1. Introduction

Electrochemical storage and conversion of clean and renewable energy, as a promising approach to deal with energy shortage and environmental pollution, has been attracting great attention of researchers. Oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are critical techniques in electrochemical systems for advanced energy conversion,[1] such as fuel cells, metal-air batteries, and water electrolysis.[2,3] However, such oxygen electrode reactions are hard to proceed due to the high overpotential resulting from the complicated four-electron transfer in one catalytic cycle.[4] Although there has been all kinds of benchmark catalysts with good electrocatalytic activity (e.g., Pt for ORR, RuO2 and IrO2 for OER[5]), these noble metal-based electrocatalysts suffer from high cost, scarcity, short lifetime, and limited bifunctional performance, especially in reversible oxygen electrode systems, which is the biggest obstacle for industrial applications.[4,6] Thus, economically and bifunctionally efficient non-noble metal electrocatalysts are urgently needed to be developed to meet practical requirements.

Among all kinds of potential non-noble metal-based electrocatalysts, transition metal oxides with spinel[7–9] or perovskite[10–12] structures have been reported to show excellent oxygen evolution/reduction performance with attractive electrochemical stability, especially for OER processes. However, their typical limitations lie in the poor conductivity and quick aggregation.[10] Meantime, metal-free heteroatom-doped carbon catalysts have attracted more and more attention due to low OER/OER bifunctional overpotential and good conductivity.[5,13] Recently, it has been found that the hybrids of transition metal oxides and N-doped carbon materials are promising bifunctional catalysts for oxygen electrocatalysis.[14,15] Unique synergistically coupling effects of metal–N–C bonds formed at the interface are reported to be responsible to the improved ORR and/or OER performance.[13] Up to now, the electrochemical performances of a set of hybrid composites of spinel oxides (Co3O4,[16,17] NiCo2O4,[14,18] Fe3O4[19] etc.) and carbonaceous materials have been studied. The active centers have been identified to be the interfacial Co–N–C or Fe–N–C species, where Co/Fe bonded with pyridinic N has been identified as the primary contributor to the activity enhancements.[14] Nevertheless, studies on hybrids of nickel–iron-based oxides (NiFe2O4) and carbon materials for reversible oxygen electrocatalysis remain deficient. Generally speaking, NiFe2O4 normally presents acceptable OER activity but poor ORR activity, which is attributed to its low electric conductivity and poor dispersity.[20] Combined with carbon materials can not only improve the dispersity of NiFe2O4 nanocatalysts but also enhance its electrocatalytic activity. There has been several
reports proposing that the composites of nickel–iron oxides and carbon nanotubes[21–24] or porous carbon[25] present low overpotential for basic OER, whereas insufficient attention has been paid to improving the ORR performance. Wang et al.[26] proposed a composite catalyst of NiFe2O4/N–Gr (N-doped graphene [NG]) with an ORR onset overpotential of ≈0.4 V and the electron transfer number was significantly elevated compared to NiFe2O4 and N–Gr. However, the underlying synergistic catalysis mechanism for activity enhancements remains unclear.

In this article, a hybrid catalyst (NiFe2O4/N-doped graphene [NFO/NG]), composed of nickel ferrite (NiFe2O4) and NG, is synthesized via a two-step hydrothermal method. The catalyst demonstrates superior bifunctional OER and ORR activities. X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), and Raman spectroscopies reveal that, Ni is chemically bonded to pyridinic or pyrrolic N atoms, and the doped N exhibits an electron-withdrawing effect on nickel sites. The electrochemical tests show that the catalyst exhibits an overall potential difference $E_{10} - E_{12}$ of only 0.67 V, which is lower than most previously reported bifunctional spinel-based electrocatalysts. When the catalyst is used as the air cathode in a rechargeable Zn–air battery, it demonstrates high discharge power density and specific capacity, and long-term charge/discharge cycling stability. Significantly, the nitrogen doping and Ni–N–C bonding are proposed to be the key factors for the enhancement of bifunctional catalytic performance.

