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Research paper

Strengthening absorption ability of Co–N–C as efficient bifunctional oxygen catalyst by modulating the d band center using MoC

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Abstract

Co–N–C is a promising oxygen electrochemical catalyst due to its high stability and good durability. However, due to the limited adsorption ability improvement for oxygen-containing intermediates, it usually exhibits inadequate catalytic activity with 2-electron pathway and high selectivity of hydrogen peroxide. Herein, the adsorption of Co–N–C to these intermediates is modulated by constructing heterostructures using transition metals and their derivatives based on d-band theory. The heterostructured nanobelts with MoC core and pomegranate-like carbon shell consisting of Co nanoparticles and N dopant (MoC/Co–N–C) are engineered to successfully modulate the d band center of active Co–N–C sites, resulting in a remarkably enhanced electrocatalysis performance. The optimally performing MoC/Co–N–C exhibits outstanding bi-catalytic activity and stability for the oxygen electrochemistry, featuring a high wave-half potential of 0.865 V for the oxygen reduction reaction (ORR) and low overpotential of 370 mV for the oxygen evolution reaction (OER) at 10 mA cm−2. The zinc air batteries with the MoC/Co–N–C catalyst demonstrate a large power density of 180 mW cm−2 and a long cycling lifespan (2000 cycles). The density functional theory calculations with Hubbard correction (DFT+U) reveal the electron transferring from Co to Mo atoms that effectively modulate the d band center of the active Co sites and achieve optimum adsorption ability with “single site double adsorption” mode.

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Keywords: Bifunctional oxygen catalysts; Pomegranate-like shell; D band theory; Enhanced synergistic effect; Rechargeable zinc air battery

1. Introduction

Economical rechargeable zinc air batteries have attracted intensive attentions as advanced electrochemical energy devices due to the low cost [1], high safety [2], and desirable theoretical energy density [3,4]. For these battery systems, the oxygen electrochemistry, including oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), is considered to be the core process and the critical “bottleneck” [5] because its reaction kinetics predominantly determines the energy conversion efficiency [6,7]. Until now, precious metals or their oxides have been reported as the benchmark catalysts for the oxygen electrochemistry, but not the best candidates due to their high cost, poor cycling durability, and disappointing bifunctionality [8–10]. Therefore, it is imperative to explore desirable and cost-effective electrocatalysts with the bifunctional capability and long-term stability for the ORR and OER.
During the past decades, non-precious transition metal-based [11–14] and metal-free carbon materials [15,16] have been developed to be active for both the ORR and OER. Among them, transition metal-nitrogen-carbon (M-N-C) materials are highly regarded as alternative bifunctional catalysts to precious metal-based catalysts for massive practical applications, because of the synergistic co-doping effect between metal and nitrogen dopants [17–21]. Systematically theoretical calculations for the intrinsic catalytic activity of various M-N-C catalyst systems showcase a volcano-type plot with the activity order of Fe > Co > Cu > Mn > Ni, indicating that the Fe–N–C materials are supposed to the highest catalytic activity toward the oxygen electrochemistry [22–24]. Nonetheless, such Fe–N–C catalysts often display poor stability and durability due to the Fenton effect relating to complex reactions between iron and the major hydrogen peroxide hyproduct of the ORR [25–27]. In comparison, the Co–N–C catalysts can effectively alleviate the Fe-involved Fenton reaction and have been proved as appealing alternatives to precious metal-based catalysts for the oxygen electrochemistry of zinc air battery chemistry [28]. However, these Co–N–C catalysts intrinsically exhibit inadequate catalytic activity with a 2-electron ORR pathway and high selectivity of hydrogen peroxide [29–31] due to the limited absorption ability of the oxygen-containing intermediates [32]. Therefore, it is essential to improve the adsorption performance of the oxygen-containing intermediate to improve electrochemical performance. The metal–oxygen bond variation between the active metal sites and oxygen-containing intermediates depends mostly on the strength of the coupling between the oxygen 2p states and the metal d states, forming both bonding and antibonding states. According to the d band theory developed by Nørskov and coworkers [33], an upward shift of the d states of active metal with respect to the Fermi level could result in an upward shift of the antibonding states and less filling of these states, which bring about the strong bonding between active metal and oxygen-containing intermediates [34]. Consequently, the adsorption abilities of the active metal for the oxygen-containing intermediates are efficiently strengthened and, eventually, change the catalytic performance for the oxygen electrochemistry.

