Pt/Zn heterostructure as efficient air-electrocatalyst for long-life neutral Zn-air batteries

Yongyin Liang¹, Hang Lei², Songjie Wang¹, Zilong Wang^{1*} and Wenjie Mai^{1*}

ABSTRACT Neutral Zn-air batteries (ZABs) have attracted much attention due to the enhanced lifespan and stability. However, their development is suppressed by the poor catalytic properties of the air-electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Hence, the exploration of highly efficient electrocatalysts for neutral ZABs is critical. Herein, we designed an economical heterostructure of Pt nanoparticle-modified Zn nanoplates (Pt/Zn NPs). Compared with commercial Pt/C electrocatalyst, our Pt/Zn heterostructure exhibits comparable catalytic properties and ultrahigh stability in neutral media. The heterostructure can reduce the dosage of Pt and offer sufficient active sites, resulting in enhanced catalytic properties for ORR/OER in neutral media. When applied to neutral ZABs as air cathode, our heterostructure exhibits a high power density of 45 mW cm⁻² and excellent stability of more than 850 cycles with negligible decay, making it the most efficient and robust one in neutral electrolyte. This approach opens a new avenue to strategically design catalysts with high activity for neutral ZABs, rendering them potential in portable and wearable electronic devices.

Keywords: Pt/Zn heterostructure, oxygen electrocatalyst, neutral electrolyte, zinc-air battery, flexible

INTRODUCTION

With the rapid depletion of fossil fuels, the application of high-performance energy storage and conversion devices is at the heart of sustainable development [1–3]. In recent years, rechargeable Zn-air batteries (ZABs) are deemed to be the up-and-coming power technology with high theoretical energy density (1084 W h kg⁻¹), low cost and high safety [4,5]. There is abundant research about liquid and solid-state ZABs in alkaline electrolyte with outstanding

performance [6,7]. However, alkaline ZABs are still facing some challenges: the reaction between the dissolved CO₂ and OH⁻ in strong alkaline media leads to the formation of carbonates (CO₃²⁻) which slows down electrolyte conductivity; zinc dendrites also grow during the process of charging and discharging, which may penetrate the cell membrane and eventually cause a short circuit. These outcomes degrade the performance and shorten the service life of alkaline ZABs [8,9].

To alleviate the above problems, ZABs with neutral electrolyte are considered as the feasible alternatives to replace the alkaline ones [10–12]. Nevertheless, the catalytic properties of electrocatalyst for oxygen evolution reaction (OER)/oxygen reduction reaction (ORR) in the air cathode are unsatisfactory in neutral electrolyte [13].

Up to now, carbon-supported Pt nanoparticles (Pt/C) is regarded as the state-of-art electrocatalyst in neutral electrolyte with the unique feature of high catalytic activity toward ORR. However, Pt/C is plagued with high cost, poor catalytic properties in OER and undesirable long-term stability, which limit its implementation for neutral ZABs [14,15]. In this regard, developing economical electrocatalysts with distinguished activity toward neutral ZABs is necessary. One efficient approach is to combine the advantages of noble metal and earth-abundant materials, coupling interfacial electronic to engineer heterostructures within catalysts [16,17]. Recent studies have indicated that Pt with transition metals can tune the electronic interface within catalysts to improve the intrinsic catalytic performance of Pt, such as the Co(OH)₂/CoPt/N-doped carbon nanosheet (N-CN) electrocatalysts which outperformed Pt/C due to the heterostructure-induced interfacial effect [18].