2. Results and Discussion

For fabrication of the NiFe2O4/NG hybrid catalysts with different loading contents (NFO/NG-x, x = 1, 2, and 3), a two-step hydrothermal method was used to in situ grow NiFe2O4 nanoparticles (NPs) onto NG in which the NG NPs were prepared in the first step hydrothermal process. Then, as shown in Table S1, Supporting Information, FeCl2·4H2O and Ni(CH3COO)2·4H2O were added into the NG dispersion at a molar ratio of 2:1. The mixture was transferred to a 50 mL Teflon-lined autoclave and heated at 180 °C for 3 h after homogeneous dispersion by ultrasonic. In the preparation of the control sample NiFe2O4/reduced graphene hybrid (NFO/G), to obtain pure NiFe2O4 phase instead of Fe2O3 phase (Figure S1, Supporting Information), a certain amount of KOH was used to regulate pH to about 11. The prepared NG presents porous and 2D-lamella structure (Figure S2, Supporting Information), which is favorable for high loading and good dispersion of metal oxides. The specific content of Fe and Ni elements in NiFe2O4/NG hybrid catalysts is shown in Table S2, Supporting Information. Figure 1a,b show transmission electron microscopy (TEM) images of NFO/NG-1 and NFO/NG-2 (with 25 and 45 mg of FeCl2·4H2O added, respectively, during preparation). NiFe2O4 NPs loaded on the edge and defect of graphene. The high-resolution TEM (HRTEM) image illustrates that the NPs are well crystallized (Figure 1c), and lattice spacing with $d = 0.29$ nm.

Figure 1. a) TEM image of NFO/NG-1. b) TEM image of NFO/NG-2. c) HRTEM image of NFO/NG-1. d) TEM image of NFO/NG-3. e) XRD patterns of NFO/G, NFO/NG-1, NFO/NG-2, NFO/NG-3, and NFO. f1–f6) scanning transmission electron microscopy and EDS mappings of elements of NFO/NG-2.
matches well with (220) crystal planes of NiFe₂O₄. It is obvious that the excessive increase in ferric and nickel salts can cause large sizes and agglomeration of the oxide particles in hybrids (Figure 1d). Moreover, the X-ray diffraction (XRD) pattern (Figure 1e) verifies the spinel crystal structure of NiFe₂O₄ (PDF#10-0325), and the diffraction peaks become higher and narrower as the amount of NiFe₂O₄ rises, also indicating a gradually increased particle size. The average crystalline sizes of NFO/NG-1, NFO/NG-2, and NFO/NG-3 are calculated to be 10.7, 14.3, and 22.9 nm, respectively, according to Debye–Scherrer equation. Energy dispersive spectroscopy (EDS) elemental mapping images (Figure 1f) reveal that Fe, Ni, and O are dominantly distributed in the position of particles, whereas N is uniformly dispersed all over the carbon nanosheets. Furthermore, oxygen-containing functionalities (─OH, C=O, etc.) of graphene oxide (GO) are effectively reduced during high-temperature hydrothermal treatment, which is proven by Fourier transform infrared spectroscopy (FTIR) results (Figure S3, Supporting Information). In addition, for Raman spectroscopy shown in Figure S4, Supporting Information, the D band (~1348 cm⁻¹) and G band (~1598 cm⁻¹) were assigned to the defects in the graphitic lattice and in-plane vibration of the sp² carbon skeleton, respectively. The relative ID/IG ratio can be quantified to reflect the degree of defects in graphene, and a larger ID/IG ratio means more structural defects. The ID/IG ratio slightly increases from 1.07 for NFO/G to 1.09 for NFO/NG-2.

Next, it is vital to explore the chemical bonding at the interface of the hybrid, therefore information on the chemical state and electronic structure was obtained by Raman, EELS, and high-resolution XPS techniques. First of all, the intense chemical interaction between NiFe₂O₄ NPs and NG in NFO/NG is verified by the Raman spectra (Figure 2a). Five characteristic peaks (A₁g, F₂g(1), F₂g(2), and F₂g(3)) can be identified in all samples with the spinel structure of NiFe₂O₄ in the range of 100–800 cm⁻¹. A₁g is attributed to the symmetrical stretching of oxygen atom along Fe─O bond in the tetrahedral coordination, whereas the F₂g(2) mode corresponds to the asymmetrical stretching of (Ni, Fe)─O bond in the octahedral coordination. Obviously, compared with that of NFO and NFO/G, the F₂g(2) peak of NFO/NG-2 has a redshift from 479.4 to 469.7 cm⁻¹, with no significant shift happened on the A₁g peak of NFO/NG-2 (Figure S5, Supporting Information). This suggests metal ions (Fe²⁺ or Ni²⁺) in octahedral position, instead of ions in tetrahedral, may be involved in bonding with N atoms, due to a redshift in Raman spectra as a manifestation of forming bonds between

