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Facile synthesis of NiCo₂O₄ nanosphere-carbon nanotubes hybrid as an efficient bifunctional electrocatalyst for rechargeable Zn–air batteries

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ARTICLE INFO

Article history:

Received 26 October 2015

Accepted 7 December 2015

Available online 27 March 2016

Keywords:

NiCo₂O₄ nanosphere

Hydrothermal process

Bifunctional catalysts

Rechargeable zinc–air battery

ABSTRACT

Developing low-cost non-precious metal catalysts for high-performance oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is highly desirable. In this work, both the primary and rechargeable Zn–air batteries with NiCo₂O₄ nanosphere and carbon nanotubes hybrid (NiCo₂O₄-CNTs) as cathode catalyst are reported. The catalysts are synthesized through a facile one-pot precipitation reaction and hydrothermal process, which exhibited highly active bi-functional catalytic activity for both ORR and OER. Using NiCo₂O₄-CNTs hybrid as a cathode catalyst, the resulting practical primary and electrochemically rechargeable Zn–air batteries give a promising discharge peak power density as high as 320 mW cm⁻², and a high current density 210 mA cm⁻² at 1.0 V. Also, the rechargeable Zn–air batteries in a two-electrode configuration exhibits an unprecedented small charge–discharge voltage polarization of ~0.75 V at 10 mA cm⁻², high reversibility and stability over long charge and discharge cycles. The high performance is believed to be induced by the hybrid effect (coupling effect) among NiCo₂O₄ and CNTs, which can produce a synergy enhancement for both catalytic ORR and OER.

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Introduction

In the face of rising energy demands and the concurrent need for environmental protection, there is an urgent need for the

development of efficient, safe and affordable energy storage devices for portable electronics, electrical vehicles and stationary grid storage [1]. As one of the most promising electrochemical energy storage device, Zn–air batteries have been emerged as an attractive solution because of their

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<http://dx.doi.org/10.1016/j.ijhydene.2015.12.022>

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environmental benignity and high theoretical energy density up to 1086 Wh kg^{-1} , which is even about 5 times as high as those of current Li-ion batteries [2]. In addition, the abundance of Zn with characteristics of mild reactivity and non-flammability make Zn-air batteries a safe and cost-effective choice. However, the metal-air batteries face a set of challenges such as life and poor rate capability [3]. These technological hurdles mainly stem from inherently sluggish kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which are the two vital reactions that control the discharge and charge, respectively, of a metal-air battery [4,5]. It is known that catalysts for oxygen reduction and evolution reactions are at the heart of key renewable-energy technologies including fuel cells [6,7]. Therefore, the carbon-supported electrocatalysts such as Pd, Pt and Ir [8–10], which have a long developmental history and success with fuel cells, were also used as oxygen electrocatalysts in some early rechargeable metal-air systems. However, the prohibitively high cost of the platinum group metal catalysts rules them out as a long-term solution, and the research today is focused on identifying low-cost alternatives to the platinum group metal catalysts [11]. On the other hand, the catalysts for rechargeable metal-air systems are functionally more complex than the catalysts for the fuel cell air electrode. The catalysts have to be active for both the ORR during battery discharge and the OER during battery recharge. Thus, an effective catalyst for the oxygen reactions in rechargeable metal-air batteries is necessarily “bi-functional”.

