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Enhancing Bifunctionality of CoN Nanowires by Mn Doping for Long-lasting Zn-Air Batteries

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Tailoring the nanostructure and composition of transition metal nitrides is highly important for their use as potent low-cost electrocatalysts. Cobalt nitride (CoN) exhibits strong catalytic activity for oxygen evolution reaction (OER). However, its poor catalytic efficiency for oxygen reduction reaction (ORR) hinders its application in rechargeable zinc-air batteries (ZABs) as the air cathode. In this work, we deploy the effective strategy of Mn doping to improve both OER and ORR activity of CoN nanowires as the cathode material for ZAB. Theoretical calculation predicts that moderate Mn doping in cobalt nitride results in a downshift of the *d*-band center and reduces the adsorption energy of reaction intermediates. With ~10 at. % Mn dopants, stronger catalysis activities for both OER and ORR are achieved compared to pure CoN nanowires. Subsequently, both aqueous and flexible quasi-solid-state ZABs are constructed using the Mn-doped CoN nanowires array as additive-free air cathode. Both types of devices present large open circuit potential, high power density and long-cycle stability. This work pushes forward the progress in developing cost-effective ZABs.

Bifunctional electrocatalyst, Zn-air battery, oxygen reduction reaction, flexible battery, plasma processing

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1 Introduction

Rechargeable Zinc-air batteries (ZABs) have gained numerous attractions and are considered as one of the promising energy storage and conversion devices due to their high theoretical specific energy (820 mAh g⁻¹ and 5855 mAh cm⁻³), safety and low-cost.[1-4] Despite the great potential,

several obstacles remain on the road to practical application even after decades of extensive research. Limited energy conversion efficiency and short lifetimes are two of major bottlenecks, which mainly originate from the sluggish oxygen reactions on air cathode and their poor stability in harsh alkaline electrolytes. Pt-based and Ir/Ru-based materials have been regarded as the best active catalysts for ORR and OER, respectively.[5, 6] However, neither of them can simultaneously drive both OER and ORR efficiently for met-

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al-air batteries.[2] Tri-electrode configuration could address this issue but it makes the structure of ZABs device complex.[7-9] In addition, the scarcity and inferior stability of these noble metal-based catalysts in ZABs also made them unattractive. Hence, the development of low-cost and high-efficiency bifunctional electrocatalysts is of great importance and urgency for ZABs to make them more practically feasible.

Up to now, non-noble transition metal (Fe, Co, Ni, Cu and Mn) oxides and hydroxides have been widely evaluated for OER and/or ORR.[10-16] Among these transition metal oxides/hydroxides, Co_3O_4 has several advantages, such as earth abundance, cost effectiveness, and is considered as one of the most attractive bifunctional catalysts.[17, 18] Nevertheless, the current catalytic performance of Co_3O_4 is still far from satisfactory. In addition to engineer the morphology and hybridization with other additives (which indeed benefits the charge transfer), it is more meaningful to tailor the intrinsic catalytic activity of active sites. Replacing all or partial oxygen atoms in Co_3O_4 lattice by non-metal heteroatoms (B, N, S, P, etc) or oxygen vacancies have proven effective in enhancing its OER performance, which even outperforms the state-of-art IrO_2 catalyst.[19-24] For instance, CoN nanowire arrays OER electrode that was previously reported by us can reach 10 mA cm^{-2} at the overpotential of 290 mV in 1M KOH.[21] However, its ORR catalytic activity is still inferior after the introduction of non-metal heteroatoms. In order to achieve bifunctionality, synergy is a potent approach and has been widely implemented in various electrocatalysis systems. MnO_x was considered as a promising ORR catalyst except for its poor electronic conductivity.[25, 26] It has also been confirmed by Prof. Abruna via in-situ X-ray absorption spectroscopy (XAS) that $\text{Co}^{+2/3}$ and $\text{Mn}^{+2/3/4}$ redox couples could serve as coactive sites to synergistically catalyze ORR.[27] Hence, it should be a judicious strategy to develop a bifunctional catalyst by optimizing the synergy of Co and Mn elements in one material system.