Herein, we demonstrate a new and facile strategy to

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couple metal zinc nanoplates (NPs) with Pt (Pt/Zn NPs) as a hierarchical electrocatalyst for ZABs in neutral electrolyte. The Pt/Zn NPs obtained an ideal three-dimensional (3D) structure with good electrical conductivity and large surface area. Benefitting from the synergistic effects between the Pt layer and Zn NPs, our strategy can decrease the amount of Pt loading (Pt in Pt/Zn NPs is 1.8 wt%) and maintain the intrinsic activity of Pt in neutral media. The catalytic properties of our Pt/Zn NPs electrocatalyst are much higher than that of individual Zn NPs in neutral electrolyte and it is also comparable to that of Pt/C. The fabricated neutral rechargeable ZABs with Pt/Zn NPs/Ti mesh as an air cathode exhibit a maximum power density of 45 mW cm^{-2} , which is close to the one based on Pt/C. Moreover, there is no obvious decay for our neutral ZABs after over 850 cycles. Flexible and stable solid-state ZABs with neutral polymer gel electrolyte are also assembled. Two solid-state devices can drive red light-emitting diodes (LEDs) when they are bent and twisted. This strategy paves a way to exploit cost-efficient and high-performance electrocatalysts, facilitating wider application of neutral metal-air batteries in wearable and reliable energy conversion devices.

EXPERIMENTAL SECTION

Preparation of Zn NPs/Ti mesh

Zn NPs were electroplated on Ti mesh, employing an electrochemical workstation. Firstly, a piece of Ti mesh ($1.5 \times 5 \text{ cm}^2$) was cleaned by acetone, deionized water and alcohol in sequence for 10 min. Then 1.73 g of ZnSO_4 and 4.41 g of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ were added to 30 mL of distilled water and stirred until complete dissolution. The mixed solution was served as the electrolyte. At last, the electrodeposition was conducted in a three-electrode system with a constant voltage of -1.5 V for different times (30, 50 or 70 min) using a cleaned Ti mesh as the working electrode, a Pt foil (Alfa, 99%) as the counter electrode and a saturated calomel electrode as the reference electrode.

Synthesis of Pt/Zn NPs/Ti mesh

Pt was electroplated on the surface of Zn NPs/Ti mesh in the mixed aqueous solution of $0.003 \text{ mol L}^{-1} \text{ H}_2\text{PtCl}_6 + 0.001 \text{ mol L}^{-1} \text{ Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ (the pH value was controlled to be about 7 by adding Na_2CO_3) with a current density of 0.25 mA cm^{-2} for different times (15, 20 or 25 min) at 60°C . The above process was performed in a two-electrode system with Zn NPs/Ti mesh as the

working electrode and a carbon rod as the counter electrode. After washing and blowing dry by nitrogen, the Pt/Zn NPs/Ti mesh was obtained by annealing at different temperatures (250 or 300°C) for 1 h in reductive atmosphere of 5% H_2/Ar . Ti mesh, as a conductive substrate, can be substituted by carbon cloth (CC) to assemble flexible quasi-solid-state Zn-air batteries.

Physical characterization

The morphology and surface structure of the as-prepared electrodes were investigated by a field-emission scanning electron microscope (FE-SEM, ZEISS ULTRA 55) installed with X-ray energy dispersive spectrometer (EDS) and high-resolution transmission electron microscope (HRTEM, JEOL-2100, operated at 200 kV). The phase structure information of the samples was collected by X-ray diffraction diffractometer (XRD, Rigaku, MiniFlex 600) with Cu K α radiation in the range of 10° – 80° with a scanning rate of 2° min^{-1} . The data of X-ray photoemission spectroscopy (XPS, Ulvac, PHI X-tool) using Al K α ($h\nu = 1486.6 \text{ eV}$) were recorded. The element contents of Zn and Pt were studied by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 720ES).

Electrochemical measurements

Electrocatalytic ORR and OER measurements were conducted within a three-electrode system controlled by an electrochemical workstation (CHI760D, Chenhua, Shanghai), including a rotating disk electrode (RDE) as the working electrode (0.196 cm^2), a platinum foil as the counter electrode and Ag/AgCl as the reference electrode. The obtained potential (vs. Ag/AgCl) was converted to the reversible hydrogen electrode (RHE), according to the Nernst equation: $E_{\text{RHE}} = E (\text{vs. Ag/AgCl}) + 0.0592 \text{ pH} + 0.197$. And all the measured linear sweep voltammetry (LSV) curves were recorded with iR correction.