Figure 2. a) Raman spectra of NFO, NFO/NG-2, and NFO/G. b) N K-edge EELS spectra of NG, NFO + NG-2, and NFO/NG-2. c) Ni L-edge EELS spectra of NG, NFO + NG-2, and NFO/NG-2. d) N 1s XPS spectra of NG, NFO + NG-2, and NFO/NG-2. e) Ni 2p XPS spectra of NG, NFO + NG-2, NFO/NG-2, and NFO/G. f) Fe 2p XPS spectra of NG, NFO + NG-2, NFO/NG-2, and NFO/G.
metal and nonmetal. To further ascertain whether Fe—N bonds or Ni—N bonds at the interface contribute to the synergistic effect for the catalysis process, EELS and XPS spectra were also conducted to analyze the electronic status of N, Fe, and Ni atoms. In EELS spectra of N K-edge (Figure 2b), two pronounced peaks can be observed on all samples. One at 401–403 eV corresponds to the pyrrolic N and graphitic N, and the other located at ≈410 eV is assigned to the pyridinic N.[14] In contrast to NG and NFO + NG (a physical mixture of NiFe2O4 and NG, without forming metal—N—C bonds), the two characteristic peaks for NFO/NG-2 shifts toward a lower energy loss range. Meanwhile, in EELS spectra of Ni L-edge for NFO/NG-2 (Figure 2c), Ni L1 and L2 EELS edges are detected at a higher energy loss range relative to those in NFO and NFO + NG. Both indicate the formation of strong Ni—N bonding which leads to partial electron transfer from Ni atoms to N atoms. However, no discernible peak shift was observed in Fe L-edge EELS spectra for NFO/NG-2 (Figure S6, Supporting Information), implying that Fe ions seldom bond with the N atoms. In addition, Figure 2d–f show N 1s, Ni 2p, and Fe 2p XPS spectra of all samples, respectively. From N 1s spectra shown in Figure 2f, two prominent peaks at 398.5 and 399.7 eV correspond to pyridinic N and pyrrolic N, respectively, and the other at 401.6 eV is attributed to graphitic N. Compared to those for NG and NFO + NG, an obvious shift (≈0.2 eV) of pyridinic and pyrrolic N 1s XPS peaks toward higher binding energy was observed (Figure 2d), suggesting that the pyridinic and pyrrolic N are probably coordinated with Ni or Fe ions at the hybrid interface.[13,30] However, the fixed peak position of graphitic N 1s XPS spectra signifies no chemical bonds forming between the graphitic N and metal ions. In Ni 2p and Fe 2p XPS spectra, the binding energy of NFO + NG peaks is nearly the same as NFO, due to no formation of new chemical bond. The peaks of the Ni 2p (855.4 and 872.9 eV) are assigned to Ni 2p1/2 and Ni 2p3/2, respectively[31] of NFO/NG-2 and NFO/G shift to higher binding energy by 0.5 and 0.2 eV compared to NFO and NFO + NG (Figure 2e), respectively, which can be ascribed to a deviation of electron cloud from Ni because of the interactions of the chemical bond between Ni ions and NG or G. The Ni (II) 2p3/2 peak of NFO/NG moves 0.3 eV toward positive more than NFO/G, signifying a stronger coupling effect between Ni and pyridinic or pyrrolic N to result in partial electron transfer from Ni to N, thus higher oxidation state of Ni ions in NFO/NG-2. Contrarily, Fe 2p XPS spectra (Figure 2f) display no detectable peak difference on NFO, NFO + NG, NFO/NG-2, and NFO/G, suggesting that Fe is not the main bonding element at the interface. These results are in good agreement with the EELS analysis. Therefore, the evidence reveals that Ni—Pyridinic N—C or Ni—Pyrrolic N—C bonds are
formed between NFO and NG, which would greatly enhance the intrinsic ORR/OER activity, whereas Fe–N–C bond is not.