Herein, we strengthen the absorption ability of Co–N–C to achieve an efficient bifunctional oxygen catalyst by modulating the d band center using MoC. The MoC core as the oxygen cathode, the as-assembled zinc air battery chemistry [28] show that the as-prepared MoO3 nanobelts have a smooth surface with an average width of about 200 nm and a thickness of about 30 nm. The XRD pattern in Fig. S3a reveals the characteristic peaks which match well with the crystal structure of MoO3 (JCPDS no.35-0609). After overgrowth of ZIF67 onto the surface of MoO3, the core–shell MoO3@ZIF67 nanobelts present a rougher surface and a slightly larger average width than those of the pristine MoO3 nanobelt (Figs. S1b and S1c). The pristine ZIF67 was also synthesized for comparison using the same procedure, but without MoO3 core (Figs. S2 and S3). TEM images in Figs. S1d and S1e reveal the homogenous ZIF67 layer on the MoO3 surface and the obvious bright/dark contrast, which further indicates the successful fabrication of core–shell MoO3@ZIF67 nanostructures. The weak MoO3 diffraction peaks are also observed at 27.3°, 33.8°, and 39°, corresponding to the MoO3(021), MoO3(111), and MoO3(150) planes, respectively (JCPDS no. 35-0609), which verifies the MoO3 core. EDS line scan profiles in Fig. S1f present that the signal of Mo is mainly observed in the inner core region, and the signals of C, N, and Co are mostly detected in the full profile. These are in line with the result of EDS analysis in Fig. S5. In addition, as shown in Fig. S1g, The STEM-EELS element mapping shows higher densities of Mo and O elements at the center, while C, N, and Co elements are uniformly distributed across the whole area. All these results demonstrate the core–shell structural feature of MoO3@ZIF67 nanobelts.

MoO3@ZIF67 nanobelts were further subjected to the pyrolysis process at 600 °C in the N2 atmosphere (denoted as MoC/Co–N–C-600). As control experiments, MoC/Co–N–C-500 and MoC/Co–N–C-700 were also prepared at 500 °C and stability of up to 2000 cycles, and low discharge–charge voltage gap of approximately 0.71 V.

2. Results and discussion

As displayed in Scheme 1 of the heterostructured MoC/Co–N–C nanobelts synthesis process, the uniform layer of the Co-based zeolitic imidazolate framework (ZIF67) was firstly grown onto the surface of MoO3 nanobelts to form the fundamental core–shell MoO3@ZIF67 nanobelts. Then ZIF67 shell as the sources of Co, N, and C was directly carbonized at various temperatures to generate the pomegranate-like carbon shell composed of random Co nanoparticles and N heteroatoms. The MoC core was also in-situ formed by a simultaneous reduction reaction between MoO3 and carbon-containing shell. It should be noted that the C atoms of MoC core originate from the outer ZIF67 shell, therefore, there should exist a continuous carbon distribution from the pomegranate-like shell to the MoC core. This implies the seamless interconnection and the formation of strong coupling interaction between the MoC core and the pomegranate-like Co–N–C shell. Besides, the carbonized ZIF67 shell could generate high porosity, which is favorable for increasing the active sites and facilitating mass transportation during the electrocatalysis process.

The typical SEM and AFM images in Figs. S1a and S2 show that the as-prepared MoO3 nanobelts have a smooth surface with an average width of about 200 nm and a thickness of about 30 nm. The XRD pattern in Fig. S3a reveals the characteristic peaks which match well with the crystal structure of MoO3 (JCPDS no.35-0609). After overgrowth of ZIF67 onto the surface of MoO3, the core–shell MoO3@ZIF67 nanobelts present a rougher surface and a slightly larger average width than those of the pristine MoO3 nanobelt (Figs. S1b and S1c). The pristine ZIF67 was also synthesized for comparison using the same procedure, but without MoO3 core (Figs. S2 and S3). TEM images in Figs. S1d and S1e reveal the homogenous ZIF67 layer on the MoO3 surface and the obvious bright/dark contrast, which further indicates the successful fabrication of core–shell MoO3@ZIF67 nanostructures. The weak MoO3 diffraction peaks are also observed at 27.3°, 33.8°, and 39°, corresponding to the MoO3(021), MoO3(111), and MoO3(150) planes, respectively (JCPDS no. 35-0609), which verifies the MoO3 core. EDS line scan profiles in Fig. S1f present that the signal of Mo is mainly observed in the inner core region, and the signals of C, N, and Co are mostly detected in the full profile. These are in line with the result of EDS analysis in Fig. S5. In addition, as shown in Fig. S1g, The STEM-EELS element mapping shows higher densities of Mo and O elements at the center, while C, N, and Co elements are uniformly distributed across the whole area. All these results demonstrate the core–shell structural feature of MoO3@ZIF67 nanobelts.

