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# Facile Composition of CoNi and Graphene as a Free-Standing Cathode for a High-Performance Solid-State Zinc–Air Battery

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**Abstract:** The development of solid-state zinc–air batteries (SZABs) has stimulated significant interest. However, the practical use of SZABs still encounters difficulties due to the complicated preparation process and low-performance air cathode. In this study, we developed a free-standing CoNi/graphene composite cathode without current collectors and binders. The simplified cathode structure decreased the preparation process, and the self-assembled conductive matrix increased charge transfer, which holds promise for facile preparation and high-performance SZABs. Specifically, a free-standing CoNi/graphene film was fabricated by a simple composition method. The CoNi/graphene electrocatalyst exhibited comparable oxygen reduction reaction (ORR) catalytic activity to that of Pt/C. Furthermore, the CoNi/graphene film could be directly used as a cathode, which showed an open-circuit voltage of 1.41 V and a power density of 210 mW cm<sup>-2</sup> in alkaline liquid ZABs, as well as an open-circuit voltage of 1.43 V and a power density of 40 mW cm<sup>-2</sup> in alkaline SZABs. This facile preparation and excellent performance offer substantial potential for practical SZAB applications.

**Keywords:** free-standing integrated electrode; non-precious metal catalyst; graphene oxide; solid-state zinc–air batteries

## 1. Introduction

For the development of wearable electronic devices and renewable energy vehicle batteries, solid-state zinc-air batteries (SZABs) are gaining widespread prominence owing to their security, high energy density, cost-effectiveness, and eco-friendliness [1-4]. The air cathode, serving as the primary constituent in SZABs, plays an important role in elevating their electrochemical efficiency, environmental suitability, and stability [1]. In recent years, various SZAB cathodes have been developed, exhibiting excellent performance, such as an open-circuit voltage of around 1.4 V and a power density of around 30 mW cm<sup>-2</sup> [2,3]. However, the vast majority of current cathodes are prepared from powder catalysts, rather than directly usable free-standing cathodes. Electrodes prepared with powdered catalysts have many drawbacks. Currently, the cathodes of SZABs usually undergo complicated procedures, including the preparation of electrocatalysts (involving the pre-preparation and grinding of catalysts), fabrication of gas diffusion layers (usually, the hydrophobic treatment of fluid-collecting carbon paper), dispersion of catalyst slurries, and drop coating using inactive additives (such as Nafion solution, PVDF, and conductive carbon black mixture), etc. These complicated procedures usually result in high costs, environmental issues, and poor performance due to the multiple hydrophobic treatments, uneven mixing of catalysts and degradation of adhesives. Therefore, minimizing inactive binders and hydrophobic substrates is important to improve charge transfer and reduce preparation complexity.



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). To solve these two problems, self-assembling an integrated, free-standing cathode is a promising method. Recently, various methods of directly growing on a specific substrate without binders have been adopted, including hydrothermal, electrodeposition, vapor deposition, and other methods [4–6]. These directly grown films can be used for SZAB cathodes, which can obtain open-circuit voltage (OCV) (ca. 1.4 V) and power density (ca. 30 mW cm<sup>-2</sup>) [7,8]. However, the growth process required for these methods is often complex and multifaceted, involving many steps. These technologies require specific instruments, which result in low yields, and are not suitable for large-scale production. In addition, the growth of water-based systems is often hydrophilic and may affect the three-phase interface, causing a decrease in the performance of zinc–air batteries [9]. Therefore, it is crucial to develop a simple, widely used, and high-performance electrode.

