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Oxygen reduction reaction (ORR) kinetics are closely related to the electronic structure of active sites. Herein, a single-atomic Mn catalyst decorated with adjacent MoP nanocrystals (MoP@Mn_{SAC}-NC) is reported. The decoration of MoP drives the electronic structure transition of Mn sites from low-spin to high-spin states through an electronic phosphide-support interaction. The rearranged electron occupation in $3d_{xz-yz}$ and $3d_z^2$ orbitals of Mn sites leads to electrons occupying the σ orbital in Mn— $\text{*}O_2$, thereby favoring O_2 adsorption to initiate the ORR mechanism. In situ characterizations confirm that Mn $3d_z^2$ orbital occupation state can activate molecular O_2 and optimize the adsorption of the *OOH intermediate. As a result, the MoP@Mn_{SAC}-NC displays an outstanding alkaline ORR half-wave potential ($E_{1/2} = 0.894$ V), excellent peak power densities (173/83 mW cm⁻² for liquid/solid-state Zn-air batteries, respectively), and long-term stability (840 h) superior to commercial Pt/C. This work provides profound insights into spintronics-level engineering, guiding the design of next-generation high-performance ORR catalysts.

1. Introduction

The oxygen reduction reaction (ORR) is the crucial cathode halfreaction in regenerative energy conversion and storage systems, including fuel cells and Zn-air batteries (ZABs).^[1] Unfortunately, ORR involves multi-electron/proton transfer, resulting in a high energy barrier and slow kinetics, which inevitably slows down reaction rates and necessitates efficient catalysts to enhance the reaction rate.^[2] Pt-group-metal (PGM) materials, typically recognized as the cutting-edge ORR catalysts with the highest kinetic activity, face problems such as limited reserves, high cost, and

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poor stability.^[3] Therefore, to meet the needs of practical applications, it is crucial to develop highly active and durable PGM-free catalysts.^[4]

Currently, catalysts composed of single metal atoms embedded in a nitrogencarbon matrix (M_{SAC} -NC, where M = Mn, Fe, or Co) demonstrate encouraging activity among PGM-free catalysts, owing to their higher atom utilization efficiency, well-defined atomic configuration, and adjustable electronic structures.^[5] Particularly, the ORR activity of the most advanced Fe_{SAC}-NC catalysts is similar to that of Pt.^[6] However, the performance of these catalysts in ZABs remains suboptimal, evidenced by low power density and limited operational lifespan.^[7] Recently, Mn_{SAC}-NC catalysts were widely reported and demonstrated considerable application potential for ZABs.^[8] Theoretical calculations predict

that the Mn–N₄ active site acts as an active center following a straightforward four-electron transfer pathway during the ORR.^[9] Unfortunately, the activities of Mn_{SAC}-NC reported hitherto still lag far behind those of the most promising Fe_{SAC}-NC catalysts.^[8b,10] A major reason is that the currently developed Mn_{SAC}-NC catalysts exhibit suboptimal adsorption energies for O₂ molecules and oxygen intermediates (e.g., *OOH, *O, and *OH).^[11] For instance, the initial O₂ adsorption, a thermal step, is essential for triggering the ORR mechanism, and the ORR process is typically limited by the electronic transfer step (especially *OH + e⁻ → OH⁻ is correlated with the rate-determining

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step).^[12] However, the limited O_2 adsorption at Mn sites, located on the right downhill in the volcano plot, and strong adsorption of OH, corresponding to the left in the volcano plot should be precisely regulated.^[8b,11,12b]

In principle, the d-orbital electronic configuration of active sites in catalysts can be adjusted to regulate the adsorption strength for O₂ molecules and oxygen intermediates, thereby optimizing the activation energy barrier of ORR catalysis and accelerating the reaction kinetics.^[13] From a structural perspective, the d orbitals in the $Mn-N_4$ configuration with D_{4h} symmetry are split into two sets: the double degeneracy d_{xz} and d_{vz} orbits, and the simple degeneracy d_{xv} , d_z^2 , and $d_x^2-y^2$ orbits, where the electron occupancy in these orbitals introduces multiple spin configurations.^[14] Specifically, the distinct orbital interactions between oxygen-containing species and metal centers with different spin configurations will profoundly affect the adsorption/desorption of reactants, thus manipulating reaction kinetics.^[15] Previous studies have elaborated that precise control of the coordination environment in Mn_{SAC}-NC can significantly optimize the spin configuration of Mn single atomic sites, thereby enhancing ORR catalytic activity.^[11,16] Besides, the electron transfer induced by the acknowledged metal-support interaction (MSI) can significantly regulate the electronic configuration of the active centers.^[17] However, most research has primarily focused on metallic alloy or oxide as the electron acceptor.^[18] In fact, transition metal phosphides also exhibit similar characteristics, especially, the metallic character of molybdenum phosphide (MoP) is conducive to appealing to electrons and thus effectively promotes the migration of charges.^[19] Some studies have confirmed the electronic phosphide-support interaction (EPSI) exists between metal phosphides and supports such as metal phosphates and N,P co-doped carbon.^[20] In such an EPSI, metal phosphides interact with supports through the interfacial metalnonmetal bonds, which could offer accessible channels for electron transfer. Nevertheless, the EPSI involving single-atom catalyst has not been thoroughly explored and remains to be elaborated, including its influence on spin configuration and the structure-activity relationship.

Herein, a hybrid MoP@Mn_{SAC}-NC electrocatalyst was prepared for the first time by integrating an ultrafine MoP structure adjacent to the atomically dispersed Mn-N₄ system. A critical EPSI was constructed between MoP and Mn-N₄ through particular interfacial Mo-N and Mo-P bonds. Experimental and theoretical investigations demonstrate the robust EPSI between MoP and Mn single atom triggers the electron delocalization and the spin-state transition from low spin (LS) to high spin (HS) in Mn-N₄ moieties. Specifically, the injection of an electron into the d_z² orbital expedites O₂ adsorption as an additional electron fills in the σ bond formed by the coupling of $3d_z^2$ orbital in Mn–N₄ site and π^* orbit of O₂. Consequently, MoP@Mn_{SAC}-NC offers superior ORR activity in 0.1 м KOH with a half-wave potential ($E_{1/2}$) of 0.894 V, surpassing Mn_{SAC}-NC (0.824 V), and 20% Pt/C (0.872 V). Furthermore, catalyst-based aqueous ZAB delivers high power density (173 mW cm⁻²) and extended cycle life (840 h), outperforming 20% Pt/C (119 mW cm⁻² and 430 h). Similarly, the solid-state ZAB assembled with MoP@Mn_{SAC}-NC exhibits an exceptional power density at 25°C (83 mW cm⁻²) and $-25^{\circ}C$ (56 mW cm⁻²), good mechanical strength, and robust span-life. This work reveals that EPSI enables precise spin-state

modulation in single-atom catalysts, provides spintronic insights into structure-activity relationships, and is expected to guide the design of advanced ORR catalysts.

