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Wave-like free-standing $NiCo_2O_4$ cathode for lithium–oxygen battery with high discharge capacity

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HIGHLIGHTS

- Wave-like free-standing air electrode for Li-oxygen battery is designed and synthesized.
- High discharge capacity is achieved with flower-like Li_2O_2 particles as discharge products.
- The battery cycles for 100 times stably.

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ABSTRACT

A novel free-standing air electrode for Li–O_2 battery with a wave-like microstructure is designed and synthesized through a facile electrochemical deposition process. Interconnected $NiCo_2O_4$ nanosheets with planes grown almost parallel to the surface of Ni foam build up continues porous catalytic surface with open space for the growth of Li_2O_2 discharge product. Li–O_2 battery with the synthesized cathode delivers a high discharge capacity of 7004 mAh g^{-1} at 40 mA g^{-1} with a charge potential lower than 3.6 V (vs. Li/Li^+), and significantly lower impedance compared to conventional electrode. Flower-like Li_2O_2 particles with a large size are observed as discharge products, consisting with the high discharge capacity. The unique wave-like microstructure and DMSO-based electrolyte with a high-doner-number are proposed to be responsible for the high discharge capacity, and the formation of large size Li_2O_2 discharge products. In addition, the electrode also exhibits stable cycle performance up to 100 cycles at the current density of 100 mA g^{-1} due to the robust composition and microstructure of the free-standing design.

1. Introduction

Non-aqueous lithium–oxygen (Li–O_2) battery has captured worldwide attention as a promising candidate for future energy storage applications in electric vehicles because of its high energy density [1–4]. The discharge/charge process of Li–O_2 battery bases on the reversible reaction between oxygen and lithium: $2Li + O_2 \rightleftharpoons Li_2O_2$ [5]. Benefited from the favorable potential of this reaction (2.96 V vs. Li/Li^+), and the low density of the reactants, non-aqueous Li–O_2 battery has a high theoretical energy density of 3505 Wh kg^{-1} (based on Li_2O_2), which is far beyond that of commercial Li-ion batteries [6]. However, the formation of solid state Li_2O_2 on the surface of cathode as discharge products also gives rise to a number of problems in cathode designing of Li–O_2 cells.

To achieve a battery with an improved energy density, a higher discharge capacity is required. Based on the cell chemistry of Li–O_2 battery, increasing the discharge capacity means to deposit a larger amount of Li_2O_2 on the surface of air electrode. Thus, one of the first priorities of cathode designing is to optimize the surface microstructure to accommodate the deposition of large amount Li_2O_2. Carbon based materials with large specific surface area are often used to serve this purpose [7–9]. Though the application of carbon as cathode material improves the discharge capacity of Li–O_2 battery, the highly active O_2^-/O_2^{2-} as intermediates of discharge process will cause the passivation of carbon, leading to the formation of lithium carbonate on the surface of cathode, which blocks the

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electron transportation between the cathode and the discharge products [10,11]. What is worse, the carbonate layer can hardly be fully decomposed in the charge process. As a result, the round-trip efficiency and cycle life of the battery is severely limited.

To avoid the utilization of unstable carbon material, carbon-free designs of air electrodes for Li–O_2 batteries has been developed [5,6,12–14]. Among these studies, nanoporous gold (NPG) cathode shows outstanding cycle stability due to the good oxygen reduction reaction (ORR) activity and stability of noble metal material [5]. But the high cost of noble metal prevents its application in practical cells. Also, the specific discharge capacity of the NPG electrode is limited. Besides the noble metal material, metal oxides based free-standing electrodes have also been studied because of the low coat and high oxygen reduction reaction (ORR)/oxygen evolution reaction (OER) catalytic activity of metal oxides [12, 14, 15]. The free-standing cathodes were prepared by directly growing nanorods or nanosheets on the surface of conductive substrates. The resulting carbon-free electrodes did show improvements in cycle efficiency and stability, but the specific discharge capacity was lower than that of carbon-containing electrodes [15,16]. We think the limited specific capacity of those electrodes can be ascribed to two aspects. First, the metal oxide nanoparticles have a much smaller specific surface area compared with that of carbon based material, which means the surface area for Li_2O_2 deposition is limited. Second, the relatively closed packed metal oxides on the substrates prevents the full utilization of the surface of metal oxide. Since the Li_2O_2 particles only forms on the three-phase interface of the electrolyte, metal oxide catalysts and oxygen, the growth of solid-state discharge products is favorable on the top of close packed metal oxide particles due to the easy access to both oxygen and electrolyte [15]. As the Li_2O_2 particle grows, the oxygen and electrolyte diffusion close to the base of the catalyst particles is clogged, hindering the further growth of Li_2O_2.

To increase the specific discharge capacity of free-standing metal oxide cathode, we developed a novel interconnected wave-like free-standing $NiCo_2O_4$ nanosheets air electrode on the surface of nickel foam ($NiCo_2O_4$ NS@Ni) through a facile electrochemical deposition method. $NiCo_2O_4$ is chosen because of its high catalytic activity in Li–O_2 battery [15–17] and relatively high electronic conductivity among transition metal oxides [18]. The $NiCo_2O_4$ nanosheets arranged almost parallel to the surface of Ni foam forms a porous layer with easy access to oxygen and electrolyte for the deposition of Li_2O_2. As a result, the $NiCo_2O_4$ NS@Ni cathode exhibits high discharge capacity (7004 mAh g^{-1} at 40 mA g^{-1}) with large size flower-like discharge products grown on the surface. The cathode also shows stable cycle performance with limited capacity.