To achieve this goal, graphene is deemed a promising contender for the facile preparation of free-standing cathodes. Because of its distinctive 2D structure, graphene sheets can be easily self-assembled via van der Waals forces, promoting the formation of an independent hierarchical structure [10]. Moreover, graphene's high specific surface area enables the easy composite formation of active materials without the need for additives. Additionally, graphene can enhance the active sites and stability of the composites due to its accelerated ion diffusion property, and it is also easily regulated by nitrogen sources [11]. As two typical graphene materials, graphene oxide and reduced graphene oxide have different properties such as electrocatalyst adhesion, conductivity, porous structure, etc., because of the different oxygen levels and binding configurations [12–14]. Then, the optimized oxygen functional groups on the graphene surface are beneficial for film formation, and they can also reduce the conductivity to a certain extent and promote the formation of specific pore structures. Recently, bimetallic alloys such as CoNi have emerged as a promising option for promoting the formation of a reconstruction layer, which can accelerate the ORR process. Compared to their single-element counterparts, these bimetallic alloys exhibit enhanced activity and stability [12,15–17]. Here, we developed a free-standing CoNi/graphene composite cathode without current collectors and binders. The elimination of current collectors and binders decreased preparation cost and processing time, while the self-assembled conductive matrix increased the charge transfer in the cathode, which has potential for facile preparation and high-performance SZABs. The CoNi/graphene electrode demonstrated impressive performance in liquid zinc-air batteries and solid-state zinc-air batteries. The optimized electrode (CoNi/graphene) showed an open-circuit voltage of 1.41 V and a power density of 210 mW cm<sup>-2</sup> in alkaline liquid zinc–air batteries, along with an open-circuit voltage of 1.43 V and a power density of 40 mW cm<sup>-2</sup> in alkaline solid-state zinc-air batteries. The facile preparation and good performance of this electrode hold substantial promise for practical ZAB applications.

## 2. Experimental Section

## 2.1. Materials

Urea(AR 98.5%) and potassium hydroxide(AR 85.0%) were obtained from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China)  $CoCl_2 \cdot 6H_2O(AR 99.0\%)$ , Ni $Cl_2 \cdot 6H_2O(AR 99.0\%)$ , and o-phenanthroline (Phen)(AR 99.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) Pt/C (20%) was obtained from Suzhou Sinero Technology Co., Ltd. (Suzhou, China) Graphene oxide(AR 97.0%) was obtained from Suzhou Tanfeng Tech. Inc. (Suzhou, China). All chemicals were analytical reagents and used as received, without further purification.

#### 2.2. Preparation of the Cathodes

In total, 0.4 g of graphene oxide was dissolved in 20 mL of deionized water and stirred consistently for a duration of 10 min. Then, 2 g of urea and 0.27 g of Phen were mixed into the graphene oxide solution and stirred for 5 min. After mixing well, 0.16 g of cobalt chloride and 0.1 g of nickel chloride were added and stirred for 15 min. The solution was poured out onto a polypropylene substrate and coated into a film using

the squeegee coating method (coating speed is 2 cm/s). Then, it was put into an oven at 35 °C for 4 h. The desiccated film was removed and transferred into a tube furnace, which was subsequently heated to 800 °C at a rate of 4 °C per minute for 2 h under a nitrogen atmosphere. After cooling to room temperature, the integrated electrode (marked as CoNi/graphene) was gained.