2. Results and Discussion

The specific synthesis process for the nanocubic Mn_{SAC}-NC framework with evenly dispersed MoP is illustrated in Figure 1a. First, zinc nitrate hexahydrate and 2-methylimidazole form ZIF-8 crystal through coordination in an aqueous solution containing cetyltrimethylammonium bromide (CTAB). During this process, CTAB adsorbs onto the (100) crystal face of ZIF-8, thereby slowing down the growth rate of this face and leading to the formation of a cubic morphology.^[21] Subsequently, ZIF-8 is transformed into nitrogen-doped carbon (NC) with a porous structure via a pyrolysis process. Then, Mn and Mo species are impregnated onto the N-doped carbon (NC) framework, followed by mixing with red phosphorus (P), and subsequent co-pyrolysis to synthesize the target catalyst (denoted as MoP@Mn_{SAC}-NC). During the high-temperature treatment, residual Zn in the carbon host evaporated, Mn ions were simultaneously incorporated into the NC, and Mo species were reduced by the released P to form MoP nanocrystals anchored on the substrate. X-ray powder diffraction (XRD) was first employed to characterize the crystal structures of electrocatalysts. Similar to NC, Mn_{SAC}-NC exhibits two broad peaks at $\approx 25.8^{\circ}$ and 43.6° , attributed to the (002) and (101) planes of amorphous carbon, respectively (Figures S1 and S2a).^[22] Notably, the additional characteristic peaks in the XRD pattern of MoP@Mn_{SAC}-NC are consistent with MoP@NC corresponding to the hexagonal MoP, which proves the absence of any characteristic peak associated with manganese phosphide, clusters, or other crystalline Mn-containing phases (Figure 1b and Figure S2b). Raman spectra were collected to unravel the basic features of the carbon matrix (Figure S3). Two bands in the detection range, D (1346 cm⁻¹) and G (1580 cm⁻¹) bands represent disordered sp³ and sp²-hybridized carbon atoms, respectively.^[18a] The higher intensity ratio of the D band to the G band (I_D/I_G) for MoP@Mn_{SAC}-NC indicates the presence of more internal topological defects in the carbon matrix. This finding suggests that the co-doping of Mn and P introduces additional carbon defects.^[23] The N₂ adsorption-desorption isotherm indicates that MoP@Mn_{SAC}-NC (695.7 m² g⁻¹) and Mn_{SAC}-NC (732.8 m² g⁻¹) exhibit larger specific surface areas than that of NC (513.6 m² g⁻¹), which facilitates the exposure of more active sites and ensures adequate contact between reactants and key intermediates (Figure S4). Notably, the slightly lower specific surface area of MoP@Mn_{SAC}-NC compared to Mn_{SAC}-NC results from the occupation of MoP nanoparticles.

To further study the structural features at the element and atomic level, field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used. The nanocubic morphology of NC, with clear boundaries and an average particle size of \approx 300 nm, is initially confirmed (Figure S5). Figure 1c,d illustrate that the MoP@Mn_{SAC}-NC catalyst inherits its well-defined nanocubic structural integrity after successive heat treatments. In the high-resolution TEM (HR-TEM) image and magnified view of the selected region (Figure 1e), the well-defined lattice spacing of 0.227 nm corresponds to the MoP (101) plane. This deduction is further validated by the line intensity

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Figure 1. Synthetic procedure and structural characterizations. (a) Schematic illustration for the preparation of the catalyst. (b) XRD pattern, (c) SEM, (d) TEM, and (e) HR-TEM images of MoP@ Mn_{SAC} -NC. (f) The corresponding lattice spacing profiles and atomic structure of MoP in MoP@ Mn_{SAC} -NC. (g) AC-HAADF-STEM image of MoP@ Mn_{SAC} -NC. (h) The HAADF-STEM and corresponding EDS mapping images of Mn, Mo, P, N, and C elements in MoP@ Mn_{SAC} -NC respectively.

profile, which aligns with both the atomic model and the XRD pattern of a hexagonal MoP crystal (Figure 1f). No obvious lattice fringes belonging to Mn-based species are visualized in the HR-TEM image, implying that Mn is embedded in the carbon framework in isolation. Furthermore, aberration-corrected highangle annular dark-field scanning TEM (AC-HAADF-STEM) images identify that monatomic Mn species are homogeneously distributed on the MoP@Mn_{SAC}-NC and Mn_{SAC}-NC, confirmed by isolated scattered bright spots highlighted with red circles (Figure 1g and Figure S6). Notably, in the NC framework, singleatom Mn sites closely surround the nano-MoP species, and both components can coexist concordantly, indicating a strong EPSI between these two active components. In addition, the HAADF-STEM image and the corresponding energy dispersive spectrometer (EDS) elemental mapping images prove the uniform distribution of Mn, Mo, P, and N within the carbon matrix (Figure 1h).

X-ray photoelectron spectroscopy (XPS) was calibrated with reference to the C 1s peak at 284.8 eV and employed to scrutinize



