

Article

Dual-MOFs-Derived Fe and Mn Species Anchored on Bamboo-like Carbon Nanotubes for Efficient Oxygen Reduction as Electrocatalysts

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Abstract: The development of efficient non-precious metal electrocatalysts for oxygen reduction reaction (ORR) to replace Pt-based methods is crucial for the applications of fuel cells and metal–air batteries. In this study, a bimetallic M–N–C catalyst with highly dispersed dual-atom Fe/Mn–Nx sites immobilized on N-doped bamboo-like carbon nanotubes is prepared by the ball-milling and calcination of dual-MOFs as precursors. The rich N-doping and abundant M–Nx species contribute to the excellent intrinsic ORR activity of the catalyst, and the unique bamboo-like nanotubes morphology is beneficial for facilitating electron transfer and mass transport while simultaneously enabling the exposure of active sites. As expected, the optimized Z–Fe1Mn1–NC catalyst exhibits efficient ORR activity with a half-wave potential ($E_{1/2}$) of 0.80 V in acid and 0.82 V in alkaline, and a higher electrochemical stability with the current density maintained at 91% (in 0.1 M KOH) and 86% (0.1 M HClO₄) of its initial current density after 15 h of a chronoamperometric test at a high potential of 0.7 V. When further applied to Zn–air batteries, the catalyst also delivers a high open-circuit voltage, large power density, and outstanding rate performance. This work provides a novel means of designing dual metal M–Nx site-based M–N–C catalysts for ORR sustainable energy applications.

Keywords: electrocatalysts; oxygen reduction reaction; carbon nanotubes; dual-atom



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1. Introduction

The oxygen reduction reaction (ORR) is an essential half-reaction shared by renewable energy storage and conversion devices, such as fuel cells and metal–air batteries [1–5]. Platinum-group metal (PGM) catalysts have the best catalytic activity for ORR. However, their actual large-scale applications are limited by their high cost and poor durability. Therefore, the development of efficient non-precious-metal-based catalysts (NPMCs) is significant and important in the clean energy era [6–8].

Among all the available NPMCs, transition metal-nitrogen-doped carbon (M–N–C, M = Fe, Co, Mn, Ni and Cu) is regarded as one of the most promising substitutes for the PGMs for ORR [9–12]. Of specific interest are highly dispersed M–N–C catalysts, which possess maximum atomic utilization of active sites [13]. Over the past few years, atomically dispersed Fe-based catalysts have attracted extensive interest [14,15]. For instance, significant breakthroughs in ORR performance using non-macrocyclic precursors to prepare the Fe–Nx–C catalysts were reported by Li et al. [16]. But the Fenton-like reaction involving the Fe sites seriously affects the catalytic activity and stability of Fe single-atom catalysts. The addition of second metal elements (such as Co, Ni, Mn, Cu, Zn, etc.) into the Fe–Nx structure to boost the ORR activity is a common topic of investigation [17–21].

Theoretic and experimental studies have shown that the synergistic effect of bimetallic active sites can reduce the potential barrier of O–O breaking, resulting in higher ORR activity [22,23]. For example, Li et al. proposed a post-synthesis encapsulation strategy by pyrolyzing FeCl₃-encapsulated Zn/Co bimetallic ZIF-8 [24]. The resulting (Fe, Co)/N-C catalyst showed a comparable ORR activity with that of commercial Pt/C in an acid medium. Recent reports indicate that the doping of Mn–Nx species can adjust the electronic spin configuration in Fe sites, resulting in an enhanced ORR activity [25–28]. Atanassov et al. prepared a series of FeCo-, FeCu-, FeNi- and FeMn-N/C bimetallic catalysts by a sacrificial support method [29]. The results showed that all catalysts had similar surface area and pore structure, but only the FeMn-N/C catalyst showed higher ORR activity than the Fe-N-C catalyst in acidic medium. Moreover, the M/N/C catalysts with a unique carbon structure are also important for the enhancement of ORR performance. Many kinds of 1D to 3D carbon supports, such as carbon nanofibers/nanotubes, graphene, MXenes, and MOFs/biomass-derived hierarchically porous carbon, have been developed for use in enhanced ORR catalysts [30–33]. Among them, it has been reported that use of carbon nanotubes with nitrogen doping is beneficial for the formation of cross-linked conductive networks, stabilizing the metal atoms and restraining their aggregation [34]. Specifically, the carbon nanotubes with a bamboo-like structure exhibit more defects and specific areas, which enables the introduction of abundant M–Nx moieties [35–37]. However, use of bamboo-like carbon nanotubes with dual-metal atomically dispersed metal sites for efficient M/N/C catalysts is rarely reported.

In this work, highly dispersed Fe and Mn atoms anchored on N-doped bamboo-like carbon nanotubes have been prepared by employing ball-milled dual-MOFs as precursor. Here, ZIF-8 and Fe/Mn-MOFs are serving as C/N and metal source, respectively. After carefully regulating the proportion of the precursors and the pyrolysis temperature, the prepared Z-Fe1Mn1-NC catalyst delivers not only efficient ORR activity, but also increasingly excellent stability in both acidic and alkaline media, making it a strong contender for applications in a Zn–air battery.

2. Results and Discussion

The fabrication process of the Z-Fe1Mn1-NC is illustrated in Figure 1. ZIF-8 is employed as a carbon and nitrogen source. Conventionally, the M-N-C catalysts are synthesized by annealing the mixture of ZIF-8 and inorganic metal source (such as FeCl₃, phenanthroline-Fe), which usually yields a substantial agglomeration of metal particles. In this study, a dual metal containing Fe/Mn-MOF, in which metal ions are separated by organic ligands, is used to replace the inorganic iron source. Then, the synthesized ZIF-8 and Fe/Mn-MOF are mixed by ball milling, which further guarantees the uniform distribution of metal in the C/N precursor. After pyrolyzing the ball-milled mixture at an appropriate temperature and acid leaching, the prepared catalyst shows a structure of bamboo-like carbon nanotubes with highly dispersed Fe and Mn active sites.

The morphologies of the prepared Z-Fe1Mn1-NC catalyst were examined by SEM and TEM. The original ZIF-8 crystals exhibited rhombic dodecahedral morphology with a particle size of about 600 nm (Figure S1a,b). The Fe/Mn-MOF crystals exhibited rhombic vertebra morphology (Figure S1c,d). The XRD characterization in Figure S2 further verifies the crystal structure of the ZIF-8 and the Fe/Mn-MOF precursor. After ball milling and the pyrolysis process, the samples did not maintain their previous morphologies. The SEM image (Figure 2a) shows that the resultant Z-Fe1Mn1-NC catalyst is composed of bamboo-like carbon nanotubes with a length of several micrometers. The TEM (Figure 2b) further characterizes the interconnected hollow bamboo-like nanostructures of Z-Fe1Mn1-NC, which are beneficial for the mass transport of ORR. Additionally, a small number of black nanoparticles in the TEM image mainly correspond to aggregates of metal nanoparticles, which are inevitably formed during the growth of carbon nanotubes. This is further demonstrated by the HRTEM images and inverse fast Fourier transform (IFFT) patterns of Z-Fe1Mn1-NC in Figures S3 and S4. The smaller particles belong to metallic Fe, while

the larger particles are associated with FeMnO_3 , and they are all encased in the highly crystalline graphitic carbon of the bamboo-like carbon nanotubes. The high-resolution TEM image (HRTEM) in Figure 2c reveals that the diameter of these carbon nanotubes is about 40 nm. Moreover, the clear lattice fringes demonstrate lattice spacing of about 0.336 nm, which is calculated from inverse fast Fourier transform (IFFT) patterns, a result similar to the standard (002) plane of graphite-2H (PDF#41-1487). This result proves the crystalline structure of the carbon nanotubes in Z-Fe1Mn1-NC, which could accelerate the speed of electron transfer during ORR. The corresponding EDS mapping shows that iron, manganese and nitrogen are distributed homogeneously across the range of the bamboo-like carbon nanotubes.