Inspired by intrinsic catalyst activity enhancement by Co and Mn synergy, herein, we introduced Mn doping into CoN to significantly improve its OER, particularly the ORR activity, towards applications in Zn-air battery full devices. First, density functional theory (DFT) calculations verify that indeed Mn doping can evidently enhance the intrinsic ORR/OER activity of Mn-doped CoN compared to the undoped sample by modulating the adsorption energy of intermediates. Our experiments confirmed the prediction and further achieved an optimal atom ratio of Mn:Co as ~1:9 to reach the best bifunctional catalytic performance. Based on this success, both aqueous and quasi-solid-state ZABs are assembled using the Mn-doped CoN nanowire arrays as air cathode material. The devices show robust cyclic performance up to 100 h. The flexible ZAB displays excellent cycling durability with a stable discharge voltage as high as 1.15 V under different bending conditions, suggesting a

promising application in wearable electronics.

2 Results and discussion

Figure 1. Thermodynamics of the Mn doping effect by first-principle calculation. a) Optimized atomic configurations of OOH, O, and OH intermediates adsorbed on the active sites (*) in Mn-doped CoN surface. b) Comparison of partial density of states (PDOS) of Mn-doped CoN and undoped CoN. c) Free energy diagrams at 1.23 V for ORR on pristine Co_3O_4 , CoN and Mn-doped CoN.

A series of DFT calculations are performed in advance to predict whether the Mn dopants can thermodynamically modify the intrinsic catalytic activity of CoN for OER/ORR by adjusting the electronic structure. Bare CoN and Co_3O_4 are also considered for comparison to identify the critical role. Similar to the common practice in literature,[28-30] our calculations do not consider the surface oxidation during the electrochemical measurement as it is a huge challenge to include an approximately 5 nm thick oxide layer in the model, and the in-situ oxidation is most likely a dynamic process. There are four elementary steps during the process, for both ORR and OER. The ORR proceeds through the formation of *OOH, *O, and *OH (*denotes the active site) and the OER occurs in the reverse direction. Optimized adsorption of reaction intermediates is the key to good reactivity of both OER and ORR.[31] Our calculations show that the most energetically favorable adsorption site for intermediates is the Mn dopant on the Mn-CoN surface (Figure 1a). The density of state calculations reveal that the Mn dopant effectively tunes the *d*-band structure of CoN, resulting in a downshift of the *d*-band center from -1.54 to -1.67 eV. Based on the *d*-band theory[32, 33], this downward shift in Mn-CoN hybrid is favorable to OER/ORR reactions, since the downshift of *d*-band results in more antibonding states below the Fermi level, and lead towards an optimal adsorption of intermediates. According to the calculated free energy diagram (Figure 1c), Co_3O_4 exhibits the most negative free energy, suggesting the strongest chemi-

cal adsorption of oxygen-containing reactants, and subsequently a sluggish reaction kinetic. In comparison, when Mn and N dopants are introduced, all reaction barriers are largely reduced, especially for the Mn-CoN. For CoN in OER catalysis, the rate-determining step (RDS) is the oxidation of $\ast\text{O}$ to $\ast\text{OOH}$ with the limiting barrier of 2.68 eV, whereas the largest uphill barrier further decreases to 1.68 eV for Mn-CoN and the RDS changes to be adsorption of $\ast\text{OH}$. Regarding the OER, a similar analysis of the energy simulation indicates the favorable kinetic properties on Mn-CoN. These computational results reveal that the Mn-doped cobalt nitride with a moderate content of Mn should be able to enhance its bifunctional catalytic activity. In this study, a series of Mn-CoN nanowire array samples with different Mn contents were synthesized by a general hydrothermal growth of doped Co_3O_4 nanowires which were then converted to nitrides by N_2 -plasma treatment. RF plasma has been demonstrated as an efficient tool for rapid surface conversion reaction.[21, 34, 35] To introduce the Mn dopant, certain volume of 0.1 M $\text{Mn}(\text{NO}_3)_2$ was added into the hydrothermal solution for cobalt nanowire array precursor (the synthesis details were described in Supporting Information). In the following context, samples are labeled as Mn-CoN-X (1, 1.5 and 2) with X being the volume in mL of 0.1 M $\text{Mn}(\text{NO}_3)_2$. After the introduction of Mn, there was no obvious change in morphology (Figure S1). The oxide nanowires uniformly grew on the carbon cloth with a quasi-vertical alignment, and the diameter of the nanowires is in the range of 50 – 100 nm. In addition, no other additional Mn phase can be observed from the XRD patterns in Figure S2; All peaks are indexed to Co_3O_4 (PDF 14-1467).

