



# Growth of Al and Co co-doped NiO nanosheets on carbon cloth as the air electrode for Zn-air batteries with high cycling stability

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## ARTICLE INFO

### Article history:

Received 3 August 2018

Received in revised form

2 September 2018

Accepted 8 September 2018

Available online 10 September 2018

### Keywords:

NiO nanosheets

Co-doping

Binder-free

Zn-air battery

Cycling stability

## ABSTRACT

The air electrodes with high activity toward oxygen electrocatalysis and high stability are essential for high-performance Zn-air batteries. Herein, we report an electrode made of Al and Co co-doped NiO nanosheets, which are directly grown on the surfaces of carbon cloth without the addition of binders, facilitating the transport of electrons. Additionally, the hierarchical structure shortens the length for species transport and provides abundant active sites for reactions. In the alkaline solution, the Al and Co co-doped NiO electrode exhibits higher activity in both oxygen reduction and evolution reactions than the pristine NiO electrode without doping and superior stability. When assembled in a Zn-air battery, impressively, this electrode results in stable charge-discharge voltage gaps and energy efficiency of 62% over 1000 cycles (330 h) at 5 mA cm<sup>-2</sup>. In comparison, a battery with the electrode made of Pt/C and Ir/C shows large voltage gaps and can only be operated for 400 cycles. The characterization of the electrode after cycling illustrates that both the nanosheet morphology and the NiO phase are well maintained. The results demonstrate that the carbon cloth with Al and Co co-doped NiO nanosheets is a promising air electrode to enable the high cycling stability of rechargeable Zn-air batteries.

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## 1. Introduction

The increasing demand of electric vehicles and electronic devices requires highly efficient energy conversion/storage systems [1]. To enhance the energy density dramatically, research interest has been devoted to metal-air batteries [2–4]. In particular, Zn-air batteries have become the hot topics due to the high theoretical capacity of zinc (820 mAh g<sup>-1</sup>) [5]. In addition, oxygen, as the other active component, can be directly got from the ambient air without occupying the mass and volume of the battery, further improving the energy density. Moreover, the battery is using aqueous electrolytes instead of organic ones, avoiding the safety issue of flammability [6]. The operation of a rechargeable Zn-air battery involves the dissolution and deposition of metallic zinc on the negative (Zn) electrode and the oxygen reduction (ORR) and evolution reactions (OER) on the positive (air) electrode. To make this technology

applicable, however, a wide variety of issues should be well solved. In addition to the irreversibility of Zn electrode [7], the sluggish kinetics in the ORR and OER is an obstacle, which not only results in large discharge-charge voltage gaps and low energy efficiency but also the poor cycling stability due to the corrosion occurred at high charge voltages [8]. Therefore, the air electrodes with high activity toward oxygen electrocatalysis and high stability are essential for high-performance Zn-air batteries [9–11].

Transition metal-based materials, due to their high electrochemical performance, low price, and facile synthesis process, have attracted great attention in research and applied as advanced electrode materials in various energy conversion and storage applications [12–18]. For the hydrogen evolution reaction, Xi et al. synthesized ultrathin metallic CuFeS<sub>2</sub> nanosheets (NSs), which presented a lower onset potential of 28.1 mV, an overpotential of only 88.7 mV at the current of 10 mA cm<sup>-2</sup>, and remarkable long-term stability [19]. Guo et al. developed hierarchical hollow carbon nanospheres (HCSs) with intimately coupled ultrathin carbon nanosheets and Mo-based nanocrystals, among which the MoP/C HCSs showed much higher electrocatalytic activity and stability in both acidic and alkaline solutions [20]. For alkali-metal-ion