the chemical states of materials (Figure S7).^[24] The XPS survey spectrum of MoP@Mn_{sac}-NC reveals that the catalyst contains Mn, Mo, P, C, and N elements (Figure S8). Meanwhile, the mass loadings of Mn, MoP, and N in MoP@Mn_{SAC}-NC are 0.3, 4.5, and 2.3 wt.%, respectively, as detected by inductively coupled plasma mass spectrometry (ICP-MS) and elemental analyzer (Table S1). In the Mn 2p spectra, the peaks at 641.8 and 643.4 eV are assigned to Mn²⁺ and Mn³⁺, respectively (Figure S9a).^[22] For the Mo 3d spectra, high-resolution peaks of Mo³⁺ and Mo⁶⁺ can be identified at 228.4 and 232.7 eV, respectively (Figure S9b).^[25] Notably, MoP@Mn_{SAC}-NC exhibits increased Mn³⁺ and Mo³⁺ segments (35.5% and 47.9%) compared to Mn_{SAC} -NC (28.1%) and MoP@NC (17.3%), suggesting the EPSI between these components, with the electron transfer trend from Mn-N₄ moieties to nearby Mo species (Figure S10).^[22] It can be explained that Mo acts as a stronger electron acceptor than Mn due to its larger electronegativity, leading to a weaker electron density on the Mn center. The P 2p XPS spectra of materials display peaks at 131.9 and 133.4 eV (Figure S11a), which can be assigned to P-C and P-O groups, respectively, suggesting the incorporation of P atoms into the carbon matrix and the inevitable oxidation of P species.^[26] Unlike Mn_{SAC}-NC and PNC, the P 2p spectra of MoP@Mn_{SAC}-NC and MoP@NC can be deconvoluted into additional peaks corresponding to metal phosphide at 128.9 eV (2p_{3/2}) and 129.5 eV (2p_{1/2}).^[27] The N 1s XPS spectra of catalysts are deconvoluted into five nitrogen species: metal-N (397.6 eV), pyridine-N (398.7 eV), pyrrolic-N (399.7 eV), graphite-N (401.3 eV), and oxidized-N (403.8 eV) (Figure S11b). The presence of pyridine N and metal-N is generally considered as evidence for the formation of Mn-N₄ moieties.^[28] Of note, the N 1s XPS spectrum of MoP@NC exhibits a distinct peak at 397.6 eV belonging to the Mo-N bond, indicating that MoP is anchored on the carbon matrix through interfacial Mo-N bonds.^[20a]

To explore the electronic and coordination configuration of metal species in MoP@Mn_{SAC}-NC, synchrotron X-ray absorption spectroscopy (XAS) was resorted. In the normalized Xray absorption near-edge spectroscopy (XANES) of the Mn Kedge, the near-edge absorption threshold position of resultant MoP@Mn_{SAC}-NC falls between those of the Mn foil and MnO₂ and is positively shifted compared to Mn_{SAC} -NC (Figure 2a). This result validates the electron transfer from Mn to MoP in MoP@Mn_{SAC}-NC due to MoP's stronger electron-attracting ability compared with that of Mn²⁺, which remarkably modulates the local electron density of Mn sites. In addition, the Fouriertransformed k³-weighted extended X-ray absorption fine structure (FT-EXAFS) spectra of MoP@Mn_{SAC}-NC and Mn_{SAC}-NC all exhibit one dominant peak at 1.65 Å in R space, ascribed to the MnN first coordination shell (Figure 2b). More importantly, similar to standard Mn-Pc, no related peak corresponding to Mn-Mn (2.35 Å) or Mn-P (≈2.00 Å) scattering is observed in both samples.^[29] The coordination configuration and radial distance were further determined by quantitative leastsquares EXAFS curve fitting analysis using Mn-N scattering path (Figures S12 and S13). This analysis suggests that each Mn atom in both MoP@Mn_{SAC}-NC and Mn_{SAC}-NC is coordinated with about four N atoms forming an Mn-N₄ moiety (Table S2). The wavelet transform EXAFS (WT-EXAFS) was utilized to monitor the atomic configuration. The WT contour plot of MoP@Mn_{SAC}-NC shows an intensity maximum at 5.5 Å⁻¹,

which is attributed to the Mn-N bonding, while the Mn-Mn signals are absent (Figure 2c). These spectroscopic analyses unravel that the Mn exists as atomically dispersed single Mn site species, in agreement with the TEM results. Similarly, XANES at the Mo K-edge was conducted to study the intrinsic electronic structure of the MoP@Mn_{SAC}-NC. The synthesized MoP@Mn_{SAC}-NC exhibits an absorption edge between those of MoP and MoO₃, implying that the average valence of Mo species lies between +3 and +6 (Figure 2d). Furthermore, the FT-EXAFS spectrum of MoP@Mn_{SAC}-NC reveals two prominent peaks at \approx 1.2 and 2.1 Å, attributed to the Mo-N/O and Mo-P scattering path, respectively (Figure 2e).^[30] WT-EXAFS analysis intuitively investigated the configuration of Mo in MoP@Mn_{SAC}-NC, in which two effective intensities appear at ≈ 5 and ≈ 6 Å⁻¹, corresponding to Mo-N/O and Mo-P standard spectrum, respectively (Figure 2f). The coordination number values for these MoP@Mn_{SAC}-NC catalysts are ascertained based on the quantitative EXAFS fitting analysis in R-space and k-space. The resulting average Mo-P and Mo-N/O coordination numbers of Mo within the sample are 0.8 and 1.8, respectively (Figure S14 and Table S2). These results suggest that MoP species are anchored on the N,P co-doped carbon matrix with Mn single atom through specific interfacial Mo-P and Mo-N bonds and are partially oxidized, which is in agreement with previous reports.^[20a]

The Mn L-edge XAS spectra were conducted to further investigate the chemical valence of catalysts. Generally, Mn L-edge spectra split into two separate sets of peaks named L₂ and L₃-edge as a result of the 2p spin-orbital coupling interaction. Compared with the L₃-edge, the L₂-edge feature is normally broadened because of the shorter lifetime of the $2p_{1/2}$ core hole and the near-threshold Coster-Kronig decay (Figure \$15).^[31] We therefore mainly focus on the L₃-edge evolution in the following discussions. As shown in Figure 2g, both samples exhibit nearly identical spectral shapes, with predominantly peaks attributed to Mn²⁺ ions, similar to the MnO reference.[32] Notably, the peak of the Mn L-edge spectrum in the MoP@Mn_{SAC}-NC shows a positive shift of 0.1 eV relative to that in $Mn_{SAC}\text{-}NC$, indicating a higher valence of Mn in MoP@Mn_{SAC}\text{-}NC.^{[33]} Ultraviolet photoelectron spectroscopy (UPS) was performed to understand the band structure (Figure 2h). The cutoff energies (E_{cutoff}) of MoP@Mn_{SAC}-NC and Mn_{SAC}-NC are 17.98 and 17.44 eV, respectively. Therefore, according to the equation of $\Phi = 21.22 \text{ eV} - E_{\text{cutoff}}$, the work functions (Φ) of MoP@Mn_{SAC}-NC and Mn_{SAC}-NC were calculated to be 3.24 and 3.78 eV, respectively.^[7a] These results indicate that MoP@Mn_{SAC}-NC tends to donate more electrons to the O₂ molecule and oxygen intermediates. Furthermore, the highest occupied molecular orbital energies are determined to be 2.80 and 1.27 eV for MoP@Mn_{SAC}-NC and Mn_{SAC}-NC, respectively, indicating the incorporation of MoP induces a Mn 3d electron delocalization with a thinner electron density of the Mn center.^[1a] Typically, this charge redistribution is concomitant with the transformation of the 3d electron spin configuration.^[15a] The shape and position of electron paramagnetic resonance (EPR) spectra are vital indicators for predicting the quantity and occupancy of unpaired electrons. Compared to the pristine Mn_{SAC}-NC, an apparent signal peak at g = 2.035 is detected in MoP@Mn_{SAC}-NC, attributed to the unpaired electron in the Mn 3d orbital (Figure S16).^[34] To eliminate the contributions of carbon defects, P-doping, and potential Mo-doping to the EPR signal, a