Figure 2. Morphology and characterization of Mn-CoN-1.5. a) XRD patterns for Co_3O_4 , Mn- Co_3O_4 -1.5 and Mn-CoN-1.5; b) SEM image; c) low- and d) high-magnification TEM images; e) HAADF-STEM image and the corresponding EDX maps for Co, Mn and N.

After 1 min N_2 -plasma treatment, all peaks are indexed to CoN (PDF 16-0116), indicating that samples have been fully converted into nitrides (Figure 2a). The nanowire array morphologies were overall preserved with slight twisted tips

due to the processing by N_2 plasma (Figure 2b and Figure S3). The diameter of the plasma processed nanowires is about 50-80 nm. The lattice fringes of 0.248 and 0.213 nm in Figure 2d can be indexed to (111) and (200) planes of the cubic CoN phase, respectively. Co, Mn and N elements are uniformly distributed within the nanowire, according to the energy dispersive X-ray (EDX) maps (Figure 2e), which confirms the Mn incorporation. According to the EDX analysis, the atomic ratio of Mn/Mn+Co for Mn-CoN-1, Mn-CoN-1.5 and Mn-CoN-2 was determined to be about 7.7, 10.3 and 14.7%, respectively (Figure S4 and Table S1). X-ray photoelectron spectroscopy (XPS) measurements were conducted to characterize the chemical compositions and surface chemical states of all samples. The XPS survey spectra in Figure 3a confirm the co-existence of Co, Mn and N elements and the Mn/Mn+Co atomic percentages of Mn-CoN-1, Mn-CoN-1.5 and Mn-CoN-2 were determined to be around 6.80%, 9.15% and 14.5%, respectively, which is also in agreement with the above results of TEM-EDX (Table S1). Figure 3b displays the high-resolution Co 2p spectra of Mn-CoN-1.5 and Mn- Co_3O_4 -1.5. After the N_2 plasma treatment, a new peak appears at 778.9 eV indicating the formation of the covalent bond (Co-N). The peaks at 781.0 and 796.9 eV are both attributed to the cobalt (oxy)hydroxide, which may originate from the inevitable surface oxidation in ambient condition. In Figure 3c, the peak of Mn 2p for Mn-CoN-1.5 shows a negative shift by ~ 0.7 eV compared with that of Mn- Co_3O_4 -1.5, corroborating the formation of Mn^{3+} and Mn-N bond[36]. For the N 1s spectrum in Figure 3d, the broad peak at 397.4 eV is assigned to the N peak in a metal nitride environment and the weak peak at 399.4 eV is attributed to the bond of C-N, which is formed due to carbon fibers' exposure to N-plasma.[37]

Figure 3. Survey analysis by XPS. a) Survey spectra of CoN, Mn-CoN-1, Mn-CoN-1.5, Mn-CoN-2; High-resolution XPS spectra of b) Co 2p, c) Mn 2p and d) N 1s of Mn- Co_3O_4 -1.5 and Mn-CoN-1.5.