## 2.3. Electrode Characterization and Electrochemical Measurement

The characterization of the CoNi/graphene was carried out using a field emission scanning electron microscope (SEM, Hitachi Regulus8100, Hitach Limited, Tokyo, Japan), a transmission electron microscope (TEM, Tecnai F20, FEI, Hillsborough, OR, USA), an X-ray diffractometer (XRD, X'Pert PRO MPD, Panalytical, Almelo, The Netherlands), and X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher Scientific, Waltham, MA, USA). Electrochemical measurements were carried out on a CHI760E electrochemical workstation using a conventional three-electrode system at room temperature. An RDE/RRDE electrode, coated with catalysts, served as the working electrode, while graphite slices functioned as the counter electrode, and Hg/HgO was used as the reference electrode in a basic electrolyte. The fabrication of the working electrode and carbon-paper-air electrode was conducted according to the following steps. First, 5 mg of the catalyst was combined with 50 µL of a Nafion solution (5 wt%), 950 µL of absolute ethanol, and ultrasonicated at room temperature for 15 min to achieve a uniform mixing slurry. Then, 20  $\mu$ L of the slurry was applied to a GC (0.071 cm<sup>-2</sup>) or 40  $\mu$ L to a carbon paper (1 cm<sup>-2</sup>) to acquire the working electrode and air electrode (load capacity  $0.4 \text{ mg cm}^{-2}$  on the GC, or  $2 \text{ mg cm}^{-2}$ on the carbon paper). And all drip slurries were naturally dried at room temperature. As a comparison, GC and air electrodes loaded with Pt/C catalyst were fabricated with the identical method (load capacity  $0.2 \text{ mg cm}^{-2}$  on GC or  $2 \text{ mg cm}^{-2}$  on carbon paper). The assembly of a liquid zinc-air battery involved the following steps. The air cathode was composed of carbon paper coated with a catalyst and a gas diffusion layer. After polishing, the zinc sheet served as the anode, and a 6 mol  $L^{-1}$  KOH solution acted as the electrolyte. The assembly of the liquid zinc-air battery was conducted using a zinc-air battery mold. For comparison, a zinc-air battery based on a commercial Pt/C catalyst was assembled using the same steps and load. The solid-state zinc-air battery was produced according to the following steps. Firstly, 5 g of polyvinyl alcohol (PVA) was dissolved in 45 mL  $H_2O$ and heated and stirred for 30 min. Subsequently, 1 mL KOH solution (6 mol  $L^{-1}$ ) was poured into the above solution. After drying at room temperature, PVA gel was obtained. A solid-state zinc-air battery was assembled using a polished zinc sheet (0.1 mm thick) as the anode, coated with catalytic film as the cathode, and PVA gel as the electrolyte. As a reference, the carbon paper modified with catalyst Pt/C was used as the cathode. The PVA gel was moistened with a 6 mol  $L^{-1}$  KOH solution before testing.

#### 3. Results and Discussion

Generally, traditional composite catalyst cathodes were prepared by blending active catalytic materials (mainly non-precious metals, nitrogen source materials, carbon materials, etc.), combining additives (such as Nafion solution, ethanol), and conductive additives (mainly acetylene black, Figure 1a(iii)) [18]. The mixed slurry was then cast onto a collector (like Ni foam loaded with carbon cloth, Figure 1a(iv)). In this traditional structure, blending inactive components often impedes the transmission of electrolyte [9]. The planar collector offered a limited contact interface with active materials, leading to a low charge transmission. Compared to traditional electrode preparation, a self-assembled layered integrated electrode was designed through straight blending the active catalytic materials (including non-noble metals and nitrogen source) with a graphene oxide solution (Figure 1b(i)). Then, the slurry self-assembled into a free-standing film after low-temperature evaporation (Figure 1b(ii)). By this approach, the electrode established a layered composition of the active material within the conductive matrix, enhancing charge transmission and ion

diffusion (Figure 1b(iii)). Moreover, the thickness of the electrode could be conveniently modified, which was conducive to preparing electrodes with tunable mass load without the need for any adhesive. Thus, this approach could be regarded as a straightforward and versatile composition technique suitable for a wide range of active materials.



Figure 1. (a) Preparation diagram for traditional cathode and (b) CoNi/graphene cathode.

We then analyzed the morphological structure of the prepared CoNi/graphene film using SEM measurements (Figure 2a). These images showed that the graphene sheets exhibit a coiled state and some folded morphology, which is conducive to the loading of electrocatalysts. This is evidenced by the uniform distribution of particles on the sheets. Additionally, the TEM images in Figure 2b reveal that the CoNi compounds were evenly dispersed and attached to the carbon framework, which may promote charge transfer and active site exposure [8].



Figure 2. (a) SEM images of CoNi/graphene; (b)TEM images of CoNi/graphene.