In this work, drop-casting ink with catalyst powder on a glassy carbon electrode (GCE) was prepared as following: firstly, 5 mg of the catalyst sample was scraped off from Ti mesh, mixed with $950 \mu\text{L}$ of ethanol and $50 \mu\text{L}$ of Nafion (5 wt%) solution under ultrasonic treatment for 30 min. Four microliter of catalyst ink was taken out and drop-casted onto the GCE. The 0.2 mol L^{-1} phosphate buffer solution (PBS) electrolyte was purged with O_2 for 30 min before the ORR testing and the LSV curves were carried out with a scanning rate of 10 mV s^{-1} at different rotation rates of 400–2025 rpm. The K-L equations were used to calculate the electron transfer number (n) of the samples.

Liquid Zn-air battery fabrication

Conventional alkaline ZABs were assembled with Pt/Zn NPs loaded on Ti mesh or CC as the air cathode and the Zn plate with the thickness of 0.05 mm as the anode in 1 mol L⁻¹ KOH, while neutral ZABs using 4 mol L⁻¹ NH₄Cl + 2 mol L⁻¹ KCl (pH of mixed solution was adjusted to 7.0 by NH₃·H₂O) as the electrolyte.

Flexible neutral Zn-air battery fabrication

A cleaned Zn foil (3.5 × 1.5 cm²) was served as the battery anode and Pt/Zn NPs/CC was employed as the flexible air cathode. The neutral gel electrolyte was synthesized as following: 1 g of polyvinyl acetate (PVA) powder (*M_w* 145,000) was dissolved in 10 mL of deionized water under magnetic stirring for 1 h at 95°C. Then, 1 mL of 4 mol L⁻¹ NH₄Cl + 2 mol L⁻¹ KCl + 0.2 mol L⁻¹ Zn(AC)₂ solution (pH was adjusted to 7.0 by NH₃·H₂O) was added and the electrolyte solution continued to be stirred for 15 min at 95°C. Afterward, the gel polymer electrolyte was inserted into a rectangle glass mold and put into a freezer at -18°C overnight, then thawed at room temperature. The process of freezing-thawing repeated thrice and the neutral gel electrolyte was obtained. Finally, Pt/Zn NPs/CC and Zn plate were placed onto the opposite sides of the electrolyte, while the cell membrane was used to prevent the contact between two electrodes.

RESULTS AND DISCUSSION

As depicted in Scheme 1, the Pt/Zn NP arrays were prepared on Ti mesh by electrochemical deposition. The Pt layer was also electrodeposited *in situ* on the surface of the prepared Zn NPs. To optimize the performance of the Pt/Zn NPs catalyst, we regulated the deposition time of Zn NPs and Pt and the annealing temperature. Appropriate annealing temperature can improve the crystal-

Scheme 1 Schematic for the preparation of the Pt/Zn-Ti mesh.

linity of Pt/Zn NPs. Such convenient synthetic method is also suitable to CC, endowing the air electrode with more wide applications in flexible devices [19].

The morphology and structure of bare Ti mesh, Zn NPs and Pt/Zn NPs were observed by SEM and TEM. As shown in Fig. 1a and Fig. S1a, b, Zn NPs were uniformly grown on Ti substrate with the thickness of 100 nm after electrodeposition. SEM images of Pt/Zn NPs are shown in Fig. 1b and Fig. S1c, which display a continuous and uniform Pt coating layer on the hierarchical Zn NPs. This 3D structure increases the surface area of the substrate to expose highly accessible active sites and contact area between the electrolyte and electrode, which can accelerate the electrocatalytic reactions [20,21]. Moreover, the HRTEM images (Fig. 1c, d) show that the lattice spacings of 0.25 and 0.22 nm agree well with the (002) plane of Zn and (111) plane of Pt, respectively. The Pt nanoparticles with diameters of 3–6 nm are uniformly distributed on the Zn NPs.

