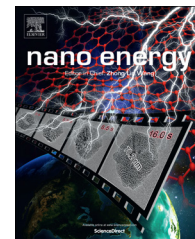


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RAPID COMMUNICATION

Decoupled bifunctional air electrodes for high-performance hybrid lithium-air batteries



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Received 19 May 2014; received in revised form 21 June 2014; accepted 7 July 2014
Available online 16 July 2014

KEYWORDS

Lithium-air batteries;
Hybrid cells;
Bifunctional catalysts;
Electrode configurations;
Decoupled design

Abstract

Lithium-air batteries have become appealing in recent years, but one of the major challenges is the large overpotential associated with the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Tremendous efforts have been made on developing highly active and durable catalysts to lower the overpotentials for ORR and OER. In addition to the intrinsic activity and stability of the catalysts, construction of the air electrodes plays an important role in the overall performance of the air electrodes. Accordingly, three kinds of electrode configurations are herein compared: single, combined, and decoupled bifunctional air electrodes. The decoupled design of the air electrodes shows the best performance in terms of both the discharge and charge performance compared to the other configurations.

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Introduction

Hybrid Li-air batteries, in which the lithium-metal anode in a nonaqueous electrolyte is separated from the air cathode in an aqueous catholyte by a solid electrolyte membrane, show attractive properties for applications like electrical vehicles or grid-energy storage [1–4]. They offer several advantages such as high cell voltage, high energy density, stability in ambient air, and reversibility in aqueous catholytes. However, the development of hybrid Li-air batteries is still at its infant stage. Many efforts have been made on extending the cycle

life of rechargeable hybrid Li-air batteries. The research directions include the development of highly active and stable bifunctional catalysts [5–8], highly porous cathodes for better air diffusion [9,10], suitable aqueous catholytes to maintain the stability of the solid electrolyte [11–13], and highly conductive solid electrolytes that are stable with lithium-metal anode and aqueous catholytes [14,15]. Noble-metal catalysts were first applied in hybrid Li-air batteries as a proof of concept [9,11,16]. Thin carbon nanotube (CNTs) buckypaper cathodes, which intertwined in a horizontal direction and formed large open channels for air diffusion, could reduce the Pt loading to as low as 5 wt% [9]. However, the noble-metal catalysts are scarce and expensive, limiting the practical applications.

Carbon-based catalysts are good candidates for the oxygen reduction reaction (ORR) during the discharge process in

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alkaline solutions, considering their low cost and high activity [17,18]. There are two examples of using pure carbon materials as air cathodes in alkaline catholyte based hybrid Li-air batteries. Li et al. [10] recently reported that less populated, vertically aligned nitrogen-doped carbon nanotube arrays (CNTAs) with dislocated graphene stacking can be grown directly onto carbon fiber papers and investigated them as air cathodes for hybrid Li-air batteries with alkaline electrolytes. They found that these CNTAs exhibit high electrocatalytic activity, which is comparable to that of 20 wt% Pt/C during battery test [10]. Zhou et al. [7] utilized an all graphene-based catalyst in hybrid Li-air batteries. They found that a high-temperature heat-treatment increases the stability of graphene at high voltage by decreasing the oxygen functional groups and planar defects in graphene. However, the loss of oxygen functional groups and planar defects also decrease the ORR catalytic activity of carbon materials [19]. As already proved, carbon has very low oxidation potential, which makes it vulnerable during the high-voltage charge process. One promising way to suppress the oxidation of carbon at high voltage is to couple it with metal oxides [20], which are more active and stable to the oxygen evolution reaction (OER). The most attractive catalysts with this approach are the cobalt oxides (e.g., CoO or Co₃O₄) coupled with graphene or carbon nanotubes [21-23]. However, the connection between the oxides and carbon support is subject to loss under the high charge potential, leading to degradation of the catalysts [24]. Therefore, the rechargeable Li-air batteries require alternative strategies to realize acceptable cycle life.