MoO3@ZIF67 nanobelts were further subjected to the pyrolysis process at 600 °C in the N2 atmosphere (denoted as MoC/Co–N–C-600). As control experiments, MoC/Co–N–C-500 and MoC/Co–N–C-700 were also prepared at 500 °C and
700 °C, respectively. The typical SEM and TEM images in Fig. 1a–c show the one-dimensional structure of MoC/Co–N–C-600 nanobelts, but with a smaller width (300–400 nm) than that of pristine MoO$_3$@ZIF67 nanobelt (400–500 nm) due to the carbonization process. It is worth noting that the products obtained at 500 °C and 700 °C present the same morphologies as MoC/Co–N–C-600 nanobelts (Fig. S6). The corresponding selected area diffraction (SAED) pattern gives two sets of
diffraction patterns that are assigned to MoC (101), MoC (110), MoC (201), and Co (200), respectively (the inset of Fig. 1c, JCPDS no. 08-0384). Besides, the features of the pomegranate-like Co–N–C shell and the MoC core are clearly illustrated by the magnified TEM (Fig. 1d). The darker color MoC core is tightly wrapped by the lighter color pomegranate-like shell, suggesting the typical core–shell feature for MoC/Co–N–C-600 nanobelts. The high-resolution TEM (HRTEM) image in Fig. 1e indicates a carbon-wrapped Co nanoparticle with the interplanar distance of 0.202 nm of the Co (200) crystal planes. It should be noted that the pomegranate-like carbon shell is beneficial for protecting Co nanoparticles against the agglomeration and expediting electron transfer during the electrocatalysis reaction. Furthermore, a closer observation of the pomegranate-like carbon shell in Fig. 1f, nanoscale pores (highlighted by the dotted ovals) with an average diameter of less than 10 nm can be seen in the Co–N–C shell, which is of benefit to the mass transportation during electrocatalysis process. The STEM-EELS element mapping (Fig. 1g) of MoC/Co–N–C-600 nanobelt shows C, N, and Co elements, which uniformly distribute on the whole contour of nanobelt, along with a higher density of Mo signal at the core area. This confirms the core–shell feature and elemental compositions. Additionally, the EDS analysis as shown in Fig. S7 verifies the existence of Mo, Co, N, and C elements in MoC/Co–N–C-600 nanobelts. All these elements are also observed in MoC/Co–N–C-500 nanobelts and MoC/Co–N–C-700 nanobelts (Figs. S7–S9).