Most recently, the mixed valence oxides of transition metals with a spinel structure have attracted much attention due to their high abundance, low cost, environmental friendliness and considerable catalytic activity for both the ORR and the OER [8–14]. More specifically, cobaltite spinel oxides $\text{M}_x\text{Co}_{3-x}\text{O}_4$ have been shown as promising electrocatalysts for the ORR when $\text{M} = \text{Co}, \text{Ni}, \text{Mn}$, and the OER when $\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Mn}, \text{Fe}$ [12–15]. The electrocatalytic performances of several cobalt-based spinel oxides such as Co_3O_4 , NiCo_2O_4 , CuCo_2O_4 , $\text{Co}_3\text{O}_4/\text{MnCo}_2\text{O}_4$ and $\text{MnCo}_2\text{O}_4/\text{CoMn}_2\text{O}_4$ have been reported [2,12,16,17], where the MnCo_2O_4 also has been widely utilized in alkaline fuel cells [18]. To improve the electrochemical performance of semiconducting metal oxides, the synergistic coupling between metal oxides with graphene or CNTs based materials and chemically doping with nitrogen in graphene are a promising approach to create more active sites, and excellent chemical stability due to interaction between carbon structure and other molecules [19,20]. For example, Chen et al. [1] showed that a NiCo_2O_4 nanoplatelet and graphene hybrid had outstanding ORR and normal OER activity. However, it does not apply in rechargeable zinc-air battery. The nanostructured NiCo_2O_4 and 3-dimensional mesoporous NiCo_2O_4 nanoplatelets, specifically nanowires, have also been studied extensively to investigate the morphological effect on their electrochemical activities [21–23]. Unfortunately, there is less report on the combination of spinel NiCo_2O_4 nanostructures with carbon based materials to improve the electrochemical properties of the metal oxide electrocatalyst. Graphene and CNTs, with its intriguing properties such as large surface area, high electrical conductivity, and thermal and chemical stability [24,25] has been reported

as an excellent support material as well as an active and stable electrocatalyst [26]. Extensive studies of graphene sheets and CNTs have been reported as a support material for precious metal catalysts such as Pt, which demonstrated excellent electrochemical activity and stability [27]. Also, graphene sheets and CNTs as a metal-free catalyst have shown to reveal a wonderful performance [28]. It is believed that by combining a transition metal oxide catalyst with a carbon-based support as opposed to simple mixing will lead to a strong hybrid effect with catalytic contributions from both of their unique properties.

In this work, we report a novel hybrid material composed of NiCo_2O_4 nanosphere and CNTs (NiCo_2O_4 -CNTs) as an active bi-functional electrocatalyst for both ORR and OER. This hybrid material is synthesized via a simple one-pot synthesis method where the precursors of the metal-oxide (Ni and Co) and carbon nanotubes are mixed into a single reaction to produce the final material. The one-pot synthesis utilizes facile methods based on the precipitation reaction and hydrothermal process, which are very simple, cost effective, and highly efficient for producing large quantities of material. The hybrid effect of combining NiCo_2O_4 nanosphere with CNTs (i.e., NiCo_2O_4 -CNTs) by comparing its performance to bare CNTs and that of NiCo_2O_4 without CNTs are thoroughly investigated. The evaluation of electrochemical activities of the hybrid towards ORR and OER is conducted by employing half-cell testing. In addition, the temperature effect on the electrocatalytic activity is investigated by comparing the performance of the different temperature to controlled the morphology of NiCo_2O_4 nanostructures. The tested results show that these catalysts have very high ORR and OER activities and stability. It is believed that the electrocatalytic activities of these catalysts are contributed by the novel phases of the inorganic nanosphere and their intimate to the underlying CNT networks, which could induce an enhanced catalyst performance. Using this hybrid electrocatalyst for the air cathode, a rechargeable Zn-air battery is constructed for catalyst validation. Compared to baseline catalyst, both remarkable high rechargeability and durability of a practical zinc-air battery are demonstrated, which are even better than the Pt/C catalyst in alkaline solutions. In particular, the significantly reduced ORR and OER over potentials are achieved, resulting in high battery performance with a discharge peak power density of 320 mW cm^{-2} and, a current density 250 mA cm^{-2} at 1.0 V. Besides, a high durability (long cycle-life) was also obtained when the charging and discharging currents is 10 mA cm^{-2} and a cycling pattern of 10 min per cycle, suggesting that NiCo_2O_4 -CNTs is one of the most promising non-precious catalysts, particularly for the OER.

Experimental section

Synthesis of NiCo_2O_4 nanomaterials

In a typical synthesis of NiCo_2O_4 nanosphere, 0.25 g $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.25 g $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 15 mL of 1.3 mol L^{-1} ammonia solution, then the hybrid were dispersed in the above solution by ultrasonication for 30 min. This mixture was then transferred into a 100 mL autoclave, which

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