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batteries [21], Lin et al. prepared hierarchically porous  $\text{ZrNb}_{24}\text{O}_{62}$  nanowires for lithium-ion storage, which exhibited a high reversible capacity of  $320 \text{ mAh g}^{-1}$ , outstanding rate capability of  $182 \text{ mAh g}^{-1}$  at 30 C, and durable long-term cyclability with maintaining 90.2% of the capacity over 1500 cycles [22]. Guo et al. reported that the unique sheet-on-sheet  $\text{MoS}_2/\text{C}$  HCSs as an anode for sodium-ion batteries demonstrated a high capacity of  $410 \text{ mAh g}^{-1}$  even after 1000 cycles at a high current density of  $4 \text{ A g}^{-1}$  [20]. Yang et al. developed single-crystalline metallic graphene-like  $\text{VSe}_2$  nanosheets for potassium-ion batteries, which showed a high reversible capacity of  $366 \text{ mAh g}^{-1}$  at  $100 \text{ mA g}^{-1}$ , a high rate capability of  $169 \text{ mAh g}^{-1}$  at  $2000 \text{ mA g}^{-1}$ , and a low decay rate of 0.025% per cycle over 500 cycles [23]. For oxygen electrocatalysis and Zn-air batteries [24–29], Zong et al. applied Ni/NiO<sub>x</sub> nanoparticle-decorated carbon nanofibers in a Zn-air battery and achieved more stable charge voltages in 40 cycles than Pt/C or Ir/C [30]. Guo et al. developed porous NiO/CoN nanowire arrays to promote the electrocatalytic performance and stability. A Zn-air battery with this catalyst exhibited a power density up to  $79.6 \text{ mW cm}^{-2}$ , an energy density of  $945 \text{ Wh kg}^{-1}$ , and operating stability for 500 min [31]. Li et al. synthesized  $\text{Fe}_2\text{O}_3$  and NiO deposited carbon nanotubes, which enabled a Zn-air battery to operate for a continuous cycle of 900 min with a slight degradation of 0.05 V in discharge [32]. Based on the mesoporous spheres assembled by NiO/Ni(OH)<sub>2</sub> nanoflakes, Chen et al. developed a hybrid battery combining Zn-Ni and Zn-air reactions, which demonstrated a high power density of  $2700 \text{ W kg}^{-1}$ , an energy density as high as  $980 \text{ Wh kg}^{-1}$ , and excellent high-rate charge capability [33]. In our previous work, nanoporous NiO/Ni(OH)<sub>2</sub> plates incorporated with carbon nanotubes were developed, which enabled a battery to deliver a high voltage of 1.7 V, a capacity of over  $800 \text{ mAh g}^{-1}$ , and high cycling stability for over 192 times with maintaining the energy efficiency of over 60% [34].

Although NiO-based materials have been reported as effective catalysts, a decrease in the capacity over repeated cycling was observed [33]. This issue is caused by the phase conversion of  $\alpha\text{-Ni(OH)}_2$  in alkaline solutions, which gradually transform to the thermodynamically stable  $\beta\text{-Ni(OH)}_2$ , decreasing the electrochemical activity and reversibility [34]. To improve the electrochemical performance, introducing other element ions as dopants has been reported as an effective approach [35–37]. Kamath et al. found that nickel-based layered double hydroxides with Cr and Mn can deliver more capacities and more stable in cycling [38]. Li et al. showed that the doping of Co could improve the stability, and at the atomic ratio of 0.57/0.43 for Co/Ni, the sample exhibited 86.4% of the initial capacitance over 1000 cycles [39]. Dai et al. attached the carbon nanotubes with NiAlCo-layered double hydroxide nanoplates, and the results demonstrated that after 2000 charge-discharge cycles, Al and Co co-doping resulted in a slight capacity loss of only ~6% [40].

Herein, inspired by the Al and Co co-doping, we developed an electrode made of Al and Co co-doped NiO nanosheets on carbon cloth for Zn-air batteries in this work. The characterization reveals that porous nanosheets are directly grown on the surface of carbon fibers without the addition of binders, facilitating electron transport. Besides, the hierarchical structure shortens the length for species transport and provides abundant active sites for reactions. Moreover, Al and Co are successfully incorporated into NiO, which is beneficial for the stability in the long-term discharge-charge cycles. The electrochemical activity of the NiO nanosheets with and without doping was first measured in 0.1 M KOH. Then, a Zn-air battery fitted with the present electrode was assembled, and the discharge and charge performance was tested. Moreover, the cycling stability was evaluated using the pulse discharge-charge method, and compared with the electrode using commercial

catalysts (Pt/C and Ir/C). Further, the characterization of the electrode after cycling was carried out to illustrate the morphology and phase changes to demonstrate the stability of the Al and Co co-doped NiO nanosheets electrode.