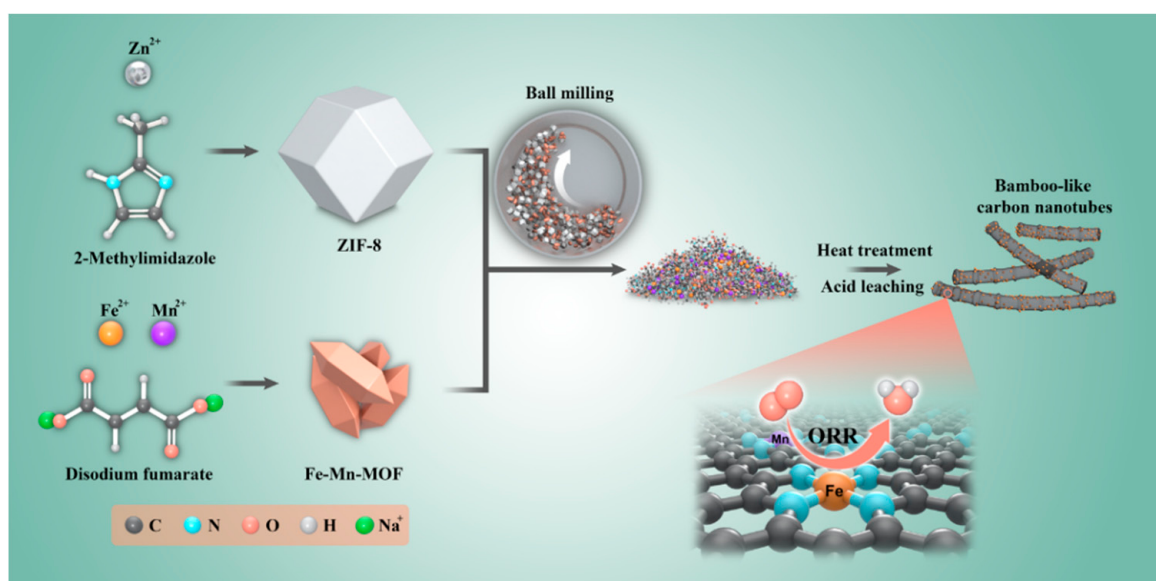


Figure 1. Schematic diagram of the fabrication process of the Z-Fe1Mn1-NC catalyst.

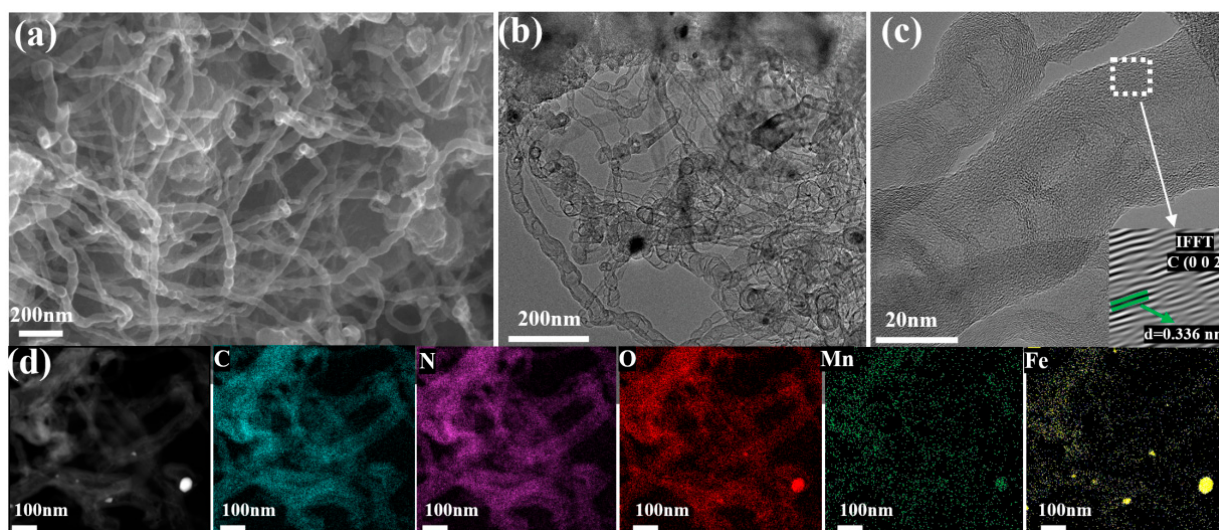


Figure 2. (a) SEM image, (b) TEM image, (c) high-resolution TEM image (the inset is an IFFT image of the marked region), and (d) EDS mapping images of Z-Fe1Mn1-NC.

The physical phases of the catalysts were investigated by XRD. The controlled NC, Fe-C, Mn-C and FeMn-C are the products of the direct pyrolysis of ZIF-8, Fe-MOF, Mn-MOF or FeMn-MOF alone, respectively. As displayed in Figure 3a, there are two broad diffraction peaks, one in the range of $20\sim 30^\circ$ and another at $40\sim 50^\circ$, for NC, which is

assigned to the (002) and (101) planes of graphitic carbon in the amorphous structure. The XRD patterns of Mn-C are similar to those of NC. These results are in agreement with the TEM images of NC and Mn-C (Figures S5 and S6), in which no graphitic lattice fringes are observed. Aside from the broad peak around 21° , a sharp diffraction peak at $\sim 26.3^\circ$ in the XRD patterns of Fe-C and FeMn-C can be assigned to the (002) lattice plane of graphite-2H (PDF#41-1487), implying that the amorphous and highly graphitized carbon coexisted in two samples, which is further proved by the TEM results in Figure S7. This result indicates that Fe serves as a better catalyst for graphitization under the pyrolysis conditions, when compared with Mn. For Z-Fe1Mn1-NC, the broad characteristic peak in the range of $20\sim 30^\circ$ confirms its low graphitization degree. And the metallic Fe/Mn or Fe/Mn carbides/nitrides/oxides/in Z-Fe1Mn1-NC do not display any peaks, which is probably due to their low content and small size. In addition, no carbon nanotubes were observed in the TEM images of control NC, Fe-C and Mn-C samples (Figures S5–S7), confirming the essential role of ball-milled dual-MOF in the formation of the morphology of the carbon nanotubes. The carbon structure of the catalysts was further investigated by Raman spectroscopy. The peak D ($\sim 1331\text{ cm}^{-1}$) and G ($\sim 1593\text{ cm}^{-1}$) were mainly caused by lattice distortions of the sp^3 carbon and the highly oriented hexagonal graphitic lattice of sp^2 carbon, respectively. For the catalysts derived from the ball-milled single MOFs' precursor, the intensity ratios (I_D/I_G) of NC, Fe-C, Mn-C and FeMn-C were 1.07, 1.04, 1.09, and 1.04, respectively. The lower I_D/I_G values of Fe-C and FeMn-C point to a higher graphitization degree, which is inconsistent with the results of the XRD and TEM [22]. Notably, the Z-Fe1Mn1-NC displays the highest I_D/I_G among all samples, indicating the existence of more defects and the doping degree in the graphitic lattice, which is crucial for improving the ORR performance. As the specific surface areas and porous structures of the catalyst also play an important role in enhancing the ORR's catalytic activities, the N_2 adsorption/desorption isotherms measurements were used. As shown in Figure 3c, the rapid absorption of N_2 at a low relative pressure region ($0 < P/P_0 < 0.05$) and the existence of obvious hysteresis loops at a higher relative pressure region ($P/P_0 > 0.45$) in the adsorption-desorption curves of all the samples demonstrate their type IV isotherms, reflecting the presence of a hierarchically porous structure. The BET specific surface areas are calculated to be 346.6, 535.3, 713.6, 673.4 and $802.2\text{ m}^2\text{ g}^{-1}$ for NC, Fe-C, Mn-C, FeMn-C and Z-Fe1Mn1-NC, respectively (Table S1). In addition, the pore width distributions analysis in Figure 3d confirms the coexistence of microporous and meso- and macroporous structures in all the catalysts. Note that the dual-MOF derived Z-Fe1Mn1-NC exhibits the highest specific surface area and pore volume, which is beneficial for providing more active sites [38,39]. And Z-Fe1Mn1-NC also reveals a relatively lower micro-porosity of 71.2%, which is helpful for promoting the mass transport during the ORR process.