The XRD pattern of MoC/Co–N–C-600 nanobelts as shown in Fig. 2a presents the characteristic peak of MoC at around 37.3° (JCPDS no. 08-0384) as well as the diffraction peaks of graphitized carbon and the diffraction peaks of metallic Co, which is consistent with the result of SAED investigation. In contrast, MoC/Co–N–C-500 and MoC/Co–N–C-700 products respectively exhibit the diffraction peaks of CoMoO₄ (denoted by ▼) and the peaks of Mo₂C (denoted by #), except the diffraction signals of the metallic Co and graphitized carbon. These can be attributed to the inadequate reduction and the excessive reduction for the MoO₃ core. Note that the peaks of the C (002) plane in all samples are observed and shown in the low-angle XRD patterns (Fig. S10). Fig. 2b showcases the Raman spectra of three samples indicate the characteristic G and D bands at approximately 1350 cm⁻¹ and 1595 cm⁻¹, respectively, which are attributed to the graphitic sp²-carbon and the defect or disordered carbon. Intensity Ratio (I_G/I_D) values of the different products increase with the elevating of pyrolysis temperatures, suggesting the decreased density of disordered or defect carbons and the improved graphitization.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the effect of the annealing temperatures on the surficial valence states and compositions in the samples. Survey XPS spectra reveal the co-existence of C, N, O, Co, and Mo elements in all the corresponding products (Fig. S11). The high-resolution C 1s spectra reveal three deconvoluted peaks corresponding to C=C, C≡N, and C=0 for all three samples (Fig. S12). The proportion of the surficial sp²-carbon was calculated and shown in Table S1. For all as-prepared samples in Fig. 2c, Co 2p₃/2 XPS spectra of the as-prepared samples manifest three spectral features, both the main peaks and the small peaks in magenta curves are assigned to Co⁹ species [35]. The sub-peaks in blue curves is corresponding to Co⁷⁺ species due to the partial oxidation of the metallic Co, which is in well agreement with previous observation for Co–N moiety (782–783 eV) [36–38]. In addition, for MoC/Co–N–C-600, the positions of the binding energy of Co⁷⁺ sub-peaks displays a more positive shift (783.1 eV) compare to MoC/Co–N–C-500 and MoC/Co–N–C-700 (782.6 eV). It is probably attributed to the coupling between the Co–N–C shell and the MoC core since MoC was observed only for MoC/Co–N–C-600 (Fig. 2a). This positive shift is also observed in the N 1s spectrum of MoC/Co–N–C-600 nanobelts (Fig. 2d). Moreover, the N 1s spectra display two main peaks indicated by magenta color lines and blue color lines, which are assigned to pyridinic N and pyrrolic N, respectively, indicating the co-existence of the different nitrogen species in the carbon shell. It is most noteworthy that the atomic percentage of pyridinic N of MoC/Co–N–C-600 nanobelts approaches approximately 42.6%, which is higher than those in MoC/Co–N–C-500 and MoC/Co–N–C-700 (Table S1). It is widely accepted that the pyridinic N, rather than the pyrrolic N, is favorable for serving as the active sites for the oxygen electrochemistry [39]. The dual-site mechanism has demonstrated the synergistic coupling between Co, C, and N that facilitates the reduction of oxygen to peroxide and further transformation to OH⁻ at the active Co–N sites [40]. Moreover, as shown in Fig. 2e, Mo 3d₅/₂ XPS spectrum of MoC/Co–N–C-600 nanobelts exhibits a negative shift of binding energy of Mo⁶⁺ species, indirectly indicating the electronic interaction between Mo, Co and N. Fitted characteristic peaks suggest two valence states of Mo (Mo⁶⁺: magenta color line, Mo⁷⁺: royal color line), and the quantitative content analysis indicates the much larger proportion of Mo⁶⁺ on the surface of MoC/Co–N–C-600 nanobelts (Table S1). In terms of the electronegativity of Co (1.88) and Mo (2.16), the electron transfer would occur from Co to Mo that is responsible for the negative shift of binding energy. Therefore, the high-content Mo⁶⁺ with a high oxidation state can readily oxidize the metallic Co to the high-valence Co species, which is the respect with the more positive shift on the binding energy of Co⁷⁺ species in MoC/Co–N–C-600 nanobelts. High-valence-state Co has been proved as the electrocatalytic active sites for oxygen electrochemical processes. This implies that the interaction between Mo and Co would be in favor of high electrocatalytic performance.

The electrocatalytic ORR activities of MoC/Co–N–C–X nanobelts (X represents 500, 600, and 700) were first evaluated by cycle voltammetry (CV) measurements and comparing with commercial Pt/C catalyst. As shown in Fig. S13, no obvious reduction peaks are observed for all samples in the N₂-saturated electrolyte and the well-defined cathodic peaks are found in the O₂-saturated electrolyte, suggesting that all samples exhibit catalytic activity for the ORR. Notably, the CV curve of MoC/Co–N–C-600 nanobelts shows a more positive oxygen reduction peak, indicating its superior
electrochemical ORR activity to MoC/Co–N–C-500 and MoC/Co–N–C-700.