2. Experimental

A facile chronoamperometry method was used to synthesize free-standing $NiCo_2O_4$ NS@Ni electrode [19]. The nickel foam was soaked in 4 M HCl solution for 20 min to remove the oxide layer from the surface, and then rinsed with distilled water and absolute ethanol. The electrodeposition was performed with a standard three-electrode system consisting of the pre-cleaned Ni foam as the work electrode, a platinum plate as the counter electrode and a saturated calomel reference electrode (SCE) at room temperature. The deposition process was conducted on an Autolab Electrochemical Workstation. The bimetallic (Ni, Co) hydroxide precursor was deposited on the surface of Ni foam after 10-min deposition at −1 V (vs. SCE) in aqueous electrolyte containing 10 mM $Ni(NO_3)_2$ and 20 mM $Co(NO_3)_2$. After the deposition process, the Ni foam was rinsed with distilled water and absolute ethanol for several times and dried at 65 °C in an oven. Finally, the sample was calcined at 300 °C for 2 h in the air. The $NiCo_2O_4$ loading of the final product was about 0.45 mg cm^{-2}. As a comparison, conventional $NiCo_2O_4$ NS/PVDF electrodes were prepared by casting the ball-milled slurry mixture of the $NiCo_2O_4$ deposit (scraped from the as-prepared $NiCo_2O_4$ NS@Ni electrode) and PVDF (dissolved in NMP) with a weight ratio of 4:1 onto Ni foams. All electrodes were dried under vacuum at 80 °C for 12 h before use.

Structures and morphologies of the as-prepared electrodes were characterized by X-ray diffraction (XRD, Rigaku Ultima IV, Cu-Kα, $\lambda = 1.542$ Å), field emission scanning electron microscope (FESEM, SU8220, Hitachi), and field emission transmission microscope (FETEM, JEM-2100F, JEOL). The surface area and pore size distribution was determined through a Tristar 3000 surface area analyzer.

The cell test was carried out with a Swagelok cell composed of a lithium metal foil anode, glass fiber separator (GF/A, Whatman), the as-prepared cathode, and electrolyte containing 0.5 M $LiClO_4$ in DMSO. The cell was assembled in an Ar filled glove box with oxygen and water contents less than 1 ppm. The cathode side was exposed to 1 atm of pure oxygen during the electrochemical measurements in order to rule out the complication related to CO_2 and H_2O.

The galvanostatic discharge/charge tests were conducted within a voltage window of 2.0–4.2 V (vs. Li/Li^+) using a LAND CT2001A battery test system at ambient temperature under different current densities. Cycling tests with different capacity limitations were also carried out. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) curves of the cells was evaluated using an Autolab Electrochemical Workstation. The EIS tests were conducted in a frequency range of 10^6 Hz to 10^{-1} Hz, while the CV curves was tested between 2.0 V and 4.2 V (vs. Li/Li^+) at a scan rate of 0.1 mV s^{-1}.

To study the cathodes after discharge/charge process, the cell was disassembled in the glove box, then introduced to FESEM, Raman (DXR Raman microscope, wave length 532 nm, Thermo Scientific) and Fourier Transform Infrared Spectroscopy (FTIR, Tsensor 27) test.

3. Results and discussion

3.1. Characterization of the synthesized electrode

XRD result shows that the deposit after heat treatment is pure phase spinel $NiCo_2O_4$ (F*3, JCPDF file No. 20-0781) with standard peaks indexed in Fig. 1a, indicating the coprecipitation of Ni^{2+} and Co^{2+} due to the similar solubility constant (K_{sp}) of $Ni(OH)_2$ (2.8×10^{-16}) and $Co(OH)_2$ (2.5×10^{-16}) [20]. This result is further confirmed by the selected-area electron diffraction (SAED) pattern (Fig. 1c), which shows well-defined diffraction rings, indicating the polycrystalline characteristic of $NiCo_2O_4$ deposit. The HRTEM results (Fig. 1d) reveal the lattice fringe of 0.47 nm, 0.29 nm and 0.14 nm for (1 1 0), (2 2 0) and (4 4 0) planes of spinel $NiCo_2O_4$, respectively. The FESEM images of the final electrode (Fig. 1e) indicate that the $NiCo_2O_4$ deposit forms a hierarchical porous layer consisting of interconnected nanosheets with the pore size between 100 and 700 nm. Unlike the free-standing electrodes with metal oxides grown perpendicularly to the surface of conductive support reported before [12,21], the interconnected $NiCo_2O_4$ nanosheets form a wave-like microstructure with planes arranged almost parallel to the surface of Ni foam. Moreover, the FETEM image in Fig. 1b suggests that the $NiCo_2O_4$ nanosheets are actually assembled by a number of nanoparticles of about 10 nm size. The Brunauer–Emmett–Teller (BET) surface area of the $NiCo_2O_4$ nanosheets derived from Fig. 2 is 40.83 m^2 g^{-1}. The pore size distribution result shows that most pores have a size of 10–20 nm (Fig. 2, inset). This result is in agreement with the FETEM image in