The XRD pattern of the CoNi/graphene is depicted in Figure 3a. It can be seen that the prominent diffraction peak at 26.4° represents the (002) plane of graphitic carbon [19]. Furthermore, clear diffraction peaks were discerned at 44.3°, 51.6° and 75.8°, which are contributed by Co or Ni elements (PDF#15-0806, PDF#04-0850) [20,21]. To further investigate the surface elemental composition and chemical form properties of the CoNi/graphene, we performed the high-resolution Co and Ni 2p XPS spectra of CoNi/graphene (Figure 3b,c).

The results show the signal of  $Co^{3+}$  (780.43 eV and 796.02 eV),  $Co^{2+}$  (782.93 eV and 797.71 eV) and  $Co^{0+}$  (778.88 eV and 794.78 eV). Similarly, the high-resolution spectrum of the Ni 2p peak confirms Ni<sup>3+</sup>, Ni<sup>2+</sup> and Ni<sup>0+</sup> species (Figure 3c) [22–24]. Figure 3d presents the high-resolution N-1s spectral analysis. The results reveal the presence of four forms of nitrogen, corresponding to pyridine nitrogen (398.63 eV), pyrrole nitrogen (400.29 eV), graphitized nitrogen (401.48 eV), and oxidized nitrogen (403.84 eV) [25–27]. It is widely acknowledged that the presence of nitrogen moieties exerts a significant impact on both the structure and catalytic activity of the resultant material [28,29]. In particular, pyridine-N and graphite-N species have been proven to play pivotal roles in facilitating the oxygen reduction reaction [30,31]. Therefore, CoNi/graphene with CoNi active sites, graphene matrix, and nitrogen-containing substrate have potential for electrocatalytic performance [32,33].



**Figure 3.** (a) XRD patterns of CoNi/graphene; (b) high-resolution XPS spectra of Co 2p; (c) Ni 2p; and (d) N 1s.

We then conducted a comparative study on the electrical activity of CoNi/graphene in an alkaline environment using a rotating disc electrode (RDE), and assessed its performance with commercial Pt/C (20% Pt/C) catalysts. The cyclic voltammogram (CV) profiles of CoNi/graphene and Pt/C indicate distinct ORR peaks in O<sub>2</sub>-saturated solutions. The CoNi/graphene catalyst exhibited a relatively higher position of the oxygen reduction peak, suggesting better ORR performance. To assess the activity of the catalysts, we conducted LSV experiments in O<sub>2</sub>-saturated 0.1 mol L<sup>-1</sup> KOH solutions at a rotation rate of 1600 rpm. As shown in Figure 4b, the CoNi/graphene catalyst exhibited relatively good ORR activity with a half-wave potential  $(E_{1/2})$  of 0.83 V, which was close to that of commercial 20 wt% Pt/C ( $E_{1/2} = 0.79$  V) [8,29]. We can observe from the Supporting File Table S1 that the half-wave potential and limiting current of CoNi/graphene catalyst are at an excellent level, as reported in the literature. At the same time, Only Phen and only Urea were added to the catalyst as reference catalysts, marked as CoNi-Phen-Graphene, CoNi-Urea-Graphene. From the Supporting File Figure S5, it can be seen that the half wave potential of CoNi-Phen-Graphene and CoNi-Urea-Graphene is lower than that of commercial Pt/C.



**Figure 4.** (a) Cycle voltammetric (CV) curves of CoNi/graphene and Pt/C in O<sub>2</sub>-saturated 0.1 mol L<sup>-1</sup> KOH at 50 mV s<sup>-1</sup>; (b) LSV curves of CoNi/graphene and Pt/C for ORR recorded at 5.0 mV s<sup>-1</sup> and 1600 rpm on RDE in O<sub>2</sub>-saturated 0.1 mol L<sup>-1</sup> KOH; (c) RDE polarization curves of CoNi/graphene at different rotation rates in O<sub>2</sub>-saturated 0.1 mol L<sup>-1</sup> KOH at 5 mV s<sup>-1</sup>; (d) Corresponding Tafel plots.