Subsequently, the reversible oxygen electrocatalytic performance was investigated. Figure 3a shows iR-corrected polarization curves for OER over the samples supported on carbon fiber paper (CFP) in 1.0 M KOH electrolyte. The NFO/NG-2 is endowed with higher OER activity in the alkaline electrolyte than the control catalyst and noble-metal-based commercial catalyst RuO₂. Specifically, the OER overpotential at a current density of 10 mA cm⁻² for the composite catalyst NFO/NG-2 (294 mV) is substantially reduced compared to its constituent species (NG [550 mV] and NFO [400 mV]), and the counterpart without nitrogen doping (NFO/G [330 mV]), demonstrating a significant coupling effect between NFO and NG, which may result from the existence of the Ni–N–C bonding. In addition, NFO/NG-2 displays the optimal OER performance among the hybrid catalysts with different amount of nickel salt and iron salt used (Figure S7, Supporting Information). Tafel slope as an intrinsic property of catalysts has been often adopted to identify the reaction kinetics mechanism.[32] As shown in Figure 3b, NFO/NG-2 possesses the lowest Tafel slope of 97.0 mV dec⁻¹, compared to the control samples and RuO₂, indicating more rapid kinetics for electrocatalytic oxygen evolution. The fastest charge transfer is further confirmed by the electrochemical impedance spectroscopy (EIS) (Figure 3c), which shows that NFO/NG-2 has a smaller semicircular arc, implying much smaller interface electron-transfer resistance (Rct). The NFO/NG-2 catalyst owns lower Rct than NFO/G and other control catalysts (Table S3, Supporting Information), attributed to the enhanced Ni–pyridinic N–C or Ni–pyrrolic N–C bonding at the interface of NFO/NG-2, which afford much faster electron transfer, in turn accelerating the OER kinetics. Furthermore, NFO/NG-2 also manifests high stability as measured by chronoamperometry tests (Figure 3d). The OER current density shows little attenuation less than 2% after 10 h of continuous polarization, which is much better than RuO₂ (Figure S8, Supporting Information) with significant current attenuation.

The ORR electrocatalytic activity was also explored. The ORR onset potential (E onset) and half-wave potential (E 1/2) for NFO/NG-2 are closer to that of NG, NFO, and NFO/G (Figure 4a), suggesting that the Ni–N–C species is beneficial to reduce ORR reaction barriers and facilitate ORR kinetics. Although there is still a gap with 20 wt% Pt/C catalyst, NFO/NG-2, with an E onset of 0.94 V and E 1/2 of 0.85 V, has proved itself to be a promising catalyst for ORR. Moreover, NFO/NG-2 has the optimal ORR performance in all NFO/NG systems (Figure S9, Supporting Information). Meanwhile, NFO/NG-2 also shows the lowest Tafel slope (57.2 mV dec⁻¹), even superior to the commercial Pt/C (73.3 mV dec⁻¹), indicating that the interfacial synergistic effect can effectively promote

![Figure 4](https://www.advancedsciencenews.com/)

**Figure 4.** a) ORR LSV curves of NG, NFO, NFO/NG-2, NFO/G, and Pt/C. b) ORR Tafel plots of NG, NFO, NFO/NG-1, NFO/NG-2, NFO/NG-3, NFO/G, and Pt/C. c) Electron transfer number and percentage of peroxide of NFO/NG-2, NFO/G, and Pt/C at various potentials. d) Chronoamperometric response curves (i–t) of NFO/NG-2.
ORR kinetics. In addition, rotating ring-disk electrode (RRDE) measurements (Figure S10, Supporting Information) were conducted to obtain the electron transfer number \( (n) \) and peroxide yields \( (H_2O_2%) \) (Figure 4c).\(^{[6,12,33]} \) Clearly, NFO/NG-2 presents an electron transfer number \( (n) \) of about 3.7 at 0.5 V, suggesting the synergy effects of interfacial Ni—N—C bonds also facilitate the dominant four-electron ORR pathway with a lower \( H_2O_2 \) yield than NFO/G. In addition, ORR linear sweep voltammetry (LSV) curves of all samples at different rotating speeds (400–2025 rpm) were also recorded (Figure S11, Supporting Information) to calculate the kinetic parameters \( n \) based on Koutecky–Levich (K–L) plots. The slope of K–L plots (Figures S11b, Supporting Information) gives rise to electron transfer number of 3.7 for NFO/NG-2, consistent with the RRDE results. In the chronoamperometric test, NFO/NG-2 also exhibits good long-term stability with the current retaining 83.5% of the initial value after 10 h (Figure 4d), much more stable than Pt/C (78.9%) with severer current degradation (Figure S12, Supporting Information). Moreover, the Raman and XPS spectra for NFO/NG-2 show negligible difference between before and after ORR/OER tests, suggesting the stability of interfacial N–Ni coordination during long-term electrocatalysis.