To avoid the involvement of the ORR catalyst layer in the oxidizing charge process, the concept of decoupling the ORR and OER electrodes was first explored in metal hydride-air batteries in 1995 and demonstrated in hybrid Li-air batteries recently [1,25,26]. However, a systematic study of how the air electrode configurations affect performance of cells with the same catalysts is still lacking. We present here such an investigation by directly growing spinel NiCo₂O₄ nanoflakes onto nickel foam as a decoupled OER catalyst and a comparison of the performance with that of conventional NiCo₂O₄ nanoflakes powder. Three kinds of air-electrode configurations are compared here, each containing the Pt/C as the ORR catalyst and NiCo₂O₄ nanoflakes (NCONF) as the OER catalyst. The conventional configuration (single) contains both Pt/C and NCONF in one single catalyst layer. Both catalysts are loaded onto a hydrophobic carbon-fiber paper to undergo the reducing discharge and oxidizing charge processes. The second configuration (decoupled) is to separate the ORR and OER functions into two different electrodes. While the Pt/C is loaded onto a hydrophobic carbon-fiber paper to play the role of ORR, NiCo₂O₄ nanoflakes are directly grown onto a hydrophilic nickel foam (NCONF@Ni) to play the role of OER. The cathode is switched between the ORR and OER electrodes during discharge and charge. The third configuration (combined) is to combine the current collectors of the decoupled ORR and OER electrodes during cell operation. In this way, the cathode need not be switched between the two electrodes, leading to a convenient cell handling.

We find that the decoupled configuration displays the best overall ORR and OER performances. This is because the ORR and OER require quite different electrochemical

environments, which are fulfilled by separating these two functions into two independent electrodes with different properties. The Pt/C catalyst was loaded onto a hydrophobic carbon paper to maximize the three-phase boundary for ORR. The decoupled design also avoids the involvement of Pt/C in the oxidizing OER process. The NiCo₂O₄ nanoflakes were grown onto a three-dimensional (3-D) porous nickel foam and totally immersed in the electrolyte to ensure full contact of the OER catalyst with the electrolyte. Each nanoflake was directly connected to the conductive nickel foam substrate to achieve high catalytic efficiency.

Experimental

Synthesis

To synthesize the NiCo₂O₄ nanoflakes powder, 0.5 mmol of Ni(NO₃)₂·6H₂O, 1 mmol of Co(NO₃)₂·6H₂O, and 3 mmol hexamethylene-tetramine were added into a mixture of deionized water and ethanol (30 mL, 2:1 v/v), resulting in a mole ratio of 1:2:6. A Teflon-lined stainless-steel autoclave was then used to conduct a hydrothermal treatment with the above solution at 90 °C for 10 h. After the autoclave cooled down, the greenish Ni-Co precursor precipitated in the solution was collected by centrifugation, washed with deionized water and ethanol for several times, and dried at 80 °C overnight. NiCo₂O₄ nanoflakes powder was finally obtained by firing the obtained dry powder at 320 °C for 2 h in air.

To synthesize the NiCo₂O₄ nanoflakes on nickel foam [27], a pre-cleaned nickel foam (2 cm × 4 cm) was immersed in the above solution when conducting the hydrothermal treatment. After the solution was cooled down, the nickel foam was covered with a layer of greenish Ni-Co precursor, preferably on the side facing down. After cleaning, the nickel foam was subjected to the same hydrothermal treatment second time with the other side facing down. The nickel foam deposited with the Ni-Co precursor was finally washed with copious amount of water and ethanol, dried at 80 °C overnight, and annealed at 320 °C for 2 h in air.

Characterization

X-ray diffraction (XRD) was carried out with a Philips X-ray diffractometer equipped with CuK α radiation from 10° to 70° at a scan rate of 0.02° s⁻¹. The morphology and microstructural characterizations were carried out with a FEI Quanta 650 SEM and JEOL 2010F transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) analysis was conducted with a Kratos Analytical spectrometer. The deconvolution of the XPS spectrum was performed using CasaXPS software with Gaussian-Lorentzian functions and a Shirley background.

Half cell test

The cycling performance of the air electrodes was tested in a home-made three-electrode half cell, in which 0.5 M LiOH+1 M LiNO₃, a Hg/HgO electrode, and a platinum flag

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