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Figure 2. Electron and coordination structure characterization. (a) Normalized Mn K-edge XANES spectra. (b) The corresponding Fourier transformed k^3 -weighted EXAFS signals of MoP@Mn_{SAC}-NC and Mn—Pc. (d) Normalized XANES spectra at the Mo K-edge. (e) The corresponding Fourier transformed k^3 -weighted EXAFS spectra. (f) Wavelet transform of k^3 -weighted EXAFS spectra. (f) χ^{-1} -T plots. (j) Schematic diagram of spin state transition.

series of controlled experiments were performed. Specifically, a comparison of EPR spectra between PNC and NC reveals that the introduction of P does not lead to enhanced EPR signals (Figure S17). Therefore, it can be speculated that the EPR signal in Mn_{SAC} -NC is mainly contributed by Mn. Furthermore, Modoped Mn_{SAC} -NC (Mo- Mn_{SAC} -NC) was synthesized (Figure S3c). Compared with Mn_{SAC} -NC, Mo- Mn_{SAC} -NC exhibits a weaker EPR signal, indicating that Mo-doping may inhibit the generation of unpaired electrons (Figure S17). When further compared to PNC

and NC, MoP@NC shows a slightly enhanced EPR signal, although MoP itself has no EPR signal (Figure S18). Based on these results, it can be concluded that MoP can increase the number of unpaired electrons in the samples through EPSI. Intriguingly, the EPR signal of MoP@Mn_{SAC}-NC is far stronger than that of MoP@NC, which validates that this signal mainly originates from the EPSI between Mn single atoms and MoP. With varying amounts of MoP added, the EPR signal intensity significantly changes, and the target catalyst exhibits the strongest

peak signal, indicating the largest number of unpaired electrons (Figure S19).

The magnetic hysteresis (M-H) loop was investigated by vibrating sample magnetometry (VSM) at room temperature to further investigate the spin electronic configuration of catalysts. Notably, MoP@Mn_{SAC}-NC exhibits ferromagnetic behavior (Figure S20), whereas Mn_{SAC} -NC shows a linear M-H curve indicative of paramagnetic behavior. This transition in magnetic properties, along with the higher saturation magnetization (Ms) of MoP@Mn_{SAC}-NC compared to Mn_{SAC}-NC, can be attributed to significant changes in the spin state caused by the incorporation of MoP, leading to more unpaired electrons.^[33] Additionally, as depicted in Figures S21a and S22a, Mn_{SAC}-NC, Mo-Mn_{SAC}-NC, MoP@NC, and MoP all exhibit typical antiferromagnetic behavior. To further elucidate the spin configuration effect on catalysts, the temperature-dependent magnetizations (M-T) were measured to derive the temperature dependence inverse magnetic susceptibilities by the Curie-Weiss law.^[3] The effective magnetic moment (μ_{eff}) obtained from the linear fit of inverse magnetic susceptibilities indicates that the average number of unpaired electrons in the Mn 3d orbital is \approx 5.44 and 1.23 for MoP@Mn_{SAC}-NC and Mn_{SAC}-NC, respectively, aligning well with the EPR and M-H results (Figure 2i). Furthermore, the contributions of MoP and the potential Mo doping can be eliminated by performing linear fitting on the χ^{-1} -T curves of MoP, MoP@NC, and Mo-doped Mn_{SAC}-NC (Figures S21b and S22b). Based on these results, it can be concluded that the EPSI induces charge density redistribution through interfacial Mo-P and Mo-N bonds, resulting in a transition in the spin configuration of the Mn center.^[7a,15a] Specifically, the transition of electrons from the d_{yz} and d_{yz} orbitals to the d_z^2 and $d_y^2 2_y^2$ orbitals leads to a transformation of the spin state in Mn sites from LS to HS, which has a substantial influence on the interaction of active species (*O₂, *OOH, *O, and *OH), thereby promoting ORR activity (Figure 2i).