Generally, the ORR/OER overall overpotential can be quantitatively evaluated by the potential gap between ORR and OER, defined as \( \Delta E = E_{1/2} - E_{10} \), where \( E_{10} \) stands for the potential required to deliver an OER current density of 10 mA cm\(^{-2} \), and \( E_{1/2} \) represents the ORR half-wave potential. An ideal reversible oxygen bifunctional electrocatalyst requires a \( \Delta E \) value as small as possible to achieve an excellent reversible oxygen electrocatalytic process. In the case of NFO/NG-2, \( \Delta E = 0.67 \) V, which is among the lowest values for highly active NiFe-based bifunctional electrocatalysts reported so far (Figure 5a and Table S4, Supporting Information). Finally, to realize practical application, we constructed a rechargeable Zn–air battery with NFO/NG-2 supported on CFP as the air cathode, a zinc plate as the anode, and 6.0 \( \) m KOH solution as the electrolyte. NFO/NG-2 provides a considerable battery open-circuit voltage of 1.74 V, much higher than that for Pt/C + RuO\(_2\) (Figure 5b). As seen in charge and discharge curves shown in Figure 5c, the rechargeable Zn–air battery using NFO/NG-2 as the catalyst shows better charge behavior than that using Pt/C + RuO\(_2\), and although the discharging voltage of the battery using NFO/NG-2 is lower than Pt/C + RuO\(_2\) at the beginning, the advantage of NFO/NG-2 gradually emerges with the increase in the current. And, the peak power density can reach 173.6 mW cm\(^{-2} \), outperforming that for Pt/C + RuO\(_2\) (134 mW cm\(^{-2} \)), due to the superior bifunctional capability of NFO/NG-2. Furthermore, the discharge specific capacity of NFO/NG-2 achieves 513.6 mAh g\(^{-1} \) at a discharge current density of 10 mA cm\(^{-2} \) (Figure 5d), by normalized to the consumed mass of Zn. When cyclically discharge and charge at 5 mA cm\(^{-2} \) for more than 65 cycles (Figure 5e,f ), nearly no increase in overpotential was observed, with the discharge/charge cycle stability superior to Pt/C + RuO\(_2\) reported before.\(^{[34]} \) In terms of these results, the NFO/NG-2 hybrid demonstrates excellent rechargeability performance as a bifunctional oxygen electrocatalyst in the Zn–air batteries.

**Figure 5.** a) Comparison of OER and ORR bifunctional activities of NFO/NG-2 with representative NiFe-based electrocatalysts in literatures. b) Open-circuit voltage plot of primary zinc–air batteries assembled with NFO/NG-2 and a mixture of Pt/C + RuO\(_2\). c) Galvanodynamic charge/discharge profiles and power density curves of NFO/NG-2 and Pt/C + RuO\(_2\). d) Specific capacity of NFO/NG-2 catalyzed Zn–air batteries after mass normalization at a current density of 10 mA cm\(^{-2} \). e) Galvanostatic charge/discharge cyclic curves of the Zn–air batteries at 5 mA cm\(^{-2} \) (a duration of 1200 s per cycle) in 6.0 \( \) m KOH. f) The first and last cycles of galvanostatic charge/discharge cyclic curves of NFO/NG-2 at 5 mA cm\(^{-2} \).
3. Conclusions

In conclusion, NFO/NG nanocomposites have been developed based on a two-step hydrothermal method to in situ load NiFe$_2$O$_4$ NPs onto NG. It is found that the interfacial Ni(−pyridinic or pyrrolic)−C bonding as the active sites greatly boosted the bifunctional ORR/OER intrinsic activities of NFO/NG and achieved a low overpotential for reversible oxygen electrocatalysis, surpassing most of the efficient NiFe-based catalysts reported so far. When used in rechargeable Zn-air batteries as the oxygen electrode, NFO/NG-2 also exhibited excellent charge/discharge performance and long-term stability. This work provides a new understanding for the rational design of low-cost and efficient composite bifunctional electrocatalysts for renewable energy storage and conversion.