The ORR polarization curve of MoC/Co–N–C-600 nanobelts in Fig. 3a exhibits a much higher half-wave potential of $E_{1/2} = 0.865 \text{ V}$ and a larger diffusion-limited current density ($\approx 5.3 \text{ mA cm}^{-2}$), which are superior to the state-of-the-art Pt/C ($E_{1/2} = 0.850 \text{ V}, -4.8 \text{ mA cm}^{-2}$). The excellent electrocatalytic ORR activity of MoC/Co–N–C-600 nanobelts is further highlighted by the smallest Tafel slope (58.8 mV dec$^{-1}$) than that of commercial Pt/C (86.8 mV dec$^{-1}$, Fig. 3b). ORR polarization curves of MoC/Co–N–C-600 nanobelts were obtained at different rotating speeds for all the products (Fig. 3c and Figs. S13–S18). The corresponding Koutecky–Levich (K-L) plots of MoC/Co–N–C-600 nanobelts (inset of Fig. 4c) reveal good linearity that suggests the first-order reaction kinetics in terms of the concentration of dissolved oxygen and electron transfer number ($n$). The calculated $n$ value of MoC/Co–N–C-600 nanobelts is about 4 in the potential range from 0.3 V to 0.7 V, close to the value of Pt/C (Fig. S18b), implying a nearly-four-electron ORR pathway. Besides, as shown in Fig. 3d, MoC/Co–N–C-600 nanobelts produce lower H$_2$O$_2$ yield of <4% than that derived from the state-of-the-art Pt/C catalyst (3.0% 6.0%), and the calculated $n$ of MoC/Co–N–C-600 nanobelts is about 3.95, which is in good agreement with the results from the K-L plots. In contrast, the pure MoC catalyst exhibits a low electrochemical ORR activity (Fig. S14) with an electron transfer number of about 2, indicating the predominant 2e ORR process for the MoC catalyst. Furthermore, ZIF67-600 presents a much inferior electrocatalytic activity of the ORR (Fig. S18). These results confirm the synergistic effect between the pomegranate-like Co–N–C shell and MoC core, which is crucial to facilitating the oxygen electrocatalysis. Stability and durability are the critical indexes to assess the electrocatalytic performance of the catalyst. As shown in Fig. S19, MoC/Co–N–C-600 nanobelts show a slight degradation in half-wave potential before and after 1000 polarization cycles. Besides, MoC/Co–N–C exhibits a good methanol tolerance (Fig. S20a), and the chronoamperometric response at 0.6 V for 30,000 s suggests a negligible loss in the current density (Fig. S20b). These investigations verify the long-term stability and durability of MoC/Co–N–C-600 nanobelts, this is because the pomegranate-like carbon shell protects Co nanoparticles against agglomeration and retains the MoC core.

The electrocatalytic OER activities of the catalysts are also investigated and compared with the commercial IrO$_2$ catalyst. As shown in Fig. 3e and 3f, the anodic LSV curves and the corresponding Tafel plots indicate that MoC/Co–N–C-600 nanobelts show the lowest potential ($E_{10} = 0.370 \text{ V}$) at 10 mA cm$^{-2}$, and the smallest Tafel slope (59.0 mV dec$^{-1}$), which outperforms the values achieved from other samples and the commercial IrO$_2$ ($E_{10} = 0.370 \text{ V}, 61.8 \text{ mV dec}^{-1}$). Furthermore, a nearly constant real-time potential and a negligible current density loss after 30,000 s continuous operation suggest the long-term electrochemical stability and durability of MoC/Co–N–C-600 nanobelts for the OER in an alkaline electrolyte (Fig. S20). This is further supported by the stable microstructure of MoC/Co–N–C-600 nanobelts according to the morphological characterization in Fig. S21. Electrochemically active surface area (ECSA) is measured through the electrochemical double-layer capacitance ($C_{dl}$) determined by CV in a non-faradic region (Fig. 3g and S22).

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The capacitance $C_{dl}$ is calculated to be 3.0 mF cm$^{-2}$ for the MoC/Co–N–C-600 catalyst, which is much higher than those of the other products. The higher the value of $C_{dl}$ is, the larger is the ECSA of MoC/Co–N–C-600 electrocatalyst, thus, the more active sites for oxygen electrochemistry processes. In addition, Nyquist plots were performed to further unveil the nature of the electrocatalytic activity of samples (Fig. 3 h and S23-S24), the charge transfer resistance of MoC/Co–N–C-600 nanobelts rapidly decreases with the increase of the potential, implying that the electrode kinetics is mainly controlled by a charge-transfer process. The smallest radius of the semicircle of MoC/Co–N–C-600 nanobelts reveals the remarkably decreased charge transfer resistance and the faster charge and ion transfers in the catalyst surface when comparing with the other catalysts. These can be ascribed to the increased electrical conductivity derived from the pomegranate-like carbon nanobelts.
shell. Moreover, MoC/Co–N–C-600 nanobelts present the lowest potential gap of 0.735 V among the as-prepared samples and the commercial Pt/C and IrO\textsubscript{2} catalysts calculated from the ORR and OER polarization curves (Fig. 3). The potential gap value is generally considered as the benchmark to evaluate the reversible oxygen electrode property for rechargeable zinc air batteries. The lower potential gap means the better oxygen cathode performance. Thus, the optimal MoC/Co–N–C-600 electrocatalyst for the oxygen electrochemical processes is achieved with the superior bifunctional activity to the state-of-art Pt/C and IrO\textsubscript{2} catalysts and many of the well-developed electrocatalysts (Table S2). Such outstanding electrocatalytic performance is mainly attributed to the dramatically enhanced synergistic effect of the Co–N–C shell by the MoC core, which endows active Co and N-doped C sites with the optimum adsorption abilities for the intermediates of oxygen electrochemistry, such as OH, O and OOH. Besides, the particular pomegranate-like carbon shell increases the electrical conductivity for fast charge/mass transfers, prevents Co nanoparticles from agglomerating and