The ORR activities of catalysts are evaluated in an O₂-saturated electrolyte using a rotating disk electrode (RDE) system. The cyclic voltammetry (CV) curves signify that MoP@Mn_{SAC}-NC has an obvious reduction peak in O2-saturated solution, while such peak is absent in N2-saturated solution, validating the effectiveness of the fabricated catalyst toward ORR (Figure 3a). The ORR polarization curves show that MoP@Mn_{SAC}-NC exhibits superior ORR activity compared with other counterparts (Figure 3b).^[35] As quantified in Figure 3c, MoP@Mn_{SAC}-NC possesses a high $E_{1/2}$ of 0.894 V and ultrahigh mass activity (MA) of 18.2 mA cm^{-2} at 0.9 V, both of which outperform those of Mn_{SAC} -NC, MoP@NC and Pt/C. Besides, the kinetic current densities (j_k) were calculated to gain insight into the effects of reaction kinetics and mass transfer processes on catalyst activity, and notably, among various catalysts, the MoP@Mn_{SAC}-NC possesses the highest j_k of 5.53 mA cm⁻² at 0.9 V (Figure S23).^[1a] The superior ORR kinetics of MoP@Mn_{SAC}-NC is confirmed by the Tafel slope (67.1 mV dec⁻¹), which is significantly smaller than Mn_{SAC}-NC (72.8 mV dec⁻¹) (Figure 3d). The MoP@Mn_{SAC}-NC catalyst exhibits advanced performance in comparison with Mn_{SAC}-NC, MoP@NC, and Pt/C, suggesting that an EPSI between the MoP and Mn_{SAC} -NC matrix optimizes the spin state of $Mn-N_4$ active sites, thereby enhancing ORR activity.[22] Furthermore, MoP@Mn_{SAC}-NC exhibits outstanding ORR activity when compared not only with the reference materials here tested but also with previously reported catalysts (Figure 3e and Table S3). Besides, we investigated the effect of varving amounts of MoP on the spin structure and ORR performance of the materials. By controlling the addition of $(NH_4)_2$ MoO₄ as 0.5, 1.0, and 1.5 times that of Mn(NO₃)₂, 0.5-MoP@Mn_{SAC}-NC, 1.0-MoP@Mn_{SAC}-NC, and 1.5-MoP@Mn_{SAC}-NC catalysts were synthesized, respectively. The results showed that the MoP@Mn_{SAC}-NC catalyst exhibited the strongest EPR signal, indicating the largest number of unpaired electrons.^[15a] Electrochemical measurements further revealed a strong correlation between the ORR performance and the intensity of EPR signals of catalysts (Figures S19 and S24). In addition, MoP@Mn_{SAC}-NC demonstrates superior ORR performance compared to Fe/Co_{SAC}-NC-based catalysts (Figure S25a). Turnover frequency (TOF) is then calculated to quantitatively evaluate the intrinsic activity of the HS Mn sites. The TOF characterizes the unit electrons transferred per active site and per second.^[36] Specifically, the individual Mn sites for MoP@Mn_{SAC}-NC achieved the highest activity with a TOF of 4.4 e⁻¹ s⁻¹ site⁻ at 0.9 V (Figure S26), which is significantly higher than that of Mn_{SAC} -NC (2.1 e⁻¹ s⁻¹ site⁻¹). This result clearly demonstrates that the Mn sites with HS are intrinsically more active than those with LS. The CV curves of MoP@Mn_{SAC}-NC and control samples in the non-Faraday zone are shown in Figure S27. Notably, the MoP@Mn_{SAC}-NC exhibits the largest electric doublelayer capacitor (C_{dl}) value of 37.7 mF cm⁻² (Figure 3f). Moreover, by calculating the $C_{\rm dl}$ values to evaluate the electrochemical surface area (ECSA) of electrocatalysts, the MoP@Mn_{SAC}-NC possesses the largest ECSA, indicating the most active site exposure (Figure S28).^[8a] The ORR pathway was evaluated by conducting polarization curve measurements at different rotation rates (Figure 3g). The calculated electron transfer number (*n*) is \approx 4.1 based on the Koutechy–Levich (K–L) equation (inset of Figure 3g),^[1a] proving that the MoP@Mn_{SAC}-NC catalyst favors the direct four-electron pathway. Furthermore, the measurement performed using the rotating ring-disk electrode (RRDE) reveals that the electron transfer number (*n*) for MoP@ Mn_{SAC} -NC is close to 4, which is better than those of Mn_{SAC} -NC and MoP@NC (Figure 3h). Meanwhile, it was verified that the H₂O₂ yield of MoP@Mn_{SAC}-NC is <9%, indicating a high selectivity for the 4e⁻ ORR.

Additionally, stability during continuous operation is important for the industrial application of catalysts. The resultant MoP@Mn_{SAC}-NC catalyst demonstrates reliable stability in benchmark i-t measurements, in which the relative current remains at 98% even after 10 h. In contrast, the commercial Pt/C and Fe_{SAC}-NC exhibit a rapid decline in performance (Figure 3i and Figure S24b). The polarization curve of MoP@Mn_{SAC}-NC shows a negligible attenuation of $E_{1/2}$ after 1000 CV cycles, further evidencing its good durability (inset of Figure 3i). The morphology and element composition of MoP@Mn_{SAC}-NC after i-ttest are investigated. Remarkably, the SEM (Figure S29) indicates marginal aggregation on the surface morphology, and no obvious change in the valence states of Mn and Mo could be observed by XPS (Figure S30), indicating the excellent stability of the resultant catalyst. The outstanding activity retention and robust structural stability of MoP@Mn_{SAC}-NC are attributed to the graphitized nanocarbon framework with excellent oxidation resistance and the strong interactions between the MoP and the Mn_{SAC}-NC.



Figure 3. ORR performances of catalysts in 0.1 M KOH. (a) CV curves in N₂/O₂ saturated electrolytes. (b) Background-corrected ORR polarization curves (rotation rate: 1600 rpm). (c) Comparisons about MA and $E_{1/2}$ of electrocatalysts. (d) Tafel slopes. (e) Activity comparison of MoP@Mn_{SAC}-NC with many representative electrocatalysts. (f) Cdl results. (g) ORR polarization curves of MoP@Mn_{SAC}-NC at different rotating sweeps (inset shows the fitted K-L plots). (h) H₂O₂ yield and electron transfer number. (i) *i-t* curves of catalysts (inset shows polarization curves before and after 1000 CV cycles over MoP@Mn_{SAC}-NC).

To further elucidate the factors contributing to enhanced activity upon spin tuning, the key reactive species involved in the ORR over MoP@Mn_{SAC}-NC and Mn_{SAC}-NC catalysts were monitored using in situ Fourier transform infrared absorption (FTIR) in O₂ saturated 0.1 M KOH at differing applied potentials. In the spectra of both catalysts, the bands at ≈ 1043 cm⁻¹ can be reasonably assigned to the O–O bending mode of surface-adsorbed $*O_2$ (Figure 4a).^[37] Notably, the bands slightly increase in intensity with decreasing potential, indicating that O2 undergoes rapid adsorption and transformation on the surfaces of two catalysts. Additionally, an absorption band at \approx 1220 cm⁻¹ can be attributed to O-O stretching vibration of *OOH.^[38] For MoP@Mn_{SAC}-NC, this band related to *OOH appears when a potential of 0.8 V is applied, whereas, for Mn_{SAC} -NC, it appears at 0.7 V (Figure 4a). The peak intensity significantly increases with the applied potential, indicating the *OOH intermediates are gradually accumulated over both MoP@Mn_{SAC}-NC and Mn_{SAC}-NC catalysts. Such a phenomenon confirms the sluggish kinetics in the dehydroxylation process from *OOH to *O (*OOH + $e^- \rightarrow *O + OH^-$).^[39] Unexpectedly, the bands assigned to adsorbed hydroperoxide (typically at 1386 cm⁻¹) are not explicitly detected, indicating that virtually no H₂O₂ is adsorbed on the surface of the Mn single-atom catalyst under all potential conditions. Consequently, this reduces the damage caused by H₂O₂ accumulation and ensures the longlasting performance of the catalytic system.^[40] To further investigate the differences in the reaction process of the two catalysts, we compared the peak intensities of $*O_2^-$ and *OOH at various potentials with corresponding peak intensities at 1.0 V (Figure 4c,d). The results show that as the applied potential decreases, the adsorption intensity of *O₂⁻ and *OOH on MoP@Mn_{SAC}-NC is significantly lower than that on Mn_{SAC}-NC, reflecting that Mn active center with HS exhibits a more efficient capacity in handling $*O_2^-$ and *OOH active intermediates.