4. Experimental Section

Preparation of NG: GOs were synthesized from graphite powder (Sigma-Aldrich) via the modified Hummer's method.[13] To prepare the NG, a 15 mg GO was dispersed in 30 mL of deionized water, 2 mL NH$_3$·H$_2$O (Macklin, AR, 25–28%) was added, and then the dispersion was heated at 180 °C for 12 h in a 50 mL autoclave. The products were washed with deionized (DI) water for several times and dried by lyophilization.

Preparation of NFO/NG-x: FeCl$_2$·4H$_2$O (Macklin, AR) and Ni(CH$_3$COO)$_2$·4H$_2$O (Adamas, 98%) were added at the cation molar ratio (Fe$^{2+}$:Ni$^{2+}$:4H$_2$O) of 2:1 into the prepared NG dispersion. In the experiment, the samples with 25, 45, and 65 mg of iron salt added were prepared for comparison, which were denoted as NFO/NG-1, NFO/NG-2, and NFO/NG-3, respectively. The mixture was dispersed by ultrasonic and heated at 180 °C for 3 h to load NiFe$_2$O$_4$ NPs on the NG. After cooling down to room temperature, the resulting NFO/NG samples were washed repeatedly with water and collected by lyophilization.

Preparation of NFO/C and NFO: A 15 mg GO was dispersed and heated at 180°C for 12 h in the autoclave without the addition of NH$_3$·H$_2$O to produce reduced graphene (G). After that, appropriate KOH was dropped to regulate the pH of the system to about 11 to create a suitable basic environment for the formation of NFO. Then, 25 mg FeCl$_2$·4H$_2$O and 28.2 mg Ni(CH$_3$COO)$_2$·4H$_2$O were added and mixed with G dispersion, followed by 3 h heating at 180°C. The cooled samples were washed and dried by lyophilization. Individual NFO was prepared as shown earlier without G.

Materials Characterization: The morphology and EELS of the catalyst samples was acquired using an S-4800 field emission scanning electron microscopy (FESEM) from Hitachi, Ltd and a Tecnai G2 F20 HRTEM equipped with a Schottky emission electron gun. To understand the crystal structure, XRD was conducted on a Bruker D8 advance XRD diffractometer with Cu Kα as the light source. Fourier transform infrared (FT-IR) spectra were obtained by using a BRUKER TEMSOR 27 FT–IR spectrometer with resolution of 1–0.4 cm$^{-1}$. XPS measurements were conducted using a Thermo Scientific K-Alpha XPS system with Al Kα microfocused monochromator. Raman spectra were recorded using an inVia Reflex Raman spectrometer produced by Renishaw.

Electrocatalytic Performance Evaluation: All the electrochemical tests were conducted using three-electrode system including a carbon rod counter electrode, a saturated calomel reference electrode, and a working electrode with O$_2$-saturated 1.0 M KOH as the electrolyte. ORR experiments were conducted on a wave drive 20 workstation (Pine Research Instruments, USA), using the rotating disk electrode and the ring disk electrode as working electrodes with an area of 0.196 and 0.246 cm$^2$, respectively. For testing OER performance, a CH1600 electrochemical workstation was used with a hydrophilic carbon fiber (area: 0.15 cm$^2$) as the working electrode. The loading density of the catalysts was fixed at 0.4 mg cm$^{-2}$. The ink was prepared by dispersing 1 mg target catalyst in 200 μL of DI water, followed by adding 10 μL of Nafion solution (5 wt%), and then sustainably ultrasonicated to obtain a well-dispersed catalyst ink.

Detailed electrochemistry tests included cyclic voltammetry (CV), LSV, EIS, RRDE experiment, and chronoamperometry (i-t curve). CV curves were first performed to stabilize the working electrode at scanning rate of 50 mV s$^{-1}$. Then, LSVs curves were measured at a scan rate of 5 mV s$^{-1}$. Specially, for ORR LSV testing, the electrode was rotating at 1600 rpm to achieve a steady-state mass transfer around the surface of electrode in liquid. EIS measurements were conducted at 1.55 V versus RHE within a frequency range of 0.1–10$^6$ Hz.