We conducted electrocatalysis characterizations for both

OER and ORR for all samples in order to evaluate the effect of Mn doping. The OER test was conducted in 0.1 M KOH aqueous solution with a typical three-electrode setup. The linear sweep voltammograms (LSVs) in Figure 4a confirm that the performance of metal nitrides is better than that of corresponding oxides. And the OER performance of both oxides and nitrides is improved after introducing Mn dopants. Mn-CoN-1.5 displays the most negative overpotential to reach the current density of 10 mA cm^{-2} (η_{10}) of 390 mV than of CoN (423 mV), Mn-Co₃O₄-1.5 (434 mV) and Co₃O₄ (445 mV). This value is also better than the commercial OER catalyst IrO₂ (410 mV). The optimized Mn dopant content was deduced by comparing the electrocatalytic activity of a series of samples with different amount of Mn precursor added into the hydrothermal growth (see Figure S5). A higher doping level (Mn-Co₃O₄-2) results in a larger overpotential than the Mn-CoN-1 and Mn-CoN-1.5 samples. This is probably caused by the worse electronic conductivity of the CoN matrix with more Mn, which is confirmed in the following impedance tests. Moreover, Tafel slopes of all samples were also studied to reveal the OER mechanism (Figure 4b). The Tafel slope of Mn-CoN-1.5 is 57.5 mV dec^{-1} , which is smaller than that of CoN (61.1 mV dec^{-1}), Mn-Co₃O₄-1.5 (68.5 mV dec^{-1}) and Co₃O₄ (74.9 mV dec^{-1}), implying the favorable OER kinetics of Mn-CoN-1.5.

Figure 4. The bifunctional electrocatalysis. a) LSV curves and b) Tafel slopes for OER. c) CV curves in N₂-saturated and O₂-saturated 0.1 M KOH electrolyte and d) LSV curves in O₂-saturated 0.1 M KOH at 1600 rpm for ORR. Stability test of Mn-CoN-1.5 for e) OER at 10 mA cm^{-2} and f) ORR at $\eta_{1/2}$.

It should be noted that, while the calculation is conducted on pure CoN, the CoN nanowires may be partially oxidized during the electrochemical OER measurement to form a thin layer of cobalt hydroxide or oxyhydroxide, which was clearly characterized in our previous study.[21] Such a surface oxidation is inevitable for most metal chalcogenides and nitride materials, and the formed MOOH group on the surface may be the active sites for OER. However, we believe the original material (CoN herein) still contribute to the electrocatalytic process by involving in the charge transfer with the reactants.[38-40]

Aside from the enhanced OER performance, it is expected by theoretical calculation that Mn doping can also modify the ORR performance of CoN. The working electrodes were fabricated by directly attaching the nanowires array grown on carbon cloth on a glassy carbon electrode. Cyclic voltammogram (CV) measurements were first conducted in N₂- and O₂- saturated solution of 0.1 M KOH. Figure 4c shows that, compared with the featureless CV curves in N₂-saturated solution, every electrode displays a distinct cathodic ORR peak at potentials between 0.7-0.9 V vs RHE in the O₂-saturated solution. This verifies their evident ORR electrocatalytic activities. In particular, the Mn-CoN-1.5 electrode exhibits the highest catalytic activity, in term of the most positive onset potential. Again, it was confirmed from a series of control samples that the Mn-CoN-1.5 has the optimal Mn doping level (Figure S6). In addition, the ORR performance was also compared by rotating-disk electrode (RDE) tests at 1600 rpm. Figure 4d shows that Mn-CoN-1.5 exhibits an onset overpotential of $\sim 0.9 \text{ V}$ (vs. RHE), which is higher than that of Co₃O₄ ($\sim 0.83 \text{ V}$), Mn-Co₃O₄-1.5 (0.85 V) and CoN (0.87 V), and also comparable to the commercial ORR catalysts Pt/C ($\sim 1 \text{ V}$). At the same time, Mn-CoN delivers a larger ORR saturating current density of 15.9 mA cm^{-2} (based on the geometrical area), indicating its potential for practical application. The half-wave potential ($E_{1/2}$) on the ORR curve is another important parameter to assess the activity of a catalyst. The more positive of $E_{1/2}$ means the more active of a catalyst. The $E_{1/2}$ of Mn-CoN-1.5 is 0.65 V , which is more positive than that of Co₃O₄ ($\sim 0.53 \text{ V}$), Mn-Co₃O₄-1.5 (0.56 V) and CoN (0.61 V). The reversible oxygen electrode can be assessed by the potential gap ΔE ($\Delta E = 1.23 \text{ V} + \eta_{10} - E_{1/2}$). [41, 42] The Mn-Co₃O₄-1.5 shows the smallest gap (0.98 V) than others (Co₃O₄: 1.15 V ; Mn-Co₃O₄-1.5: 1.05 V and CoN: 1.10 V). The above results imply that an appropriate amount of Mn doping makes CoN a potent bifunctional electrocatalyst for both ORR and OER.