The corresponding XRD pattern of Pt/Zn-Ti mesh in Fig. 2a indicates that the diffraction peaks at 36.3°, 39° and 43.2° can be attributed to the (002), (100) and (101) planes of metallic Zn. Nevertheless, the XRD pattern of Pt/Zn-Ti mesh shows that no Pt-containing crystal phases can be detected, which is ascribed to a thin layer of Pt onto the Zn NP surface. The Pt/Zn molar ratios were quantitatively measured by ICP-MS technique (Table S1), revealing only ~1.8 wt% Pt content in Pt/Zn NPs (the total mass of Pt/Zn NPs is 4.1 mg cm⁻²). According to the EDS results in Fig. 2b, Pt atoms are uniformly distributed on the Zn NPs, further proving that the ultrathin Pt layer

Figure 1 (a) SEM images of the Zn-Ti mesh at different magnifications. (b) SEM images of the Pt/Zn-Ti mesh at different magnifications. (c, d) HRTEM images of Pt/Zn NPs.

Figure 2 (a) XRD patterns of Pt/Zn-Ti mesh. (b) The corresponding EDS mappings of Zn (green), Pt (red) and O (blue) elements distributed at the Pt/Zn-Ti mesh. High-resolution XPS spectra of (c) Pt 4f and (d) Zn 2p in Pt/Zn NPs.

is attached to the surface of Zn NPs. The presence of oxygen derives from the adsorbed oxygen from environmental atmosphere. XPS was also conducted to investigate the composition of our sample and the spectra results are presented in Fig. 2c, d and Fig. S2a, b. The core-level spectrum of Pt 4f exhibits two valence states, which show the peaks with binding energies of 70.88 and 74.18 eV, belonging to metallic platinum while the other two peaks are ascribed to Pt^{2+} ions from PtO. The results of the integrated peak area indicate that the metallic Pt is dominant [18,22]. The Zn 2p spectrum shows the fitting peak of 1021.8 eV, confirming the existence of metallic Zn [23]. The peak of O with binding energy of 532 eV is also detected, which originates from the environmental atmosphere. And the ratio of oxygen in Pt/Zn NPs is 25 at%.

To evaluate the catalytic properties of our Pt/Zn NPs, we firstly collected their LSV results for ORR and OER in neutral media. Compared with N_2 -saturated neutral media, an obvious cathodic peak of Pt/Zn NPs was detected in O_2 -saturated one (Fig. S3). As indicated in Fig. 3a, the Pt/Zn NPs exhibit a higher diffusion-limited

current density at 4.98 mA cm^{-2} and half-wave potential ($E_{1/2}$) at 373 mV, which are much better than the individual Zn NPs ($E_{1/2}$ at 220 mV). Moreover, the $E_{1/2}$ of our Pt/Zn NPs is just slightly lower than that of Pt/C ($E_{1/2}$ at 500 mV). The LSV curves of Pt/Zn NPs at different rotation rates reflect the number of electron transfer in ORR process (Fig. S4a, b). According to the above LSVs at different rotation rates, the fitted Koutecky-Levich (K-L) plots at 0.2 V is obtained and the calculated electron transfer number of Pt/Zn NPs is 3.5. This nearly four-electron process is more appropriate to output high power density for ZABs because it means there is thimbleful H_2O_2 , which may cause less battery damage during ORR [24,25]. On the other hand, such a high stability of Pt/Zn NPs at a constant potential of 0.2 V during ORR is demonstrated in Fig. 3b. The Pt/Zn NPs electrocatalyst maintains a slow attenuation after 9-h testing, whereas Pt/C reveals 25% loss of initial current density.

In addition, the OER properties of our Pt/Zn NPs were also evaluated. As shown in Fig. 3c, the Pt/Zn NPs exhibit much higher current density and lower overpotential in OER compared with that of Zn and commercial Pt. The

Figure 3 (a) ORR polarization curves of Zn NPs, Pt/Zn NPs and Pt/C in PBS. (b) ORR stability of Pt/Zn NPs and Pt/C at a constant potential of 0.2 V (vs. RHE). (c) OER polarization curves of Zn NPs, Pt/Zn NPs and Pt/C in PBS. (d) OER stability of Pt/Zn NPs and Pt/C at a constant overpotential of 550 mV.

