ions into the nickel cobaltite matrix, have superior oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) bifunctional activity, and allowed the formation of 3D dimensional networks for oxygen diffusion, electrolyte impregnation, and has very ORR/OER low overpotential due to Zr insertion. Moreover, the ZrO₂ coated shell increases the electronic conductivity, porosity, specific surface area, and protects the core and interstitial decoration against lithium peroxide passivation (Li₂O₂). The electrochemical performance of the 3D hierarchical ZrO₂@NiCo₂O₄/GNS nanocomposite delivers a higher discharge capacity of 9034 mAh g⁻¹ at 50 mA g⁻¹ and a superior cycling performance up to 100 cycles with a limited capacity of 1000 mAh g⁻¹ at 100 mA g⁻¹. An ORR/OER mechanism was suggested to illustrate the interesting growth of spherical-like particle and film-like Li₂O₂ deposits at the different cycles for the ZrO₂@NiCo₂O₄/GNS cathodes. Such MOF-derived; hierarchical porous nanocomposites can lead to high-performance efficient bifunctional electrocatalysts and enables the formation and decomposition of discharge products (Li₂O₂) during the discharge-charge process.

1. Introduction

Non-aqueous Li-O₂ batteries (LOBs) have fascinated remarkable attention due to their ultrahigh theoretical energy density of 3600 W h kg⁻¹ with a thermodynamic potential U₀ of 2.96 V in comparison with traditional Li-ion batteries (LIBs, 250 W h kg⁻¹) [1–4]. However, because of small round-trip efficiency and poor cycling performance, due to greater polarization, these batteries are not marketed. The ORR/OER process of a Li-O₂ battery is based on the reversible reaction of formation and decomposition of discharged by-products (Li₂O₂) (2Li + 2e⁻ + O₂ → Li₂O₂) [5,6]. The formation of by-products during the ORR is a highly insulating material having a wide bandgap; it can affect the electron

conductivity of the cathode material significantly-for example by diminishing the number of active sites through the construction of passivating layers, thereby leading to a discharge specific capacity lower than that prophesied theoretically. Moreover, the deposited discharge products need an extreme charge overpotential during the OER to endure complete decomposition; furthermore, the Li₂O₂ particles are extremely sensitive to water, provoking parasitic reactions, foremost to low coulombic efficiency, low-rate ability, short life cycles, and severe batteries capacity fade [7–9].

Unfortunately, there are still other obstacles to overcome before a carbon-based cathode can be used in a Li-O₂ battery. Noble metal-free catalysts (Ru,[10] Pt,[11], Au,[12] and Pd[13]), transition metal

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