The stabilities of Mn-CoN-1.5 electrode for the OER and ORR were also examined by constant current and constant potential measurements, respectively. Figure 4e shows that the Mn-CoN-1.5 electrode exhibits very stable catalytic activity without significant increase in overpotential after 10 hours test at the current density of 10 mA cm^{-2} . Continuous

oxygen reduction on Mn-CoN-1.5 was carried out at 0.65 V vs RHE ($\eta_{1/2}$) and only ~12% decrease in current density is observed after 10000 s (Figure 4f). Hence, it can be concluded that an appropriate amount of Mn doped in CoN can significantly improve its catalytic activity toward both ORR and OER.

Next, it would be worth identifying the source of the enhanced performance: is it a result of Mn doping effect or other extrinsic reasons? First thing to check is the electrochemical specific surface area (ECSA). From typical scan-rate-dependent CV curves (Figure S7a-d), we plotted the capacitive current at 1.13 V (vs. RHE) as a function of scan rate to extract the double layer capacitance (C_{dl}) from the slopes of fitting lines. While the current density during CV tests increased with the increasing contents of Mn, the fitting lines are nearly parallel to each other (Figure S7e), which indicates that Mn doping has little influence on the ECSA of the CoN nanowires. Secondly, the electrode kinetics were evaluated by electrochemical impedance spectroscopy (EIS) (Figure S8). It is found that the resistance of solution (R_s) for each sample is nearly the same but the charge transfer resistance (R_{ct}) increases gradually with increasing content of Mn, from 24 Ω of CoN to 27.5 Ω of Mn-CoN-2. Increase in electric resistance is unfavorable for the catalytic activities. Based on ECSA and EIS results, we can infer that the improved OER/ORR performance by Mn doping should be mainly attributed to the enhancement of the intrinsic catalytic activity of electrode, which is in accordance to theoretical calculation discussed earlier.

Figure 5. Performance of rechargeable ZAB devices. a) Schematic of the aqueous ZAB using Mn-CoN-1.5 as the air-cathode. b) Open circuit voltage of Mn-CoN-1.5 and 20% Pt/C cathode ZABs (upper two branches). Also shown (bottom two branches) are discharge curves of the Mn-CoN-1.5 cathode ZAB at the current density of 5 and 20 mA cm⁻². c) Polarization curves and corresponding power-density plots of ZABs using Mn-CoN-1.5 and 20% Pt/C as the air electrode catalysts. d) Photograph of an electric

fan powered by one ZAB (see also Movie S1 in Supplementary Information). e) Cycling performance of aqueous ZAB at 5 mA cm⁻². Insets are selected discharge-recharge profiles at different times. f) Discharge polarization curve and power-current density curve of flexible quasi-solid-state ZAB (See also Movie S2 in Supplementary Information). g) Mechanical flexibility and stability tests of the flexible quasi-solid-state ZAB at a charge/discharge current density of 2 mA cm⁻². Insets are the photos of the flat and folded state of the device.