## 2. Experimental

### 2.1. Growth of Al and Co co-doped NiO nanosheets on carbon cloth

The Al and Co co-doped NiO nanosheets on carbon cloth (denoted as NiO-Al-Co/carbon cloth) was fabricated by a modified hydrothermal reaction as previously reported [41]. The carbon cloth was pre-treated through calcination at  $500 \text{ }^\circ\text{C}$  in the air for 4 h to improve its wettability. Then, the well-cleaned carbon cloth was placed vertically into a Teflon-lined stainless steel autoclave with the capacity of 50 mL. Previous work has demonstrated that Al and Co co-doping with the atomic ratio of 20/2/1 for Ni/Al/Co is effective to stabilize  $\alpha\text{-Ni(OH)}_2$  [40]. To this end, we chose the same atomic ratio in the fabrication of NiO. Namely, 2 mmol  $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.2 mmol  $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 0.1 mmol  $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 8 mmol  $\text{CO(NH}_2)_2$ , and 4 mmol  $\text{NH}_4\text{F}$  were dissolved in 40 mL of distilled water to form a homogeneous solution. After transferred into the carbon cloth-contained autoclave and sealed, it was maintained at  $120 \text{ }^\circ\text{C}$  for 7 h in an oven and cooled down naturally to room temperature. The precursor-decorated carbon cloth was taken out, rinsed with distilled water carefully, and dried thoroughly. The calcination process was performed at  $350 \text{ }^\circ\text{C}$  in air for 2 h with a heating rate of  $2 \text{ }^\circ\text{C min}^{-1}$ . For comparison, the growth of NiO nanosheets on carbon cloth (denoted as NiO/carbon cloth) was fabricated using the similar method without adding  $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . After synthesis, the mass loadings of NiO-Al-Co and NiO nanosheets were measured to be 1.72 and  $1.51 \text{ mg cm}^{-2}$ , respectively.

### 2.2. Material characterization

X-ray diffraction (XRD, Rigaku Smartlab) with a Cu-K $\alpha$  source operating at 45 keV was applied to analyze the compositions of the synthesized samples. The morphologies and nanostructures of NiO-Al-Co and NiO nanosheets decorated carbon cloth were observed by a scanning electron microscope (SEM, VEGA3 TESCAN) under 20 kV and a transmission electron microscope (TEM, JEOL 2100F) with a LaB<sub>6</sub> filament at 200 kV. The elemental concentration and distribution were analyzed on SEM and TEM with energy dispersive X-ray spectrometry (EDS), respectively. The X-ray photoelectron spectroscopy (XPS) data were collected by a Physical Electronics PHI 5600 multi-technique system using Al monochromatic X-ray at a power of 350 W. The adsorption-desorption isotherm was tested on ASAP 2020 Automatic Micropore and Chemisorption Physisorption Analyzer, and the specific surface area and pore distribution were calculated by the Brunauer-Emmert-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

### 2.3. Electrochemical measurements

A three-electrode cell was applied to measure the electrochemical activity by using the Solartron SI 1287 potentiostat, and the rotation speed was controlled by the instrument from Pine Instrument Co. The working electrode was made by fixing the prepared carbon cloth with NiO-Al-Co or NiO nanosheets on the glassy carbon electrode, the counter and reference electrodes are a platinum wire and a Hg/HgO electrode, respectively, and the electrolyte was 0.1 M KOH. For the ORR test, pure oxygen gas was purged to saturate the electrolyte. Linear sweep voltammetry (LSV) for the ORR polarization was recorded at a scan rate of  $5 \text{ mV s}^{-1}$  in

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