Potential-dependent in situ Raman spectra of MoP@Mn_{SAC}-NC and Mn_{SAC}-NC were measured in an O₂-saturated alkaline medium to offer direct surface-bonding information of oxygencontaining intermediates during the ORR process (Figure 4b). The band located at ≈ 1175 cm⁻¹ can be ascribed to the O–O stretching vibration of the superoxide anion O2- species adsorbed on active center $(*O_2^{-})$.^[41] The other band, at 1478 cm⁻¹,

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Figure 4. Intermediate species tracking and catalytic mechanism deciphering. (a) In situ FTIR spectra of MoP@Mn_{SAC}-NC (left) and Mn_{SAC}-NC (right). (b) In situ Raman spectra of MoP@Mn_{SAC}-NC (left) and Mn_{SAC}-NC (right). The corresponding infrared signal fluctuations of (c) $*O_2^-$ and (d) *OOH at various potentials. In situ EIS measurements of (e) MoP@Mn_{SAC}-NC and (f) Mn_{SAC}-NC. (g) Summary of the R_{ct} and R_{mt} values in the mixed-diffusion region.

is ascribed to *OOH adsorbed on the catalytic surface.^[1b] Notably, for MoP@Mn_{SAC}-NC, the Raman peak associated with *O₂⁻ disappears at 0.6 V, while the *OOH signal emerges at 1.1 V. In contrast, the *O₂⁻-related peak in the spectra of Mn_{SAC}-NC remains evident at 0.5 V, and the *OOH signal appears at 1.0 V. The more positive transition potential confirms that the HS Mn–N₄ sites in MoP@Mn_{SAC}-NC significantly accelerate the transformation of O₂ and intermediates.

To further elucidate the kinetic and mass transport characteristics of the MoP@Mn_{SAC}-NC and Mn_{SAC}-NC catalysts over the electrode surface, in situ electrochemical impedance spec-

troscopy (EIS) was performed in an O₂-saturated 0.1 м KOH electrolyte across the potential range of 0.40 to 1.20 V.^[42] The classical ORR process can be divided into three regions, the kinetic region (≈1.05–1.20 V), the mixed-diffusion region (≈0.80–1.00 V), and the mass transport region (≈0.40–0.70 V).^[43] This process involves multiple steps of oxygen-containing species adsorption and transport on the catalyst's active sites, which is assessed through fitting parameters of the charge transfer impedances (R_{ct}) and mass transfer impedances (R_{mt}).^[44] According to previously reported work, two semicircles were fitted in the high-frequency and low-frequency regions of the Nyquist plot,

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identified as the charge transfer and diffusion process, respectively. Therefore, a feasible fitting model based on the equivalent circuit was proposed to extract the various charges and mass transfer impedances of the catalyst layers (Figure S31).^[45]

The fitted EIS of MoP@Mn_{SAC}-NC and Mn_{SAC}-NC under various bias conditions are depicted, and all corresponding data are summarized in Table S4. Specifically, in the kinetic region (1.05-1.20 V), the high potential results in a sluggish reaction rate. Therefore, the slow electron transfer is considered the primary limiting factor. At 1.20 V, the MoP@Mn_{SAC}-NC and Mn_{SAC}-NC catalysts exhibit large R_{ct} values of 33.74 and 41.94 Ω , respectively (Figures S32a and S33a). As the applied potential decreases, the $R_{\rm ct}$ values of both catalysts gradually reduce to 31.57 and 38.36 Ω at 1.05 V, respectively. Conversely, the R_{mt} values show an increasing trend with more negative applied potentials, which can be attributed to the accumulation of reactants on the electrode surface. In the mixed-diffusion region (0.80-1.00 V), oxygenated reactants diffuse to the active sites and rapidly convert. This is evidenced by the significant reduction in R_{mt} for the MoP@Mn_{SAC}-NC (from 21010 to 1208 Ω) and Mn_{SAC}-NC catalysts (from 8828 to 849 Ω) (Figures S32b and S33b). Simultaneously, the R_{ct} for both catalysts also decreases significantly. These findings indicate that the decrease in potential enhances the electron transfer rate, thereby promoting the rapid conversion of adsorbed species on the electrode surface (Figure 4e-g). In the mass-transport region (0.40-0.70 V), the reaction on the electrode surface is very fast, in which reactants reach the electrode surface and rapidly transform into products. Therefore, the primary limiting factor for the reaction is the convection and diffusion of the reactants. Consequently, as the potential decreases, the R_{mt} values for the MoP@Mn_{SAC}-NC and Mn_{SAC}-NC catalysts rapidly increase from 676 and 905 Ω to 3791 and 2039 Ω , respectively (Figures S32c and S33c). The above in situ EIS results reveal that the R_{ct} of MoP@Mn_{SAC}-NC is lower than that of Mn_{SAC}-NC at all potentials, while R_{mt} shows the opposite trend. We speculate that this may be due to the faster transfer rate of intermediates on MoP@Mn_{SAC}-NC, leading to substantial product accumulation.

Density functional theory (DFT) calculations were performed to better understand the regulation mechanism of the MoP structure on the electronic spin state and ORR activity at Mn-N₄ moiety. The corresponding atomic models, based on the conclusion of XAS, are shown in Figures S34 and S35. Specifically, the ideal composite model of MoP@Mn_{SAC}-NC was constructed by coupling the MoP model with the single-layer graphene model through specific interfacial Mo-N and Mo-P bonds, where the MoP species is adjacent to an isolated Mn–N₄ site. Besides, through structural optimizations on different MoP crystal planes anchored at the Mn-N-C, we determined that MoP@Mn_{SAC}-NC achieves its most stable configuration on MoP (101) plane, consistent with its dominant exposure in XRD (Figures S36 and S37). Next, the charge density difference is calculated to explore the electron transfer behaviors (Figure 5a). Compared to the pristine Mn–N₄ moiety, the incorporation of the MoP results in significant charge depletion at the central Mn sites. It suggests that EPSI via interfacial chemical bonds causes charge delocalization on the single Mn atom, inducing the rearrangement of the 3d orbital electrons, consistent with the experimental findings.