The electron transfer number (n) was determined by RRDE experiment and K–L equation. The electron transfer number and H$_2$O$_2$% could be calculated based on Equation (1) and (2)

\[ n = \frac{4N_j}{N_j + j_r} \]  
\[ H_2O_2\% = \frac{2j_d}{N_j + j_d} \times 100\% \]

where $N_j$, $j_d$, and $j_r$ stand for the H$_2$O$_2$ collection coefficient (0.37) of the ring, disk current, and ring current, respectively.

In contrast, the K–L equation is shown as Equation (3)

\[ J^{-1} = J_d^{-1} + J_r^{-1} = 0.62nFACS_0D_0^{3/2}ν^{1/2}ω^{-1/2} + J_r^{-1} \]

where $J$, $J_d$, and $J_r$ refer to the measured current, diffusion-limiting currents, and kinetic current density, respectively. $F$, $C$, $S$, $D$, $ν$, and $ω$ represent the Faraday constant (96 485 C mol$^{-1}$), area of the electrode (0.196 cm$^2$), saturated O$_2$ concentration (1.21 $×$ 10$^{-5}$ mol cm$^{-3}$), diffusion coefficient of O$_2$ in electrolyte at room temperature (1.86 $×$ 10$^{-5}$ cm$^2$ s$^{-1}$), kinetic viscosity of electrolyte (0.01 cm$^2$ s$^{-1}$), and the rotation rate of the electrode in rpm. The working electrode was scanned at a rate of 5 mV s$^{-1}$ with changing rotating speed from 400 to 2025 rpm.

Zn–Air Battery Assembly: The Zn–air battery was assembled using a zinc plate as the anode, a NG/NFO-2 or Pt/C + RuO$_2$ (a mixture of commercial 20% Pt/C and RuO$_2$ with a mass ratio of 1:1) sample-loaded carbon fiber as the air cathode, and 6 M KOH with O$_2$ saturated as the electrolyte. The CH1 600 E electrochemistry workstation was adopted to test the polarization curves (5 mV s$^{-1}$) and cycling charge/discharge performance (600 s charge and 600 s discharge with a current density of 5 mA cm$^{-2}$).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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bifunctional electrocatalysts, nitrogen-doped graphene, spinel oxides, synergistic effects, zinc-air batteries