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Fig. 4. (a) Models for MoC/Co–N–C-500 (Co–N–C–CoMoO\textsubscript{4}), MoC/Co–N–C-600 (Co–N–C–MoC) and MoC/Co–N–C-700 (Co–N–C–Mo\textsubscript{2}C). (b) Gibbs free energy change diagrams of OER for the models MoC/Co–N–C-500 (Co–N–C–CoMoO\textsubscript{4}), MoC/Co–N–C-600 (Co–N–C–MoC) and MoC/Co–N–C-700 (Co–N–C–Mo\textsubscript{2}C) at the voltage of U = 0.00 and 1.60 V. (c) Gibbs free energy change diagram of ORR for the models MoC/Co–N–C-500 (Co–N–C–CoMoO\textsubscript{4}), MoC/Co–N–C-600 (Co–N–C–MoC) and MoC/Co–N–C-700 (Co–N–C–Mo\textsubscript{2}C) at the voltage of U = 0.00 and 0.75 V. (d) Projected density of states (PDOS) of the d bands for the active Co for the models MoC/Co–N–C-500 (Co–N–C–CoMoO\textsubscript{4}), MoC/Co–N–C-600 (Co–N–C–MoC) and MoC/Co–N–C-700 (Co–N–C–Mo\textsubscript{2}C), respectively. (e) Structures for intermediates OH, O, OOH and OO of model Co–N–C–MoC. * denotes the adsorption on the active site. Selective distances are in Å.

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retains the MoC core throughout the oxygen electrochemical processes, which is indispensable to the long-term stability.

The density functional theory with Hubbard $U$ correction (DFT + $U$) calculations were used to study the in-depth structural–properties relationship and further elucidate the functionality for MoC/Co–N–C-500, MoC/Co–N–C-600 and MoC/Co–N–C-700. To model the complex MoC/Co–N–C system, it is a big challenge as there are four factors should be addressed for the system: (1) Co nanoparticle doping; (2) N doping; (3) supporting; (4) co-existence of Co, N and MoC. Taking all factors into consideration, a Co, N co-doped graphene interfacing with MoC(001) facet was modelled for MoC/Co–N–C–Mo2C, the adsorption ability is significantly enhanced and two OH groups can be simultaneously adsorbed on one active Co site for MoC/Co–N–C–Mo2C because it preserves the alternative molybdenum layer and carbon layer of MoC structures, which is a most possible situation in the experimental environment. For comparison, the MoC/Co–N–C–Mo2C and MoC–Co–N–C–700 were modelled to further study the origin of OER/ORR activity similar to that for MoC/Co–N–C–500. As the CoMoO4 (JCPDS no. 73-1331) and Mo2C (JCPDS no. 35-0787) were found the main substrates as shown in Fig. 2a, the Co–N–C–CoMoO4 and Co–N–C–Mo2C models were established for MoC/Co–N–C–500 and MoC/Co–N–C–700 as shown in Fig. 4a. In addition, the Co13, N–C and Co–N–C models were also designed to elucidate the respective functionality for Co nanoparticle, pyridinic N dopant graphene and Co nanoparticle anchored on the N dopant graphene (Fig. S27).

With the modulation by the support CoMoO4, MoC and Mo2C, the adsorption ability is significantly enhanced and two OH groups can be simultaneously adsorbed on one active Co site. We named this adsorption mode as “single site double adsorption”. With this mode, one OH group is strongly adsorbed and the other OH group acts as the intermediates. The MoC–Co–N–C–Mo2C (Co–N–C–MoC) shows the superior performance with a theoretical overpotential of 0.33 V (1.56–1.23 = 0.33 V) as shown in Fig. 4b, which is close to the experimental value 0.37 V. The processes of *OH → O and *OH → *OOH almost show the same uphill free energy changes, indicating both these steps determine the OER reaction for MoC/Co–N–C–600 (Co–N–C–MoC). However, for MoC/Co–N–C–500 (Co–N–C–CoMoO4) and MoC–Co–N–C–700 (Co–N–C–Mo2C), there are much larger energy free energy changes for the step of *OH → *O than that for MoC/Co–N–C–600 (Co–N–C–MoC). As a result, only MoC/Co–N–C–600 (Co–N–C–MoC) shows a downhill free energy change at the experimental overpotential 0.37 V (U = 1.60 V), in line with the experimental observations.