To further analyze the electrocatalytic properties of CoNi/graphene, we then conducted polarization curve testing on the CoNi/graphene catalyst at varying rotational velocities (400, 600, 900, 1225, 1600, and 2025 rpm). The results demonstrate a clear trend of the limiting diffusion current density increasing in correspondence with elevated rotational speeds, as illustrated in Figure 4c. A Koutecky–Levich (K-L) curve was used to determine the average number of electrons transferred by the CoNi/graphene catalyst during the ORR process, which was calculated to be approximately 4.1 [34,35]. These results suggest that the catalyst follows a four-electron transfer process in the ORR reaction.

The Tafel curve was generated from the LSV plot, and a comparative analysis of Tafel slopes was conducted for the catalysts, as illustrated in Figure 4d. The Tafel slope value for the CoNi/graphene catalyst was 79 mV dec<sup>-1</sup>. And it was also observed to be lower than that of the Pt/C catalyst (83 mV dec<sup>-1</sup>), indicating that the CoNi/graphene catalyst is more effective for oxygen reduction reaction (ORR) kinetics.

To investigate the actual performance of the prepared electrode under alkaline conditions, a liquid zinc–air battery with a 6.0 mol L<sup>-1</sup> KOH solution as the electrolyte was assembled, wherein the air electrode served as the cathode and the zinc sheet as the anode. The efficacy of air electrodes employing the prepared catalysts in batteries was assessed against the performance of the Pt/C air electrode. Figure 5a demonstrates that the OCV of the CoNi/graphene is 1.41 V, which is superior to the 1.40 V achieved by Pt/C. Figure 5b displays the polarization and power density curves of the zinc–air batteries with Pt/C and the CoNi/graphene catalyst. It is observed that the CoNi/graphene cathode has a maximum power density of 210 mW cm<sup>-2</sup> at a current density of 270 mA cm<sup>-2</sup>. For comparison, the maximum power density achieved by Pt/C is 165 mW cm<sup>-2</sup> at a current density of 260 mA cm<sup>-2</sup>. In addition, at different discharge current densities (2, 5, 10, 20 and 30 mA cm<sup>-2</sup>), the performance of the batteries with the CoNi/graphene and Pt/C cathodes was documented and compared (Figure 5c). A stable voltage platform was established across different discharge currents, demonstrating the battery's high discharge stability. Figure 5c also demonstrates that the discharge voltage plateau of the CoNi/graphene battery closes to the Pt/C battery at a discharge current density of 2, 5, 10 mA cm<sup>-2</sup>. As the CoNi/graphene battery is discharged at higher current densities, such as 20 and 30 mA cm<sup>-2</sup>, its corresponding voltage plateaus are slightly higher than those of the Pt/C battery. We then compared the power density of CoNi/graphene with some reported electrocatalysts in Figure 5d, where one can find that the CoNi/graphene electrode shows good performance ranking [7,36–39].



**Figure 5.** (a) Open-circuit voltage test of CoNi/graphene and Pt/C; (b) Polarization and power density curves; (c) Discharge curves of the CoNi/graphene and Pt/C batteries in 6 mol  $L^{-1}$  KOH at different current density; (d) Maximum values from polarization and power density curves of different catalysts.