To get a thorough insight into the internal electronic properties, the density of states (DOS) of electrocatalysts

are analyzed.^[38] As depicted in Figure S38, Mn_{SAC}-NC possesses a partial DOS near the Fermi level resembling metallic behavior, possibly due to the introduction of P during the synthesis process. Compared to Mn_{SAC}-NC, MoP@Mn_{SAC}-NC exhibits significantly higher electronic states across the Fermi level, indicating enhanced electrical conductivity capability during the electrocatalytic process.^[22] Additionally, the d-band center of Mn in MoP@Mn_{SAC}-NC is upshifted and closer to the Fermi energy level compared with Mn_{SAC}-NC, suggesting it serves as highly active sites for adsorb oxygen intermediates (*O2, *OOH, *O, and *OH⁻) with improved electron-donation ability.^[33,46] To investigate the electronic configuration in the Mn 3d orbital of both MoP@Mn_{SAC}-NC and Mn_{SAC}-NC, the projected density of states (pDOS) for Mn-N₄ moiety was calculated. In Mn-N₄ configuration with D_{4h} symmetry, the five d orbitals of Mn exist in a quantized energy level, with electrons primarily residing in $d_{yz}-d_{xz}$, d_{xy} , d_{z}^{2} , $d_{x}^{2}-v_{y}^{2}$ orbits. From the pDOS of Mn²⁺, the Mn center in the Mn_{SAC}-NC system shows a $d_{xz}^2 - dyz^2 d_{xy}^1$, d_z^0 , $d_{x}^{0}^{2} - d_{y}^{2}$, configuration (S = 1/2) with a low spin state, whereas the spin state of the Mn center in the MoP@Mn_{SAC}-NC alters to a high spin state with a $d_{xz}^2 - d_{yz}^2$, d_{xy}^1 , d_{z}^2 , $d_{x}^1 - q_{yz}^2$, configuration (S = 5/2) as two electron in $d_{xz} - d_{yz}$ move up to the d_z^2 and $d_x^2 - \frac{1}{2}$ orbitals (Figure 5b,c). When the d_z^2 and $d_x^2 - \frac{1}{v}^2$ orbitals are partially occupied, they generally form anti-bond orbitals (σ * and π *) with reaction intermediates (RIs, i.e., *OOH, *O, and *OH), resulting in weaker Mnⁿ⁺-RI bond due to electrons filling in these orbitals, which promotes the transition of intermediates.^[7a,16] We first demonstrated that the Mn adsorption site exhibits the most favorable O2 adsorption energy, compared with that of N, C, and Mo sites (Figure S39). To obtain an in-depth understanding of the ORR mechanism, the free energy diagrams of the 4e⁻ ORR pathways are calculated at the Mn-N₄ center, including key intermediates of *OOH, *O, and *OH (where * denotes the adsorbed state) (Figure S40). At a potential of 0 V, all reaction steps from O₂ to OH⁻ are thermodynamically favorable, indicating each elementary step of ORR is spontaneous exothermic. Notably, the rate-determining step (RDS) for both MoP@Mn_{SAC}-NC and Mn_{SAC} -NC is the typical OH⁻ desorption step (*OH + $e^- \rightarrow OH^-$).^[8b,12b] The RDS energy barrier for MoP@Mn_{SAC}-NC is 0.72 eV, whereas the RDS energy barrier for Mn_{SAC}-NC is 0.41 eV, reflecting the easier desorption toward *OH intermediates is one of the factors contributing to the enhanced ORR activity (Figure 5d). The bond order theorem was applied to further elucidate the orbital interactions between the *OH and Mn sites on the surfaces of catalysts. By analyzing the $\chi^{-1}-T$ curve, the numbers of unpaired electrons in MoP@Mn_{SAC}-NC and Mn_{SAC}-NC are calculated as 3.41 and 1.32, respectively (Figure S41a). Under orbital interaction, the bond order between Mn sites and adsorbed state *OH is determined to be 1.5 for both catalysts. However, in the MoP@Mn_{SAC}-NC-*OH system, an extra electron occupies the σ * orbital with higher energy than the π^* orbital occupied by electrons from

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on the MoP@Mn_{SAC}-NC than on Mn_{SAC}-NC (Figure S41b,c).^[15a] Besides, the adsorption of O₂ is the first step for the initiation of the ORR mechanism, significantly contributing to catalytic activity.^[47] To gain a deeper understanding of this interaction, both the adsorption energy for O₂ in Mn site and the Crystal Orbital Hamilton Population (COHP) of Mn—*O₂ were calculated.

Mn_{SAC}-NC, thereby leading to more favorable *OH desorption

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Figure 5. Theoretical studies on the enhanced performance. (a) Top view of the charge density difference of MoP@Mn_{SAC}-NC and Mn_{SAC}-NC (The electron accumulation and depletion regions are indicated by yellow and cyan isosurfaces, respectively). Calculated pDOS and d orbital arrangement of Mn²⁺ for (b) MoP@Mn_{SAC}-NC and (c) Mn_{SAC}-NC. (d) Free energy profile of ORR. (e) Calculated absorption energies of the O₂ (left); COHP of the Mn–O bond (right) (inset shows an illustration of orbital interactions between 3d orbitals of Mn and π^* orbital of O₂). A schematic diagram of Mn spin-charge injection effect for *O₂ activation. Calculated COHP and DOS diagram of (f) MoP@Mn_{SAC}-NC and (h) Mn_{SAC}-NC with *O₂. Orbital interactions of *O₂ with (g) MoP@Mn_{SAC}-NC and (i) Mn_{SAC}-NC, respectively (major interaction between d_{xz}, d_{yz}, d_z², and π^* orbitals of *O₂).

As depicted in Figure 5e, compared to Mn_{SAC}-NC, MoP@Mn_{SAC}-NC exhibits optimized adsorption energies, encouraging the adsorption of O_2 on the catalyst surface. Furthermore, the corresponding integrated COHP for the Mn–O bonds of *O₂ intermediates displays a decreasing negative value, changing from -0.207~eV in $Mn_{SAC}\text{-}NC$ to -1.721~eV in MoP@Mn_{SAC}\text{-}NC, indicating a stronger interaction between Mn and O of *O2 intermediates in MoP@Mn_{SAC}-NC (Figure 5e and Figure S42). Furthermore, orbital interactions of *O₂ with catalysts are depicted in Figure 5f,h. According to the principle of symmetry conservation, the d_{xy} and $d_x^2 - \frac{2}{y}^2$ orbitals of Mn were omitted. Particularly, an additional electron fills in the σ bond produced between the partial electron-occupied Mn d_z² orbital of MoP@Mn_{SAC}-NC and the π^* orbital of the *O₂ compared with Mn_{SAC}-NC (Figure 5h,i), which improves the bond order between Mn sites and $*O_2$, which results in stronger bonding strength. Therefore, it can be concluded that high spin Mn^{2+} in MoP@Mn_{SAC}-NC is beneficial to the enhanced ORR activity by optimizing the *OH desorption and O₂ adsorption processes.