The surface element information of the catalysts was revealed by XPS analysis. The atomic compositions are listed in Table S2. Due to the nitrogen-rich ZIF-8 precursor, the total N content of NC and Z-Fe1Mn1-NC are as high as 15.28 and 13.03 at. %, respectively. In the absence of a nitrogen source, no signs of N are found in Fe-C, and the trace amounts of N content of Mn-C and FeMn-C are mainly surface adsorption of the carbon supports. In addition, the presence of metal was not observed in any samples of Fe-C Mn-C or FeMn-C. As for the catalyst derived from ball-milled ZIF-8 and Fe/Mn-MOF, XPS confirms the successful introduction of Fe, Mn, and N within Z-Fe1Mn1-NC, in accord with the TEM mapping images. Further elemental analysis with inductively coupled plasma mass spectrometry (ICP-MS) reveals that the loading contents of metals for Z-Fe1Mn1-NC are 1.86 (Fe) and 0.31 (Mn) wt%, respectively. The high-resolution XPS spectra for different elements are further revealed in Figure 4 and Tables S3–S6. Figure 4a shows that the C 1s XPS spectra for the samples are deconvoluted into C-C/C=C ($\sim 284.8\text{ eV}$), C-N/C-O ($\sim 286.1\text{ eV}$), O-C=O ($\sim 288.4\text{ eV}$), and C 1s plasmon ($\sim 291.2\text{ eV}$) [40]. As shown in Figure 4b, the high-resolution N 1s spectra of NC and Z-Fe1Mn1-NC display six peaks, at $\sim 398.7\text{ eV}$, $\sim 399.8\text{ eV}$, $\sim 400.4\text{ eV}$, $\sim 401.3\text{ eV}$, $\sim 402\text{--}403\text{ eV}$, and $\sim 405\text{ eV}$, which corresponds to pyridinic-N, M-Nx, pyrrolic-N, graphitic-N and oxidized-N (N-O1 and N-O2), respectively [41].

According to the previous reports, the pyridinic N can coordinate metal atoms for the construction of the M–Nx configuration. The concentration of pyridinic-N and M–Nx for Z-Fe1Mn1-NC reach 42.51% and 24.63%, respectively, which is beneficial for improving the ORR performance [42]. The Fe 2p high-resolution spectra of Z-Fe1Mn1-NC show the pair of Fe 2p_{3/2} and Fe 2p_{1/2}, where the peaks at ~708.6 eV, ~709.8 eV and ~711.5 eV are assigned to Fe–Nx, Fe²⁺ and Fe³⁺, respectively. The two main peaks at ~640.9 and ~653.3 eV in the Mn 2p XPS spectrum of Z-Fe1Mn1-NC are attributed to Mn²⁺ 2p_{3/2} and Mn²⁺ 2p_{1/2}. These results proved that Fe and Mn are coordinated with N, suggesting that these elements are successfully doped into the bamboo-like carbon nanotubes.