The enhanced OH adsorption will lead to lower ORR performance according to the previous theoretical investigation by Nørskov and co-workers [41]. However, this is not the case for MoC/Co–N–C–600 (Co–N–C–MoC) because of the “single site double adsorption” mode. On one hand, the OH will be adsorbed firmly on the active Co site under the condition of ORR, and the active Co site can also adsorb additional O2. On the other hand, the adsorption ability for O2 is significantly weakened since there is already an OH moiety adsorbed. At potential $U = 0.00$ V for MoC/Co–N–C–600 (Co–N–C–MoC), the adsorbed O2 can be reduced to H2O with adsorption free energies of 4.04, 2.49 and 0.93 eV for the intermediates OOH, O and OH, respectively (Fig. 4c). As the free energy change is downhill, it indicates a facile reaction. When the potential $U$ increases to 0.75 V, the adsorbed free energies for the intermediates OOH, O and OH are changed to 1.79, 0.99 and 0.18 eV, respectively. It still shows a downhill in the free energy change, comparable to that for precious metal Pt at the same potential [41]. Accordingly, the MoC/Co–N–C–600 (Co–N–C–MoC) is provided with excellent ORR performance similar to Pt. With the “single site double adsorption” mode, the first OH adsorption is to lower the further adsorption ability of oxygen species and the second adsorption is for the ORR reaction. Based on this mechanism, it can well explain that the strengthening of adsorption ability can facilitate both ORR and OER performance simultaneously for MoC/Co–N–C–600 (Co–N–C–MoC). However, there are uphill in the step of *OH → H2O for MoC/Co–N–C–500 (Co–N–C–CoMoO4) and MoC/Co–N–C–700 (Co–N–C–Mo2C) at $U = 0.75$ V. Comparing the free energy changes for all the steps, the ORR activity shows the order of MoC/Co–N–C–600 > MoC/Co–N–C–700 > MoC/Co–N–C–500. It is in well agreement with the experimental observations in Fig. 3. Since the main difference for models MoC/Co–N–C–500 (Co–N–C–CoMoO4), MoC/Co–N–C–600 (Co–N–C–MoC) and MoC/Co–N–C–700 (Co–N–C–Mo2C) are the substrates, the modulation of the substrates is essential for the OER/ ORR activity. The further differential charge density analysis for MoC/Co–N–C–600 (Co–N–C–MoC) (Fig. S29) shows that the electrons migrate from Co to Mo atoms to achieve the modulation. It also confirms the experimental observations in Fig. 3c, in which MoC core couples with the Co–N–C shell, producing more Co2+ instead of Co0, shifting the binding energy more positive (783.1 eV).

To uncover the origin of the adsorption properties improvement, the projected density of states (PDOS) analysis was performed for MoC/Co–N–C–500, MoC/Co–N–C–600 and MoC/Co–N–C–700. It was found that the d band centre ($\varepsilon_d$) of active Co sites for MoC/Co–N–C–500 (Co–N–C–CoMoO4) is at −2.18 eV whereas the d band centre of active Co sites for MoC/Co–N–C–600 (Co–N–C–Mo2C) is upward shifted to −1.90 eV as illustrated in Fig. 4d. As expected from the d band theory, an upward shift of the d states of active Co sites with respect to the Fermi level results in a stronger Co–O bond, strengthening the oxygen-containing intermediates adsorption. However, the over upward shift of d states of active Co sites with respect to the Fermi level will lower the electrocatalysis activity according the Sabatier principles. This is the case for MoC/Co–N–C–700 (Co–N–C–Mo2C), in which the d band center of active Co is shifted to −1.82 eV. It strengthens the adsorption of *OH and leads to larger free energy change for the step *OH → *O, decreasing the OER/ORR activity.
To sum up, the MoC could perfectly tune the OER/ORR performance by modulating the $d$ band center of the active Co site. As a result, the MoC/Co–N–C-600 catalyst exhibits the excellent bifunctionality of the OER and ORR because of the improved synergistic coupling between Co, C and MoC.