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[1] Q. Wang, Y. Ji, Y. Lei, Y. Wang, Y. Wang, Y. Li, S. Wang, ACS Energy Lett. 2018, 3, 1183.
[2] V. R. Stamenkovic, D. Strmcnik, P. P. Lopes, N. M. Markovic, Nat. Mater. 2016, 15, 57.
[3] X. F. Lu, Y. Chen, S. Wang, S. Gao, X. W. D. Lou, Adv. Mater. 2019, 31, e1902339.
[4] Z. L. Wang, D. Xu, J. J. Xu, X. B. Zhang, Chem. Soc. Rev. 2014, 43, 7746.
[5] C. Li, M. Wu, R. Liu, Appl. Catal., B 2019, 244, 150.
[6] Y. Tong, P. Chen, T. Zhou, K. Xu, W. Chu, C. Wu, Y. Xie, Angew. Chem., Int. Ed. 2017, 56, 7121.
[7] K. Li, R. Zhang, R. Gao, G.-Q. Shen, L. Pan, Y. Yao, K. Yu, X. Zhang, J.-J. Zou, Appl. Catal., B 2019, 244, 536.
[8] X. T. Wang, T. Ouyang, L. Wang, J. H. Zhong, Z. Q. Liu, Angew. Chem., Int. Ed. 2020, 59, 6492.
[9] S. Peng, F. Gong, L. Li, D. Yu, D. Ji, T. Zhang, Z. Hu, Z. Zhang, S. Chou, Y. Du, S. Ramakrishna, J. Am. Chem. Soc. 2018, 140, 13644.
[10] M. Retuerto, L. Pascual, F. Calle-Vallejo, P. Ferrer, D. Gianolio, A. G. Pereira, A. Garcia, J. Torrero, M. T. Fernández-Díaz, P. Bencok, M. A. Peña, J. L. G. Fierro, S. Rojas, Nat. Commun. 2019, 10, 2041.
[11] L. Kuai, E. Kan, W. Cao, M. Huttula, S. Ollikkala, T. Ahopelto, A.-P. Honkanen, S. Huotari, W. Wang, B. Geng, Nano Energy 2018, 43, 81.
[12] H. Miao, Z. Wang, Q. Wang, S. Sun, Y. Xue, F. Wang, J. Zhao, Z. Liu, J. Yuan, Energy 2018, 154, 561.
[13] X. Cui, S. Yang, X. Yan, J. Leng, S. Shuang, P. M. Ajayan, Z. Zhang, Adv. Funct. Mater. 2016, 26, 5708.
[14] X. R. Wang, J. Y. Liu, Z. W. Liu, W. C. Wang, J. Luo, X. P. Han, X. W. Du, S. Z. Qiao, J. Yang, Adv. Mater. 2018, 30, e1800005.
[15] Y. P. Zhu, C. Guo, Y. Zheng, S. Z. Qiao, Acc. Chem. Res. 2017, 50, 915.
[16] Y. Wang, T. Hu, Y. Qiao, Y. Chen, L. Zhang, ChemComm 2018, 54, 12746.
[17] J. Li, Z. Zhou, K. Liu, F. Li, Z. Meng, Y. Tang, H. Wang, J. Power Sources 2017, 343, 30.
[18] S. Chen, S.-Z. Qiao, ACS Nano 2013, 7, 10190.
[19] J. Guo, Y. Cheng, Z. Xiang, ACS Sustain. Chem. Eng. 2017, 5, 7871.
[20] N. Xu, Y. Zhang, T. Zhang, Y. Liu, J. Qiao, Nano Energy 2019, 57, 176.
[21] P. Li, R. Ma, Y. Zhou, Y. Chen, Q. Liu, G. Peng, Z. Liang, J. Wang, RSC Adv. 2015, 5, 73834.
[22] X. Zhang, X. Zhang, X.-G. Wang, Z. Xie, Z. Zhou, J. Mater. Chem. A 2016, 4, 9390.
[23] M. Fei, H. Shi, J. Zhao, N. Kang, W. He, H. Li, F. Yang, ChemCatChem 2018, 10, 5174.
[24] P. Sahoo, J.-B. Tan, Z.-M. Zhang, S. K. Singh, T.-B. Lu, ChemCatChem 2018, 10, 1075.
[25] B. Li, S. Chen, J. Tian, M. Gong, H. Xu, L. Song, Nano Res. 2017, 10, 3629.
[26] M. Kiani, J. Zhang, J. Fan, H. Yang, G. Wang, J. Chen, R. Wang, Mater. Express 2017, 7, 261.
[27] X.-D. Yang, Y. Zheng, J. Yang, W. Shi, J.-H. Zhong, C. Zhang, X. Zhang, Y.-H. Hong, X.-X. Peng, Z.-Y. Zhou, S.-G. Sun, ACS Catal. 2016, 7, 139.
[28] P. Li, R. Ma, Y. Zhou, Y. Chen, Z. Zhou, G. Liu, Q. Liu, G. Peng, J. Wang, RSC Adv. 2015, 5, 44476.
[29] F. N. Smith, W. Um, C. D. Taylor, D. S. Kim, M. J. Schweiger, A. A. Kruger, Environ. Sci. Technol. 2016, 50, 5216.
[30] G. Yang, W. Choi, X. Pu, C. Yu, Energy Environ. Sci. 2015, 8, 1799.
[31] Y. Cheng, S. Dou, J. P. Veder, S. Wang, M. Saunders, S. P. Jiang, ACS Appl. Mater. Interfaces 2017, 9, 8121.
[32] T. Shimagawa, A. T. Garcia-Esparza, K. Takanabe, Sci. Rep. 2015, 5, 13801.
[33] T. Feng, X. R. Zhao, C.-K. Dong, H. Liu, X. W. Du, J. Yang, Nanoscale 2018, 10, 22140.
[34] J. Qin, Z. Liu, D. Wu, J. Yang, Appl. Catal., B 2020, 278, 119300.
[35] Y. Zheng, Y. Jiao, L. Ge, M. Jaroniec, S. Z. Qiao, Angew. Chem., Int. Ed. 2013, 52, 3110.