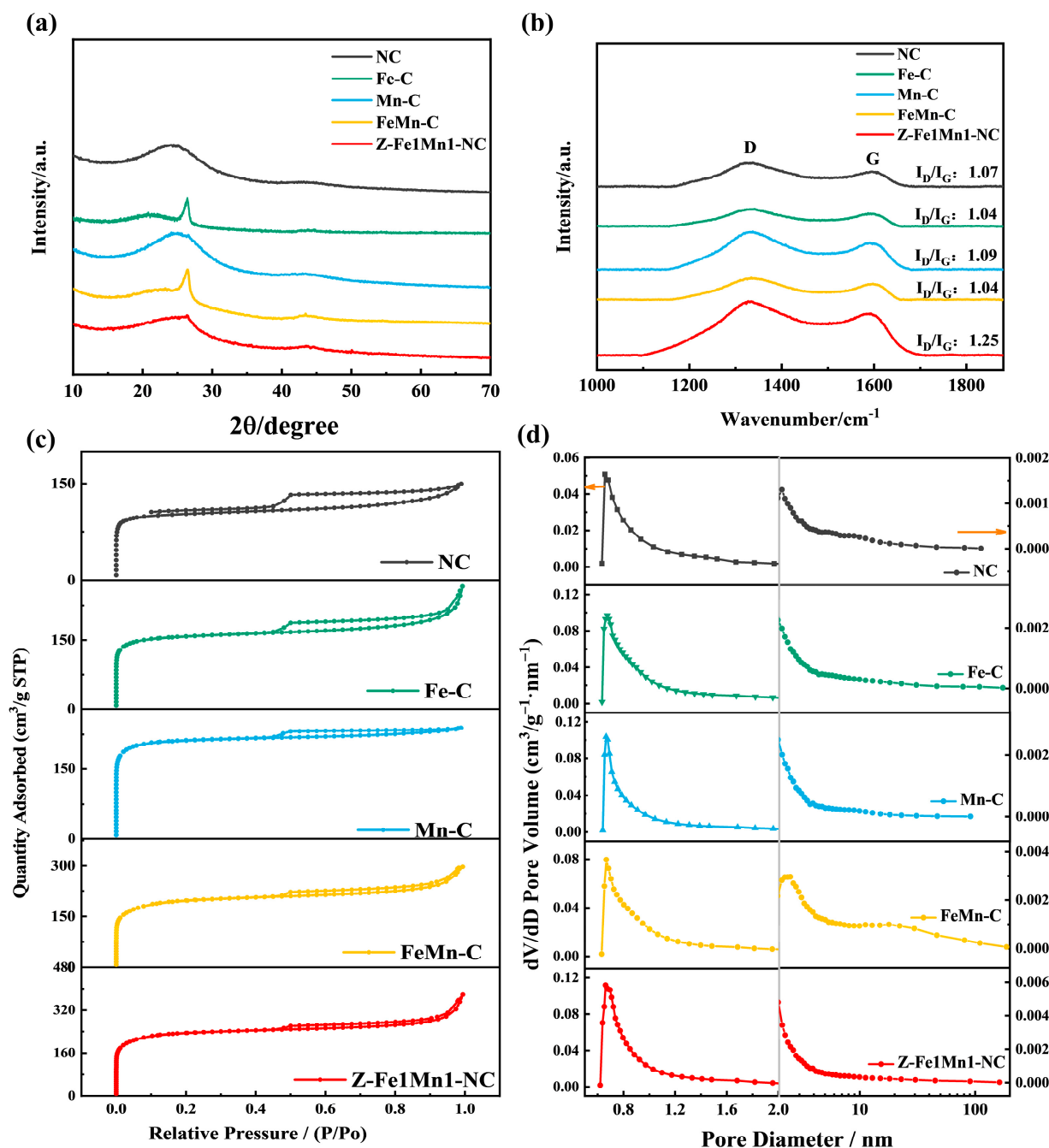


Figure 3. (a) XRD patterns, (b) Raman spectra, (c) N₂-adsorption/desorption isotherm and (d) pore size distribution of NC, Fe-C, Mn-C, FeMn-C, and Z-Fe1Mn1-NC.

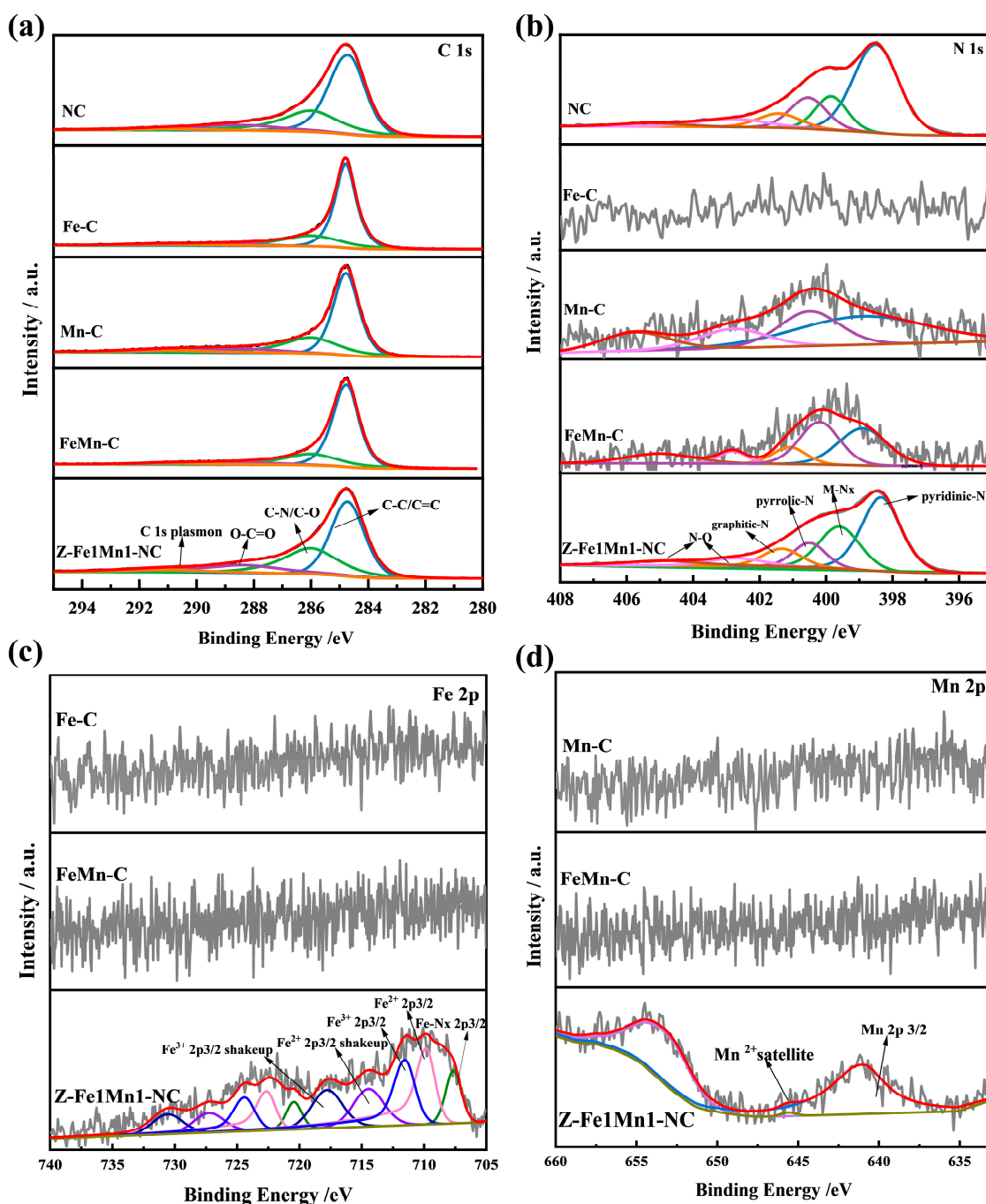


Figure 4. High-resolution XPS spectra of (a) C 1s and (b) N 1s for NC, Fe-C, Mn-C, FeMn-C, and Z-Fe1Mn1-NC. (c) High-resolution XPS spectra of Fe 2p for Fe-C, FeMn-C, and Z-Fe1Mn1-NC. (d) High-resolution XPS spectra of Mn 2p for Mn-C, FeMn-C, and Z-Fe1Mn1-NC.

The catalytic ORR performance of the prepared samples was initially evaluated by a rotating disk electrode (RDE) method in 0.1 M KOH. As seen in Figure 5a, the linear sweep voltammetry (LSV) curve (under a rotational speed of 1600 rpm) of Z-Fe1Mn1-NC shows superior ORR properties, with an onset potential (E_0) of 1.02 V, half-wave potential ($E_{1/2}$) of 0.82 V, and diffusion limited current density (J_L) of 5.42 mA cm⁻². It is also higher than those of NC ($E_{1/2}$ = 0.61 V, J_L = 3.02 mA cm⁻²), Fe-C ($E_{1/2}$ = 0.80 V, J_L = 5.04 mA cm⁻²), Mn-C ($E_{1/2}$ = 0.81 V, J_L = 4.52 mA cm⁻²) and FeMn-C ($E_{1/2}$ = 0.74 V, J_L = 4.76 mA cm⁻²) (Figure 5b). Moreover, the Z-Fe1Mn1-NC exhibits slightly lower $E_{1/2}$ and higher J_L compared to a commercial Pt/C catalyst ($E_{1/2}$ = 0.87 V, J_L = 5.68 mA cm⁻²). Additionally, Z-