Considering the outstanding bifunctional performance of MoC/Co–N–C-600 catalyst toward the oxygen electrochemistry, therefore, it was applied as the cathode material for zinc air batteries in two-electrode configuration with zinc plate anode. The as-mounted zinc air battery can continuously work with the open-circuit voltage of 1.458 V for over 24 h (Fig. 5a), implying the stable voltage supply. Fig. 5b presents higher current densities and a narrower charge–discharge voltage gap for the zinc air battery assembled from the MoC/Co–N–C-600 air cathode when compared with the Pt/C–IrO$_2$ hybrid cathode, verifying a superior battery performance to the commercial Pt/C–IrO$_2$ catalyst. A peak power density and a discharge current density at 1.0 V are achieved to be 180 mW cm$^{-2}$ and 80 mA cm$^{-2}$, respectively, for the MoC/Co–N–C-600 cathode (Fig. 5c), which much outperform those of the Pt/C–IrO$_2$ hybrid cathode (112 mW cm$^{-2}$ and 60 mA cm$^{-2}$). Besides, the galvanostatic discharge tests demonstrate the higher discharge potentials of the MoC/Co–N–C-600 cathode at various current densities than those of the commercial Pt/C–IrO$_2$ hybrid cathode.

Additionally, the galvanostatic charge–discharge test is conducted to evaluate the rechargability and cycling stability for the practical applicability of the as-assembled zinc batteries (Fig. 5e). The zinc air battery with MoC/Co–N–C-600 cathode exhibits better durability without a significant charge/discharge voltage change after continuous operation for 45 h. However, the battery assembled from the commercial Pt/C–IrO$_2$ cathode delivers a relatively poor cyclic durability with an obvious increase in the potential gap after less than 40 h cycle operation. As a practical exemplification, two as-assembled zinc air batteries connected in series can electrify two electronic watches and an electroluminescent panel lamp (Fig. 5f). Additionally, a long-term cyclic test over 2000 cycles is carried out by replenishing the electrolyte (Fig. 5g). As expected, the battery based on the MoC/Co–N–C-600 cathode...
delivers the exceptionally excellent stability with the extremely low degradation in the charge–discharge voltage gap, from 0.70 V at the initial cycle to 0.706 V at 1000 cycles, even after 2000 cycles, the potential gap climb up to only 0.716 V. Moreover, MoC/Co–N–C-600 delivers the specific capacity of 827.7 mAh g$^{-1}$ at 10 mA cm$^{-2}$ 791 mAh g$^{-1}$, outperforming that of the reference Pd/C–IrO$_2$ catalyst (775.8 mAh g$^{-1}$, Fig. S30). These results strongly evidence the feasibility of MoC/Co–N–C-600 catalyst applied as air cathode for zinc air batteries with a long lifespan.

3. Conclusions

The MoC-modulated Co–N–C catalyst system is successfully developed for oxygen electrochemistry, in which the d band center of active Co site of the Co–N–C catalyst was modulated by MoC to strengthen their adsorption capability for oxygen-containing intermediates and improve the electrocatalytic performance for the OER and ORR. A “single site double adsorption” mechanism was proposed for the deep understanding of the ORR performance enhancement, which makes OER and ORR enhancement simultaneously in the case of the adsorption ability strengthened. The optimal MoC/Co–N–C-600 catalyst delivers the impressive bifunctional electrocatalytic activity with a high half-wave potential of 0.865 V for the OER and a low overpotential of 0.37 V at 10 mA cm$^{-2}$ for the OER, accompanying with long-term stability. The excellent electrocatalytic performance and practical applicability of the MoC/Co–N–C-600 catalyst are further highlighted by the rechargeable zinc air battery using it as the air cathode, which exhibits a high peak power density of 180 mW cm$^{-2}$ and superb cyclic stability (2000 cycles). Experimental and DFT investigations result reveal that the MoC core modulated the d band center of the active Co sites by transferring electron from Co to Mo atoms, efficiently optimizing the adsorption abilities toward the oxygen-containing intermediates throughout the oxygen electrochemistry processes. This work offers important implications for developing the efficient oxygen catalysts for rechargeable metal-air batteries with long-term cyclic lifespan, through molybdenum compounds modulating the specific electronic configurations of active sites.

Declaration of competing interest

All authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gee.2021.05.008.

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