corresponding Tafel plots (Fig. S5) also display that the slopes of Pt/Zn NPs are almost as small as Pt/C, illustrating the excellent catalytic kinetics of Pt/Zn NPs. These results indicate the Pt layer can significantly enhance the catalytic performance. Meanwhile, the Pt/Zn NPs display high OER stability in Fig. 3d without obvious degradation at a constant overpotential of 550 mV for 12 h. The electrochemical impedance spectra (EIS) and the electrochemical active surface area (ECSA) were collected to evaluate the electrochemical properties of Zn-Ti mesh and Pt/Zn-Ti mesh. As shown in Figs S6, S7, the charge transfer resistance of Pt/Zn NPs is much smaller than that of Zn NPs, indicating the Pt layers can facilitate the charge transfer process. And compared with separate Zn NPs (5.4 mF cm^{-2}), the Pt/Zn NPs (28.8 mF cm^{-2}) exhibit larger ECSA, illustrating that Pt/Zn NPs expose more active sites.

After the stability tests, the morphology and composition of Pt/Zn NPs were also detected. As shown in Fig. S8a, Pt/Zn NPs still maintain the original morphology of Zn nanoplates and Pt NPs. XRD patterns in Fig. S8b confirm the main crystalline phase of metallic Zn,

accompanied by a little amount of ZnO. Meanwhile, the high-resolution spectra of Zn 2p and O 1s indicate the presence of Zn–O (1022.5 eV) and metal oxygen (530.2 eV), respectively, confirming the existence of ZnO. However, the signal of metallic Zn is still obvious, and the ratio and valence states of Pt species are almost unchanged after the stability tests. The above results illustrate that the original composition of Pt/Zn NPs are not seriously changed (Fig. S8c, d). The presence of ZnO is mainly caused by the slight oxidation of Zn during the OER process and just on the surface. Furthermore, the Zn nanoplates still can work as a support to obtain Pt/Zn heterostructures with low interface impedance, compensating the conductivity loss caused by ZnO. Therefore, Pt/Zn NPs present excellent catalytic stability without structure damage.

Based on the bifunctional Pt/Zn NP electrocatalyst, we assembled the liquid-phase ZABs with neutral electrolyte. As shown in Fig. 4a, our neutral ZABs exhibit high and flat open-circuit voltage (V_{OC}) of 1.24 V. Considering the performances of Pt/Zn NPs can be affected by the amount of Pt, the power density of neutral ZABs have been op-

Figure 4 (a) Open-circuit plots of a single ZAB and two-series neutral ZABs with Pt/Zn-Ti mesh as air-cathodes. (b) Charge and discharge polarization curves of Pt/Zn NPs and Pt/C. (c) Polarization and power density curves of neutral ZABs established by Zn NPs, Pt/Zn NPs and Pt/C. (d) Galvanostatic discharge-charge cycling curves of neutral ZABs at 1 mA cm^{-2} built by Pt/Zn NPs and Pt/C as catalyst and the corresponding magnified view. (e) Photographs of two series batteries with an open-circuit voltage and an LED panel powered by two series batteries.

timized (Fig. S9) by adjusting the electrodeposition time of Zn, Pt and annealing temperature. The power densities show that the best performance occurs at the Pt deposition time of 20 min, which is consistent with the catalytic activity (Fig. S10 and Table S2). As can be seen from Fig. 4b, the charge and discharge polarization curves for the neutral ZABs based on Pt/Zn NPs and Pt/C display the similar platform and the higher loss for the Pt/C-based ZABs at high current density. The power densities of the neutral ZABs based on Zn, Pt/Zn and Pt/C are shown in Fig. 4c. The neutral ZAB based on Pt/Zn NPs obtains a peak power density of 45 mW cm^{-2} . This value is superior to that of ZAB based on Zn NPs (25 mW cm^{-2}) and close to the one based on Pt/C (54 mW cm^{-2}).

Furthermore, neutral ZABs based on Pt/Zn NPs present a remarkable long-term cycle stability compared with that based on Pt/C. The continuous discharge-charge test in Fig. 4d shows that a discharging voltage of 0.91 V and a charging voltage of 2.1 V for Pt/Zn NPs at 1 mA cm^{-2} , with a round-trip efficiency of 43.3%. Even after 850 continuous cycles (about 300 h, 20 min per cycle), the enlargement of voltage gap is just about 0.05 V . The above-mentioned performances of Pt/Zn-based ZAB outperform the state-of-art ZABs in neutral media (Table S3). In addition, Fig. 4e and Fig. S11 demonstrate

that two series neutral ZABs with Pt/Zn NPs as air-cathode can trigger the blue light-emitting diodes (LEDs, V_{OC} is 1.8 V) for more than 15 days, highlighting their impressive performance.