Fe1Mn1-NC also displays excellent ORR kinetics, as evidenced by having the smallest Tafel slope, 68.3 mV dec^{-1} , comparable to those of NC (84.0 mV dec^{-1}), Fe-C (77.4 mV dec^{-1}), Mn-C (74.5 mV dec^{-1}), FeMn-C (87.5 mV dec^{-1}), and Pt/C (73.4 mV dec^{-1}) (Figure 5c). To give insight into the reaction routing of Z-Fe1Mn1-NC, the LSV measurements at different rotation speeds of 400–2500 rpm were performed (Figure 5d). The corresponding K-L plots exhibit excellent linearity at different potentials, implying a first-order ORR reaction kinetic of Z-Fe1Mn1-NC. And the electron transfer number is calculated to be 3.94, further confirming a direct four-electron pathway. Moreover, the effect of pyrolysis temperature on ORR performance was investigated. As displayed in Figures 5e and S6, the catalyst prepared at $T = 750^\circ\text{C}$ shows the lowest ORR activity, with a $E_{1/2}$ of 0.76 V and Tafel slope of 88.0 mV dec^{-1} . As the temperature was elevated to 850°C , the Z-Fe1Mn1-NC possessed a significantly enhanced activity. Along with the rise of the pyrolysis temperature to 950°C and 1050°C , the ORR performance was gradually decreased. These results indicating that 850°C is the optimal temperature. To verify the synergistic catalytic effect of Fe and Mn, the ORR performance of comparison samples derived from ball-milled ZIF-8 and Fe or Mn-MOF is further evaluated. As analyzed from Figure 5f, Z-Fe1Mn0-NC and Z-Fe0Mn1-NC demonstrate 10 mV more negative positive $E_{1/2}$ than Z-Fe1Mn1-NC. And the Tafel slope of Z-Fe1Mn0-NC (70.1 mV dec^{-1}) and Z-Fe0Mn1-NC (81.4 mV dec^{-1}) are larger than that of Z-Fe1Mn1-NC, which confirms the fast ORR kinetics of the bimetallic catalyst (Figure S8). Then, the same analytical method was applied to evaluate the acidic ORR activity of the catalysts. As shown in Figure 6a,b, the $E_{1/2}$ and J_L of Z-Fe1Mn1-NC were 0.80 V and 5.1 mA cm^{-2} , respectively, which demonstrates superior activity compared to NC, Fe-C, Mn-C, and FeMn-C. The ORR activity of Z-Fe1Mn1-NC is slightly inferior to that of Pt/C in acidic media, with a 50 mV difference in $E_{1/2}$. Remarkably, the Z-Fe1Mn1-NC displays the same limited current density, as well as the Pt/C electrode. Additionally, the Z-Fe1Mn1-NC delivers the smallest Tafel slope of 82.6 mV dec^{-1} , further confirming its ORR kinetics (Figure 6c). And the number of transferred electrons attained from the K-L equation for Z-Fe1Mn1-NC is determined to be 4.02, illustrating its ultrahigh selectivity for $4e^-$ ORR pathway in acid (Figure 6d). Moreover, the influence of pyrolysis temperature and bimetal MOF on the ORR performance reveals a similar law with the alkaline condition (Figures 6e,f and S9).

The durability of Z-Fe1Mn1-NC was examined by chronoamperometry test, with a speed of 900 rpm at 0.7 V for 15 h. Pt/C was tested under same conditions for comparison. As observed in Figure 7a, the Z-Fe1Mn1-NC catalyst retained 91% of its initial current density, which is much higher than that of commercial Pt/C (63%), demonstrating the excellent stability in 0.1 M KOH. It is well known that most M-N-C catalysts suffer from severe degradation under harsh acidic media. Based on this consideration, we further studied the durability of Z-Fe1Mn1-NC in 0.1 M HClO_4 (Figure 7b). Z-Fe1Mn1-NC maintains 86% of the initial current value after continuous test, whereas the Pt/C catalyst only retains 64%. The above results demonstrate the excellent stability of Z-Fe1Mn1-NC, both in alkaline and acid conditions. In comparison with previous literature reports, the prepared Z-Fe1Mn1-NC possesses superior activity and stability simultaneously in both acidic and alkaline conditions (Table S7).

Inspired by the enhanced ORR activity of Z-Fe1Mn1-NC, a homemade liquid ZAB was assembled to evaluate the possible application of the catalysts. For comparison, NC and Pt/C also served as air cathode catalysts for ZAB. As shown in Figure 8a, the Z-Fe1Mn1-NC based battery displays an open circuit voltage (OCV) of 1.475 V, which is higher than those of NC (1.359 V) and Pt/C (1.456 V). According to the discharge polarization curves in Figure 8b, Z-Fe1Mn1-NC gives a peak power density of 164.3 mW cm^{-2} , with a current density of 282.8 mA cm^{-2} at 0.58 V, which is superior to those of NC (69.7 mW cm^{-2} , 181.9 mA cm^{-2} , 0.38 V) and Pt/C (116.3 mW cm^{-2} , 236.4 mA cm^{-2} , 0.49 V). Moreover, the specific capacity (at 10 mA cm^{-2}) of ZAB with Z-Fe1Mn1-NC is 708.3 mAh g^{-1} , outperforming those of NC (596.0 mAh g^{-1}) and Pt/C (656.6 mAh g^{-1}) (Figure 8c). Notably, this level of activity exceeds the values of the latest-reported Fe-based electrocatalysts

(Table S8). Subsequently, the catalytic activity was further based on the rate performance test. As illustrated in Figure 8d, the ZAB based on Z-Fe1Mn1-NC exhibits much higher and more stable discharge voltage over the current densities from 5 to 50 mA cm⁻². Although Z-Fe1Mn1-NC delivers slightly lower voltages than that of Pt/C at smaller current densities (5 and 10 mA cm⁻²), it exhibits a higher voltage platform under high-current conditions (20 and 50 mA cm⁻²), demonstrating its better rate performance.