After the separated evaluation for OER and ORR dual functions, we now further test its practical application in ZAB full cell. For this purpose, ZAB was assembled using Mn-CoN-1.5 directly as the air cathode and a zinc plate as the anode in 6 M KOH+0.2 M Zn(Ac)₂ electrolyte solution (schematically shown in Figure 5a). For comparison, the 20% Pt/C cathode ZAB was also assembled and tested under the same conditions. Figure 5b shows that the open-circuit voltage (OCV) of Mn-CoN-1.5 based ZAB is 1.55 V, which is slightly better than that of the Pt/C ZAB (1.46 V). The higher OCV of Mn-CoN-1.5 based ZAB than the Pt/C one could be attributed to the zinc-ion reaction with Mn-CoN-1.5.[43, 44] This is also indicated by the slope before reaching a stable plateau at a small discharge current density of 5 mA cm⁻² (Figure 5b). The discharge plateau of Mn-CoN-1.5 decreases by only 0.15 V from 1.19 to 1.04 V when the discharge current density increases from 5 to 20 mA cm⁻² (Figure 5b), which indicates its considerable rate capability. The cell achieves a peak power density of 53 mW cm⁻², which is 83 % of that using Pt/C as the air cathode (64 mW cm⁻², Figure 5c). The ZAB based on Mn-CoN-1.5 can power a small electric fan (Figure 5d, see also Movie S1). A rather stable discharge-recharge cycle behavior is also achieved (Figure 5e). Going to details, the battery shows an initial voltage gap of 0.802 V at 5 mA cm⁻² with a high round-trip efficiency of 59.3 %, which outperforms the Pt/C based ZAB (1.037 V, 53.1 %, Figure S9). Moreover, no obvious fading is observed after operating for 300 cycles (3000 min). As for the Pt/C-based ZAB, although the discharge platform is slightly high in the first few cycles due to its superior ORR activity, the voltage gap increases from 1.037 V to 1.257 V after 50 cycles and gradually to 1.372 V after 190 cycles (see Figure S9). At a higher current density (10 mA cm⁻²) and longer charge/discharge process (2 h per cycle), our Mn-CoN-1.5 based ZAB also exhibits quite stable cycling performance (Figure S10), which is comparable to the recently reported ZABs (Table S2). Hence, our ZAB fabricated from low-cost transition metal-based material can deliver comparable, or even better, battery performance to the most active noble metal materials (20% Pt/C) in the laboratory test. Scalability of the device and tests under near industry condition will be the future work.

Driven by the increasing demand for flexible and portable

electronic devices,[45] we also fabricated flexible ZABs by using the Mn-CoN-1.5 as air cathode, conductive polyacrylamide (PAAm) hydrogel (saturated with 6 M KOH +0.2 M Zn(Ac)₂) as electrolyte, and Zinc foil as anode. Because of relatively low ionic conductivity of hydrogel electrolyte, the discharge plateau of this quasi-solid-state battery is slightly lower compared with the aqueous one. After 1 h activation, a stable OCV as high as 1.37 V is obtained (Figure S11). As shown in Figure 5f, the maximum power density of the flexible ZAB is determined to be 48 mW cm⁻² at 0.71 V. As a proof-of-concept demonstration for practical applications, only one as-assembled flexible ZAB can power an electronic fan to work under different bending conditions (see Inset photo of Figure 5f; and Movie S2). Figure 5g shows that, after gradual increase of voltage gap in a few initial cycles due to the activation at the electrolyte-electrode interface, a stable discharge voltage around 1.15 V can be maintained without any obvious degradation in the following 20 h (the hydrogel tends to dry out during long run). Folding or bending does not affect the performance during the whole tests (Figure 5g), indicating its potential practical application for flexible devices.

3 Conclusions

In summary, cobalt nitride nanowires array with optimized Mn doping exhibit outstanding bifunctional activity for electrocatalysis of both OER and ORR, and is proven a high-performance additive-free air cathode material for ZAB. Both theoretical calculation and experiment results confirm that a moderate Mn doping (~10 at.% in this case) is efficient in regulating the dissociation and adsorption free energy between active sites and intermediates, thus leading to much enhanced ORR and OER bifunctional activities compared to the undoped nitride and Mn-doped cobalt oxide counterparts. Both aqueous and flexible quasi-solid-state ZABs fabricated with Mn-CoN-1.5 as the air cathode show high working potentials (1.55 and 1.37 V) and excellent cycling stability. The performance of our aqueous ZAB is compatible to the one based on commercial Pt/C cathode. This is highly promising to the advance of low-cost Zn-air batteries for future static energy storage and microelectronics.

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Conflict of interest The authors declare that they have no conflict of interest.

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Table of Contents graphic

A moderate content of Mn in CoN nanowire arrays can effectively modify their electronic structure, leading to enhanced ORR and OER bifunctional catalytic activities. The Mn-doped CoN (~10 at.%) nanowires exhibit outstanding performance as the air-cathode for both aqueous and quasi-solid electrolyte Zn-ion batteries.