Considering the excellent ORR performance of MoP@ Mn_{SAC} -NC catalyst, we assembled it as an air cathode in a primary Znair battery (ZAB) to evaluate its efficiency in renewable energy devices (**Figure 6a**).^[48] As displayed in Figure 6b, MoP@ Mn_{SAC} -NC-incorporated ZAB delivers an open-circuit voltage (OCV) of 1.56 V, exceeding that of the Pt/C-based ZAB (1.54 V). Figure 6c illustrates the discharge curves of ZAB, where the maximum power density of MoP@ Mn_{SAC} -NC-based ZAB is 173 mW cm⁻², superior to that of Pt/C-based ZAB (119 mW cm⁻²). Impressively, MoP@ Mn_{SAC} -NC-based ZAB displays an outstanding OCV and power density compared with not only the reference Pt/C-counterpart but also previously reported devices (Figure 6d and Table S5). The improved performance indicates that the

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Figure 6. ZAB performance of MoP@Mn_{SAC}-NC catalyst as an air cathode. (a) Schematic diagram of the liquid-state ZAB. (b) OCV plots (inset shows photography of OCV of the liquid-state ZAB). (c) Discharge polarization curves and corresponding power density curves. (d) Comparison of OCV and power density for MoP@Mn_{SAC}-NC-based ZAB with state-of-the-art ZAB. (e) Charge-discharge cycle curves of liquid-state ZAB at a current density of 5 mA cm⁻² (inset: the curves at different time intervals). (f) Scheme of the solid-state ZAB. (g) Charge-discharge cycle curves of solid-state ZAB (@5mA cm⁻², inset: Photos of the OCV values at different bending angles of MoP@Mn_{SAC}-NC-based solid-state ZAB).

MoP@Mn_{SAC}-NC catalyst is capable of achieving sufficient efficiency to warrant its integration into ZAB. Furthermore, the long-term rechargeability of the MoP@Mn_{SAC}-NC-based battery is evaluated by continuous galvanostatic discharging/charging at a current density of 5 mA cm⁻². Remarkably, the MoP@Mn_{SAC}-NC+RuO₂-based ZAB exhibits a long lifespan of over 840 h with a scarcely fading charge-discharge voltage gap (ΔE) during operation (Figure 6e). In contrast, the ZABs assembled by MoP@NC, Pt/C, and Fe_{SAC}-NC show severe degradation after 118, 430, and 340 h operation, respectively (Figures S43 and S44). We quantitatively determined the Mn dissolution levels in the electrolyte after the prolonged MoP@Mn_{SAC}-NC-based ZAB operation to assess Mn leaching. The ICP-MS results revealed minimal Mn leaching (<46 ppm) from MoP@Mn_{SAC}-NC after continuous ZAB operation, confirming its robust structural stability. Furthermore, the Mn oxidation state experiences negligible alterations after an extended stability test, as evidenced by Mn 2p XPS spectra in Figure S45. To meet the demand for practical applications in flexible energy devices, a flexible solid-state

ZAB utilizing the MoP@Mn_{SAC}-NC-based cathode was also assembled. Figure 6f manifests the schematic fabrication of the solid-state ZAB, featuring Zn foil anode, MoP@Mn_{SAC}-NC cathode, and potassium hydroxide/polyvinyl alcohol (KOH/PVA) gel electrolyte. As seen in Figures S46 and S47, the OCV and the maximum power density of the MoP@Mn_{SAC}-NC-based solidstate ZAB are 1.53 V and 83 mW cm⁻², respectively, which are better than those of the Pt/C-based ZAB of 1.43 V and 45 mW cm^{-2} . After freezing at -25 °C for 24 h, the corresponding peak power densities of solid-state ZAB assembled with MoP@Mn_{SAC}-NC and Pt/C decrease to 56 and 27 mW cm⁻², respectively, which can be mainly ascribed to the significantly reduced ionic conductivity of electrolyte under low-temperature condition. Besides, the MoP@Mn_{SAC}-NC-based solid-state ZAB illuminated a red "GXNU" LED panel, revealing its good practical application prospects (inset of Figure S46). To investigate its flexibility, the as-fabricated MoP@Mn_{SAC}-NC-based solid-state ZAB was intentionally bent and twisted into different shapes. Surprisingly, it can be found that MoP@Mn_{SAC}-NC-based solid-state ZAB

maintained consistent voltage across varying bending angles (bent at 0, 45, and 90°), indicative of its superior flexibility and wearability (inset of Figure 6g). The galvanostatic discharge curves indicate that the MoP@Mn_{SAC}-NC+RuO₂-based solid-state ZAB shows a voltage plateau of \approx 1.04 V and a standing time as long as 12 h, illustrating its favorable structural stability (Figure 6g). Overall, these results confirm the potential of MoP@Mn_{SAC}-NC for practical energy device applications, spanning from conventional ZAB to flexible battery configurations.

3. Conclusion

In summary, we have regulated the spin state of atomically dispersed Mn sites by embedding MoP nanoparticles, thereby ameliorating the kinetics of ORR. The resulting MoP@Mn_{SAC}-NC catalyst exhibits exceptional ORR activity in alkaline electrolytes and advanced performance in liquid/solid-state ZABs. It is shown that the strong electronic phosphide-support interaction between the monodispersed Mn atoms with D_{4h} symmetry and MoP nanocrystals enables the spin electron filling in the d_{z^2} and $d_x^2 - v^2$ orbitals at the Mn active center. In situ techniques and theoretical calculations confirm a spin-state transition of Mn single atom from the LS to HS due to the involvement of MoP, which facilitates O2 adsorption and key intermediate *OH desorption. This work paves the way for optimizing single-atom catalysts, leading to the achievement of high-efficiency and stable catalysts for metal-air batteries and other renewable energy systems.

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.

Author Contributions

Z.L. contributed to conceptualization and wrote the original draft. J.X. conducted investigation. J.C. also conducted investigation. F.W. curated data. S.L. carried out investigation. J.Z. performed investigation. X.S. participated in investigation. X.Y. acquired funding and supervision.B.W. contributed to conceptualization, reviewed the manuscript, and supervised the work. Z.J.X. reviewed and edited the manuscript. The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Mn single atoms, phosphide-support interaction, spin state modulation, oxygen reduction reaction, Zn-air batteries

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