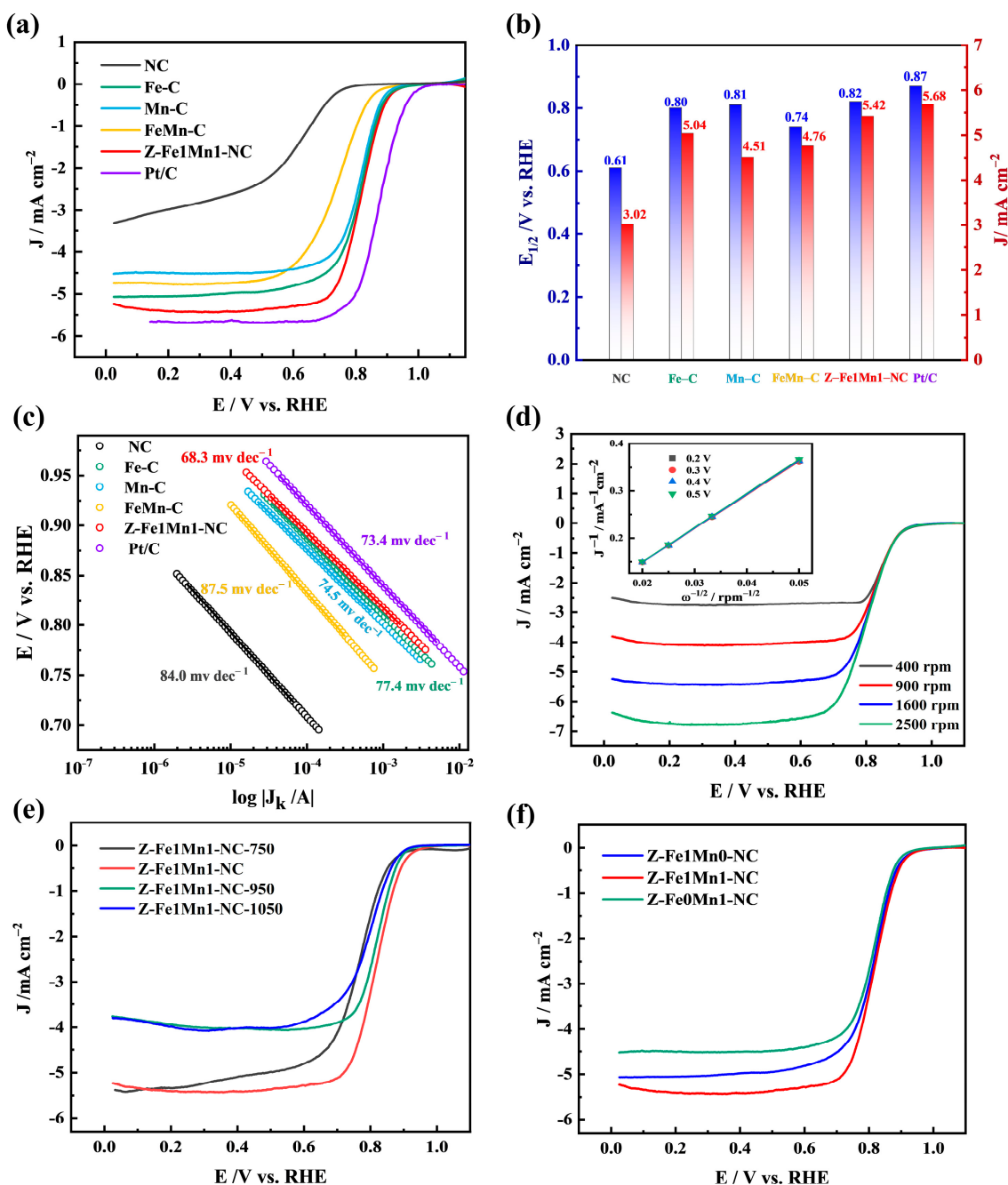


Figure 5. ORR performance in alkaline medium. (a) LSV curves (under a rotational speed of 1600 rpm), half-wave potentials $E_{1/2}$ and limiting current density J_L (b), and (c) corresponding Tafel curves of NC, Fe-C, Mn-C, FeMn-C, Z-Fe1Mn1-NC, and Pt/C. (d) LSV curves of Z-Fe1Mn1-NC at different rotating speeds (400–2500 rpm) in O₂-saturated 0.1 M KOH; the insets are the corresponding K-L plots. (e) LSV curves of Z-Fe1Mn1-NC-750, Z-Fe1Mn1-NC, Z-Fe1Mn1-NC-950, and Z-Fe1Mn1-NC-1050. (f) LSV curves of Z-Fe1Mn0-NC, Z-Fe1Mn1-NC and Z-Fe0Mn1-NC.

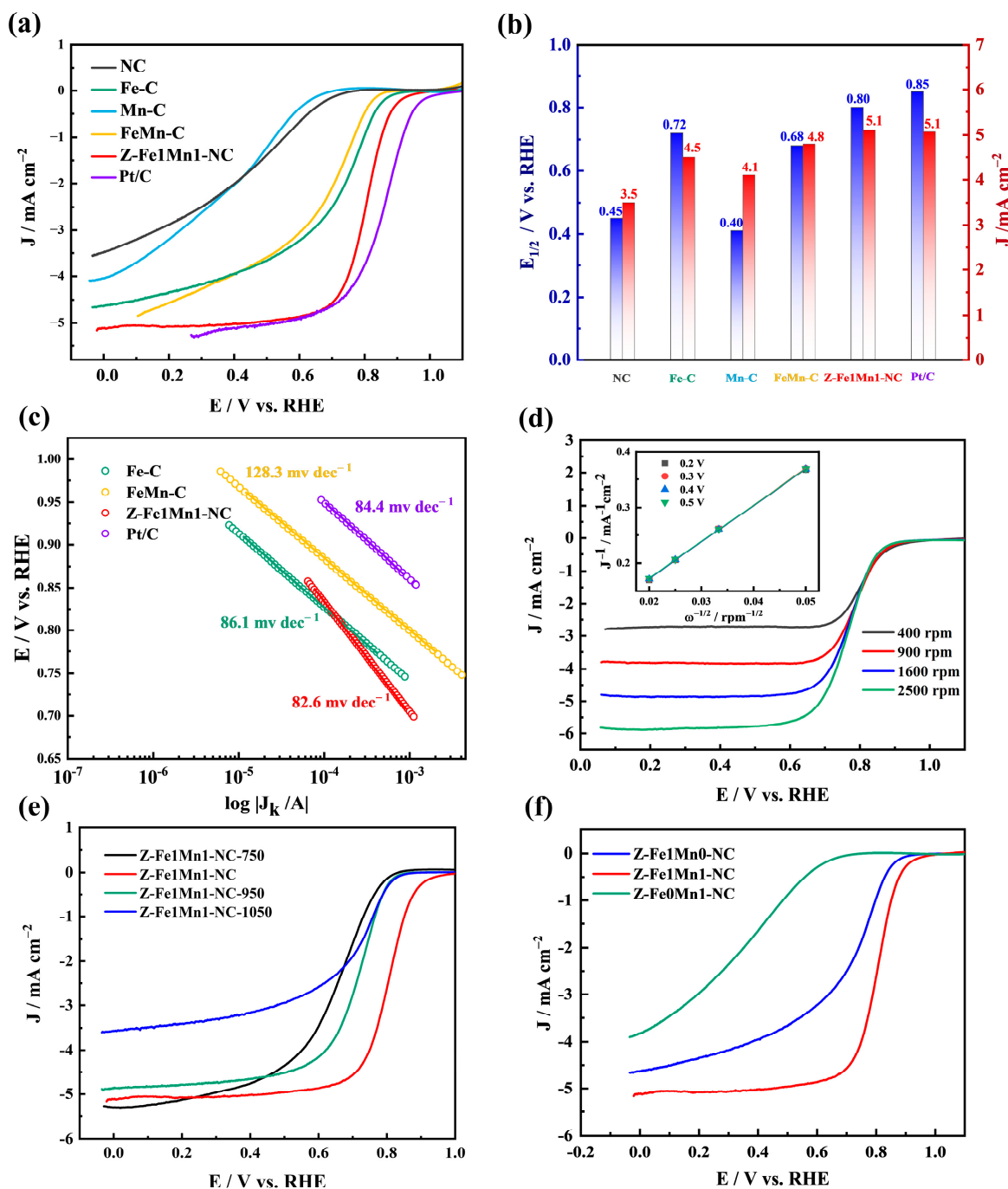


Figure 6. ORR performance in acidic medium. (a) LSV curves, (b) half-wave potentials $E_{1/2}$ and limiting current density J_L , and (c) corresponding Tafel curves of NC, Fe-C, Mn-C, FeMn-C, Z-Fe1Mn1-NC, and Pt/C. (d) LSV curves of Z-Fe1Mn1-NC at different rotating speeds (400–2500 rpm) in O₂-saturated 0.1 M HClO₄; the insets are the corresponding K-L plots. (e) LSV curves of Z-Fe1Mn1-NC-750, Z-Fe1Mn1-NC, Z-Fe1Mn1-NC-950, and Z-Fe1Mn1-NC-1050. (f) LSV curves of Z-Fe1Mn0-NC, Z-Fe1Mn1-NC, and Z-Fe0Mn1-NC.