To investigate the practical implementation of the free-standing CoNi/graphene film, we then assembled a SZAB [40,41]. A solid-state zinc-air battery was also assembled using carbon paper loaded with Pt/C for comparison. Figure 6a depicts the open-circuit voltage of the CoNi/graphene and Pt/C cathode. The OCV of the CoNi/graphene SZAB was 1.43 V, while the OCV of the Pt/C SZAB was 1.41 V. From Figure 6b, it was observed that the integrated electrode made of CoNi/graphene generated a maximum power of 40 mW cm<sup>-2</sup>, in contrast to the power output of 29 mW cm<sup>-2</sup> generated by the carbon paper loaded with platinum carbon. From Figure 6c, further analysis revealed that the integrated catalytic electrode demonstrated a smaller voltage drop (1.21 V) at a current density of  $2 \text{ mA cm}^{-2}$ . In comparison, the use of carbon paper loaded with platinum carbon resulted in a relatively low voltage output (1.20 V) at a current density of 2 mA cm<sup>-2</sup>. The results show that the solid-state zinc-air battery with the free-standing CoNi/graphene displays stable discharge performance at a current density of 2 mA cm<sup>-2</sup>. Furthermore, the specific capacity of the battery equipped with CoNi/graphene can reach 780 mAh  $g^{-1}$ (Figure 6d). Meanwhile, it can be seen from the supporting document (Figure S8) that SZAB also exhibits good charge-discharge cycle stability. These results illustrate that the



integrated free-standing electrode exhibits notable advantages over the use of platinum carbon loaded on carbon paper and some reported SZABs [42,43].

**Figure 6.** (a) Open-circuit voltage test of CoNi/graphene and Pt/C; (b) Polarization and power density curves; (c) Discharging curves of the CoNi/graphene and Pt/C batteries at 2 mA cm<sup>-2</sup>; (d) Specific capacity of CoNi/graphene and Pt/C.

#### 4. Conclusions

In summary, we have developed a free-standing CoNi/graphene cathode using a facile self-assembly process. This free-standing cathode possesses the advantages of increased performance and facile preparation because it decreases the influence of binders, anhydrous ethanol, and carbon paper. The CoNi/graphene-derived alkaline liquid ZAB delivers a peak power density of 210 mW cm<sup>-2</sup> at 270 mA cm<sup>-2</sup> and a specific capacity of 780 mAh g<sup>-1</sup> at 2.0 mA cm<sup>-2</sup>. And the performance of the SZAB prepared with this integrated electrode (1.43 V, 40 mW cm<sup>-2</sup>) is relatively superior to that of the commercial platinum carbon loaded with carbon cloth (1.41 V, 29 mW cm<sup>-2</sup>). This work provides insights into integrated, independent, and flexible electrodes, which is of great significance for advanced solid-state-energy-storage devices.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/en17092045/s1, Figure S1: XPS of C 1s; Figure S2: XPS of O 1s; Figure S3: CV curves of CoNi/graphene at different sweep speeds in the range of 0.46 V–0.58 V; Figure S4: Based on the CV curve, the relationship between current density and sweep speed at 0.525 V; Figure S5: LSV curves of CoNi-Urea-Graphene, CoNi-Phen-Graphene and Pt/C for ORR recorded at 5.0 mV s<sup>-1</sup> and 1600 rpm on RDE in O<sub>2</sub>-saturated 0.1 mol L<sup>-1</sup> KOH; Figure S6: Corresponding Tafel plots; Figure S7: Electron transfer numbers (n) of ORR on the CoNi/graphene; Figure S8: Galvanostatic discharge and charge cycling curves of SZABs with 15 min discharge and 15 min charge at 8 mA cm<sup>-2</sup>; Figure S9: LSV curves of CoNi/Graphene, Co/Graphene, Ni/Graphene and Pt/C for ORR recorded at 5.0 mV s<sup>-1</sup> and 1600 rpm on RDE in O<sub>2</sub>-saturated 0.1 mol L<sup>-1</sup> KOH; Figure S10: ORR polarization curves at 1600 rpm with a scan rate of 10 mV s<sup>-1</sup> before and after 2000 cycles accelerated degradation test; Figure S11: electrochemical impendence spectroscopy of CoNi/graphene; Figure S12: electrochemical impendence spectroscopy of Pt/C; Figure S13: XRD patterns of Graphene oxide and CoNi/graphene; Table S1: Comparison of ORR performance for CoNi/graphene with other non-precious metal electrocatalysts in alkaline media; Table S2: Comparison of ORR performance for CoNi/graphene with other non-precious metal electrocatalysts in alkaline media.

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**Conflicts of Interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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