Quasi-solid-state and flexible ZABs based on our Pt/Zn NP electrocatalyst with neutral gel electrolyte were assembled as shown in Fig. 5a. The Pt/Zn NPs were grown on the hydrophilic CC by the same synthetic method, and the relative liquid neutral ZABs also show a high power density (30 mW cm^{-2}) with good stability (Fig. 5b and Fig. S12a, b). Fig. S13 and Fig. 5c indicate that our flexible ZAB also exhibits a high V_{OC} of 1.24 V and steady charge/discharge potentials with no obvious decay after 20 h. Moreover, our flexible ZABs demonstrate similar performance when bent at 30° , 90° and 180° (Fig. 5d), indicating high mechanical stability. In addition, our flexible batteries can light up the red LEDs for more than 3 h even contorted into different shapes (Fig. 5e and Fig. S14). The above results indicate our flexible ZABs exhibit potential applications in portable and wearable electronic devices in daily life. Compared with previous studies in neutral ZABs [10,11,26], our studies display a breakthrough in flexible neutral battery assembly.

CONCLUSIONS

In summary, we prepared an effective electrocatalyst of

Figure 5 (a) Schematic representation of quasi solid-state and flexible ZAB with neutral gel electrolyte. (b) Polarization and power density curves of liquid ZABs established by Pt/Zn NPs/CC. (c) Cycling performance at 1 mA cm⁻². (d) Galvanostatic discharge-charge cycling curves of the flexible ZAB by bending to 30°, 90° and 180° every 5 cycles at 0.5 mA cm⁻². (e) Photographs of LEDs powered by bending and twisting ZAB.

Pt/Zn NPs on Ti mesh by facile *in-situ* electrodeposition which served as cost-efficient and highly active air-electrode catalyst for neutral ZABs. This strategy of coupling the Pt layer with 3D Zn NPs can not only decrease the dosage of Pt, but also facilitate electron transfer, expose more active sites, and enhance the catalytic properties. The Pt/Zn NPs exhibit enhanced catalytic properties for both ORR and OER compared with the Zn NPs in neutral electrolyte. The neutral ZABs based on Pt/Zn-Ti mesh as air cathode deliver a high power density of 45 mW cm⁻² and long-term cycle stability for 850 cycles. More impressively, the flexible sandwich-type ZABs with neutral gel electrolytes were fabricated and display good performance even after bending or twisting. This work paves a way to develop more environment-friendly energy devices.

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Author contributions Liang Y performed the experiments and wrote the article. Lei H and Wang S conducted the characterization and data analysis. Wang Z proposed the experimental design. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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Pt/Zn异质结构作为高效空气催化剂用于长寿命中性锌空气电池

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摘要 相比于传统碱性锌空气电池, 中性锌空气电池因为其长寿命和高稳定性吸引了越来越多的关注. 但中性锌空气电池的发展因空气催化剂的氧还原(ORR)和氧析出(OER)性能差而受到了限制. 因此, 开发用于中性锌空气电池的高效催化剂非常必要. 本工作利用Pt纳米颗粒修饰Zn纳米片(Pt/Zn NPs), 制备了经济型异质结构催化剂. 相对于商用Pt/C催化剂, 我们的复合材料催化剂在中性电解液中具有和Pt/C相媲美的催化性能和高稳定性. 这是因为Pt/Zn NPs复合材料不仅可以减少Pt的用量, 还提供了丰富的活性位点. 采用Pt/Zn NPs组装的中性锌空气电池, 具有45 mW cm⁻²的高功率密度和超过850个循环的持久稳定性, 可高效稳定地应用于中性电解液中. 本工作为应用于中性锌空气电池的高活性催化剂的研发提供了指导, 使其在柔性可穿戴器件中更具应用前景.