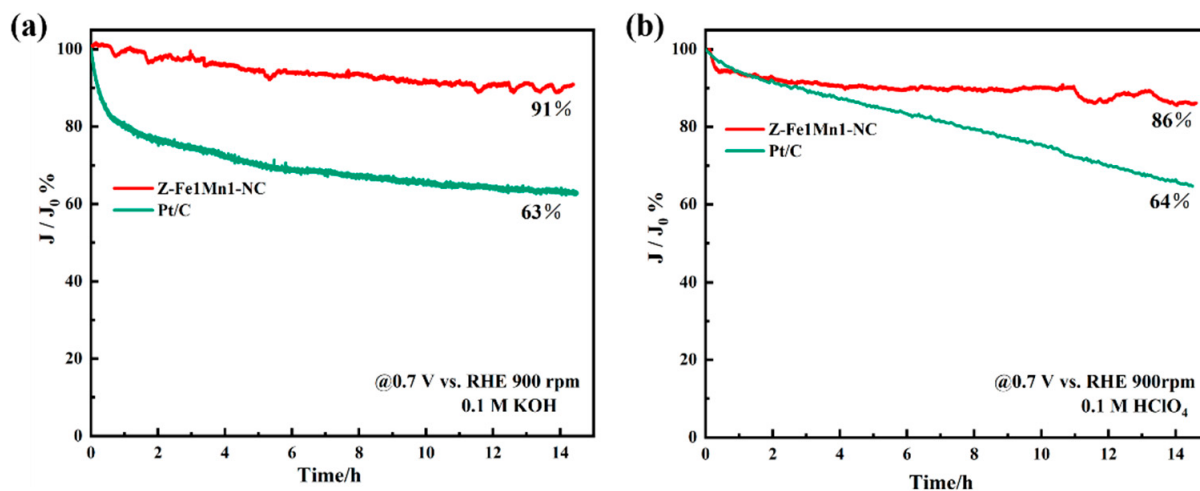


Figure 7. Current–time chronoamperometric response of Z-Fe1Mn1-NC and Pt/C at 0.7 V vs. RHE, with a rotating speed of 900 rpm in O_2 -saturated 0.1 M KOH (a) and 0.1 M $HClO_4$ (b).

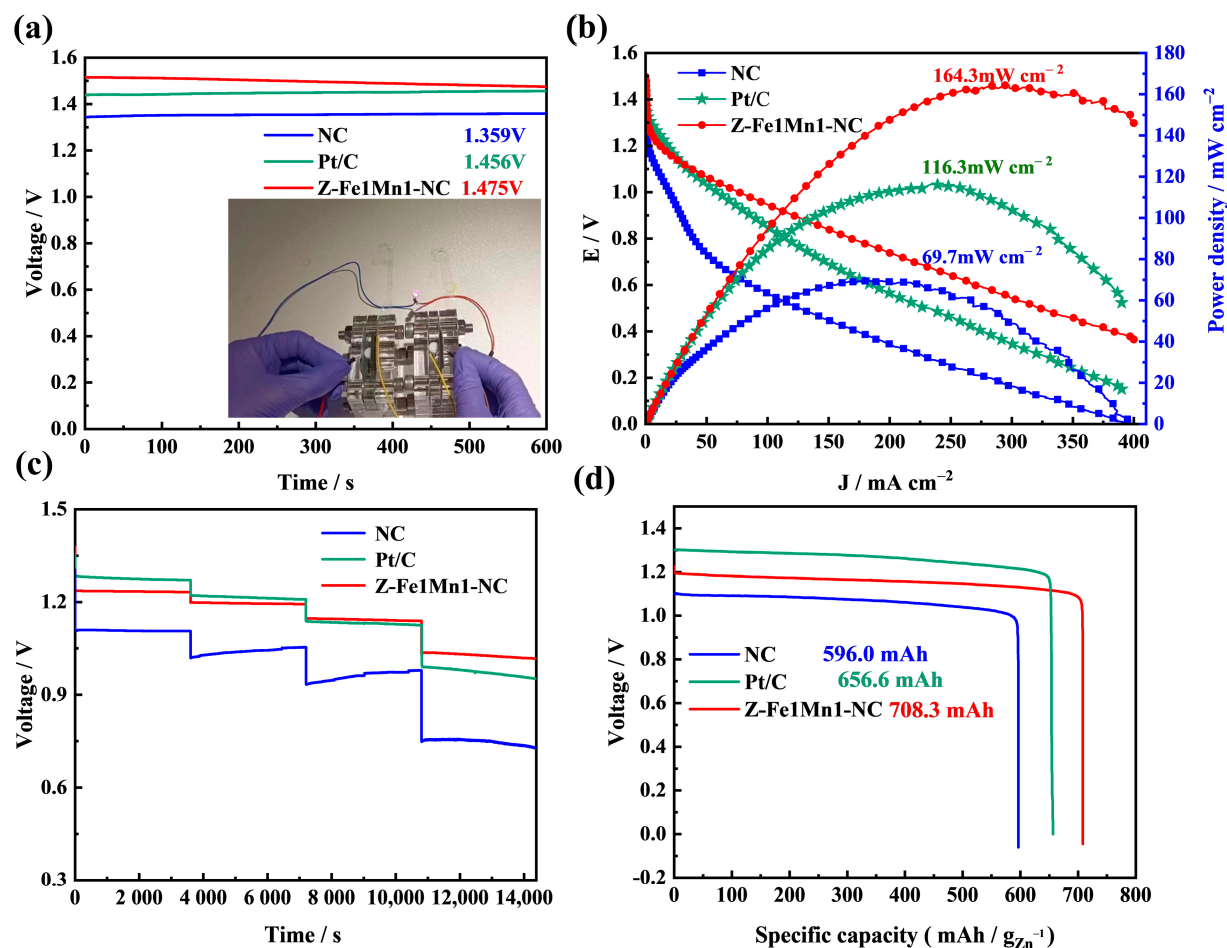


Figure 8. Performances of liquid ZABs: (a) open circuit voltage curves (the inset is the photograph of two ZABs powering a LED light), (b) discharge polarization and power density curves, (c) voltage–specific capacity curves at 10 mA cm^{-2} , and (d) discharge curves of at different current densities of ZABs with NC, Z-Fe1Mn1-NC and Pt/C as the air cathode catalysts.

3. Experimental Design

3.1. Synthesis

3.1.1. Synthesis of ZIF-8

In brief, 48.7 mmol of 2-Methylimidazole and 5.64 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were, respectively, dissolved in 60 mL and 20 mL of methanol to form two clear solutions. After mixing them together under continuous stirring for 1 h, the mixture was kept under neutral conditions for 24 h. Then, the products were collected by centrifugation and washed with methanol several times and dried at 70 °C for 12 h.

3.1.2. Synthesis of Fe/Mn-MOF

Typically, 19.9 mmol disodium fumarate was dissolved in 10 mL of deionized water under vigorous stirring at 60 °C. A quantum of 10 mmol of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was subsequently added into the above mixture and stirred adequately for 8 h. Then, 40 mL deionized water containing 10 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was mixed with the above solution and stirring was maintained. After the reaction, the mixture was centrifuged and washed for several times and finally dried at 60 °C under vacuum. For comparison, the Fe-MOF and Mn-MOF were prepared by means of an approach similar to that of Fe/Mn-MOF, but without adding $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, respectively.

3.1.3. Synthesis of Z-Fe1Mn1-NC

The obtained ZIF-8 and Fe/Mn-MOF of a certain mass ratio (10:1) were mixed homogeneously. Next, the powder mixture was placed into the ball-mill tank. The diameters of the grinding ball followed the ratio of 8 mm:10 mm:15 mm = 12:6:1. The ball-mill process was conducted at 400 rpm for 6 h. Then, the fine powder mixture was calcined in a tube furnace at 850 °C for 1 h in an Ar atmosphere. After being cooled to room temperature, the product was washed using 0.5 M H_2SO_4 with a thorough stirring for 4 h at 80 °C. Finally, the sample was washed several times with deionized water and dried under vacuum overnight to obtain the Z-Fe1Mn1-NC.

For comparison, the mixture without adding Fe/Mn-MOF and the mixture excluding ZIF-8 during the ball-milling process were also prepared and named as NC and FeMn-C, respectively. The catalysts named as Fe-C and Mn-C were prepared by pyrolyzing of ball-milled Fe-MOF and Mn-MOF alone, respectively. The catalyst named as Z-Fe1Mn0-NC was prepared by the pyrolysis of a ball-milled mixture of ZIF-8 and Fe-MOF. The catalyst named as Z-Fe0Mn1-NC was prepared by the pyrolysis of a ball-milled mixture of ZIF-8 and Mn-MOF. Additionally, samples with different pyrolysis temperatures (750, 950, and 1050 °C) were prepared by an approach similar to that for Z-Fe1Mn1-NC.

3.2. Materials Characterizations

The morphology of the resultant samples was carried out by scanning electron microscope (SEM, Sigma 500) and transmission electron microscopy (TEM, JEM-F200). The chemical composition and state of the catalysts were obtained by X-ray photoelectron spectra (XPS) on a K-ALPHA+ X-ray photoelectron spectrometer. The Fe and Mn content in the catalyst was determined by means of inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700s). X-ray diffraction (XRD) was conducted in the 2θ range of 10° to 70° (X'Pert PRO) using $\text{Cu K}\alpha 1$ X-ray source. The Raman spectra were measured on a HORIBA LabRAM HR Evolution with 633 nm laser radiation. Nitrogen sorption isotherms were recorded on a 3Flex surface analyzer.

3.3. Electrochemical Characterizations for ORR

The electrochemical measurements were conducted on an electrochemical workstation (CHI660E) with a conventional three-electrode system with 0.1 M KOH and 0.1 M HClO_4 electrolyte. An Ag/AgCl electrode and platinum foil were used as reference and counter electrodes, respectively. For comparison, a commercial electrode (40 wt% Pt/C, JM) was also tested under the same conditions. The catalyst ink was prepared as follows: 5 mg

of catalyst was blended with 10 μL of Nafion 5 wt % solution and 500 μL of ethanol. After ultrasound for 30 min, the catalyst ink was deposited consecutively on a glassy carbon electrode to prepare the working electrode. Linear sweep voltammetry (LSV) was performed in an O_2 saturated solution with a scan rate of 10 mV s^{-1} at 1600 rpm. All potentials are reported as the reversible hydrogen electrode (RHE).

3.4. Zn–Air Battery (ZAB) Assembly

The air cathode (positive electrode) was prepared by loading 2 mg cm^{-2} prepared catalyst on a carbon diffusion layer ($1 \times 1 \text{ cm}$). The polished zinc foil was employed as the negative electrode. A mixed solution containing 6.0 M KOH and 0.2 M $\text{Zn}(\text{Ac})_2$ was used as the electrolyte. The electrochemical tests were performed on the CHI760E workstation at ambient conditions.

4. Conclusions

In conclusion, we report a facile strategy by ball-milling ZIF-8 and Fe/Mn-MOFs, followed by a direct pyrolysis process to produce a catalyst with two atomically dispersed metals (Fe and Mn) anchored on N-doped bamboo-like carbon nanotubes. As a result, Z-Fe1Mn1-NC shows remarkable ORR activity in both acidic and alkaline media, with half-wave potentials of 0.80 and 0.82 V, respectively. Notably, the outstanding stability of Z-Fe1Mn1-NC during the ORR outperformed the commercial Pt/C and many other reported catalysts. Moreover, the ZAB using Z-Fe1Mn1-NC as the cathode catalyst exhibited satisfactory OCV (1.475 V), high peak power density (164.3 mW cm^{-2}), and enhanced rate performance over a wide current density range, from 5 to 50 mA cm^{-2} . This work provides an efficient strategy to produce advanced M-N-C catalysts with high activity and stability for ORR.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13081161/s1>, Figure S1: SEM images of ZIF-8 (a,b) and Fe/Mn-MOF (c,d); Figure S2: XRD patterns of ZIF-8 (a) and Fe-MOF, Mn-MOF, and Fe/Mn-MOF (b); Figure S3: TEM image (a), HRTEM image (b) and IFFT image of marked region of (b) for Z-Fe1Mn1-NC; Figure S4: TEM image (a) and HRTEM images (b,d) for Z-Fe1Mn1-NC; IFFT images of the marked region of (b) and (d) are given in (c) and (e); Figure S5: TEM image (a) and high-resolution TEM image (b) of NC; Figure S6: TEM image (a) and high-resolution TEM image (b) of Mn-C; Figure S7: TEM image (a) and high-resolution TEM image (b) of Fe-C; Figure S8: ORR performance in alkaline medium (0.1 M KOH). (a) Half-wave potentials $E_{1/2}$, limiting current density J_L , and (b) corresponding Tafel curves of Z-Fe1Mn1-NC-750, Z-Fe1Mn1-NC, Z-Fe1Mn1-NC-950, and Z-Fe1Mn1-NC-1050. (c) Half-wave potentials $E_{1/2}$ and limiting current density J_L , and (d) corresponding Tafel curves of Z-Fe1Mn0-NC, Z-Fe1Mn1-NC, and Z-Fe0Mn1-NC; Figure S9: ORR performance in acidic medium (0.1 M HClO_4). (a) Half-wave potentials $E_{1/2}$ and limiting current density J_L , and (b) corresponding Tafel curves of Z-Fe1Mn1-NC-750, Z-Fe1Mn1-NC, Z-Fe1Mn1-NC-950, and Z-Fe1Mn1-NC-1050. (c) Half-wave potentials $E_{1/2}$ and limiting current density J_L , and (d) corresponding Tafel curves of Z-Fe1Mn0-NC, Z-Fe1Mn1-NC and Z-Fe0Mn1-NC. Table S1: Summary of BET specific surface areas for various catalysts; Table S2: Summary of element content for various catalysts; Table S3: Summary of fitting results for C 1s XPS spectra for various catalysts; Table S4: Summary of fitting results for N 1s XPS spectra for various catalysts; Table S5: The fitting results for Fe 2p XPS spectra for Z-Fe1Mn1-NC; Table S6: The fitting results for Mn 2p XPS spectra for Z-Fe1Mn1-NC; Table S7: Performance comparison of ORR activities for Fe-based nonprecious catalysts both in acidic and alkaline medium; Table S8: Performance comparison of Zn–air batteries for Fe-based nonprecious catalysts as air cathode.

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