# Journal of Materials Chemistry A

## PAPER

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Cite this: J. Mater. Chem. A, 2024, **12**, 24285

Received 4th April 2024 Accepted 8th August 2024 DOI: 10.1039/d4ta02309a

rsc.li/materials-a



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scale electrochemical simulation methodologies and materials design strategies based on interface thermodynamics and endeavors to the application of new energy conversion systems including lithium metal batteries and all-solid-state batteries.

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# Evolution of high spin state single-atom catalyst active centers in Na-O<sub>2</sub> batteries†

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Due to the abundance and economic viability of Na resources,  $Na-O_2$  batteries are regarded as promising energy storage devices in achieving the carbon neutrality goals, featuring an ultra-high theoretical energy density. Nevertheless, the slow ion diffusion kinetics hinders the applications of batteries. Spin-induced single-atom catalysts (SACs) offer a promising avenue to ameliorate the activation process of the battery reaction. Herein, we study the adsorption–activation mechanism of  $O_2$  on six spin-induced SACs (*i.e.*, MnN<sub>3</sub>, MnN<sub>4</sub>, CoN<sub>3</sub>, CoN<sub>4</sub>, NiN<sub>3</sub>, and NiN<sub>4</sub>) in Na–O<sub>2</sub> batteries. We find that oxygen in mono-vacancy catalysts with high spin states favors the side-on adsorption mode. This mode enhances the coupling between the  $3d_{xy}$  orbital of metal and  $O_2$ , and alters the active center structures which further reduces the reaction overpotential by cutting down the OER potential. Moreover, we establish the scaling relationship between the oxygen adsorption–activation process which strongly determines the battery performance. The established structure–activity relationship of spin induced SACs may shed light on the catalyst modification involving the oxygen adsorption and activation to achieve a better performance.

### Introduction

The advancement of next-generation energy storage technologies with exceptional energy density plays a pivotal role in achieving the carbon neutrality goals.1-4 Nonetheless, the current lithium-ion batteries, boasting an energy density of 300 W h kg $^{-1}$ , fall short of meeting the requirements of prolonged lifespan devices such as electric vehicles. Metal-air batteries are renowned for their significant theoretical energy density, which is attributed to the use of inexhaustible oxygen from the air as the cathode active material, positioning them as one of the most promising energy storage devices capable of replacing lithiumion batteries. For the first time in 2011, a Na-O<sub>2</sub> battery with polymer electrolytes was assembled and tested at 100 °C for over 140 cycles.<sup>5</sup> Later, a pioneering room-temperature Na-O<sub>2</sub> battery with an ether-based electrolyte exhibited discharge capacities of over 300 mA h g<sup>-1</sup> and a charging overpotential lower than 0.2 V.6 Recently, a remarkable average coulombic efficiency as high as 97% during 80 cycles was achieved with a discharge capacity of 1000 mA h  $g^{-1}$  by Chen *et al.*<sup>7</sup> Moreover,

 $N_3$  at 1200 K; the mechanisms of adsorption–activation on  $CoN_x$  and  $NiN_x$ and the corresponding charge distribution; the PDOS of free  $O_2$  and  $O_2$ (a)  $MN_x$ ; the relative energy profiles of the proximal path and the distal diffusion of the Na atom on  $CoN_x$  and  $NiN_x$ ; the comparison of adsorption modes of the two coordination types. See DOI: https://doi.org/10.1039/d4ta02309a ‡ These authors contributed equally to this work.

Published on 09 August 2024. Downloaded by Zhejiang University on 11/18/2024 2:50:47 AM.



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<sup>&</sup>lt;sup>b</sup>State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China † Electronic supplementary information (ESI) available: The optimized structure of  $MN_x$  and Na,  $O_2$ , and  $Na_yO_2$  adsorbed on these six catalysts; the variations of relative energy against the time for AIMD simulations of (OMO)

Na is more widely available in the Earth's crust compared to lithium and cost-effective.<sup>8,9</sup> The abundance and economic viability of sodium resources confer an absolute advantage for the practical implementation of Na–O<sub>2</sub> batteries. Such a battery system offers the potential for advanced energy storage (theoretically up to 1100 W h kg<sup>-1</sup> based on NaO<sub>2</sub>) and the opportunity to reduce carbon emissions significantly.

Although the Na-O<sub>2</sub> battery has the above advantages, the sluggish ion diffusion kinetics attributed to the size effect of sodium hinders the battery practical application.<sup>10-12</sup> One possible way to relieve the reaction kinetics is seeking an appropriate catalyst for the Na-O2 battery. Co3O4, as a transition metal oxide (TMO) catalyst, has been demonstrated to mitigate the sluggish kinetics of both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in Na-O<sub>2</sub> batteries through a hierarchical charge and discharge mechanism, facilitated by the spin interaction between NaO2 and catalysts.13 But the role of spin in unraveling the precise mechanism of interaction remains unclear. In the meantime, the large bandgap of TMOs often represents an undeniable challenge to the cycling stability of the battery.14 Alternatively, single-atom catalysts (SACs) present a promising avenue, offering outstanding conductivity and a readily modulated coordination milieu that serve to enhance the adsorption and desorption of reactants.15 Furthermore, owing to their characteristic 2D nature, SACs exhibit a vast specific surface area that facilitates the accommodation of sizable sodium ions and discharge products.16 Inspired by the spin interaction between the metal and oxygen molecules, SACs with a magnetic metal active center, characterized by multiple spin states, may be better candidates for efficiently catalyzing Na-O2 batteries. Nevertheless, the mechanism linking the spin states to the reactivity in Na-O<sub>2</sub> battery reactions remains elusive. There is a lack of reports on the impact of spin states on the real active centers of spin SACs in Na-O<sub>2</sub> batteries. In other words, whether the spin state effects changes in the active center and how the active center evolves remain unclear.

Here, we investigate the reaction mechanism of six catalysts featuring transition metals Mn, Co, Ni, and N co-anchored on graphene in Na-O<sub>2</sub> batteries. Two coordination types, specifically threefold-coordinated and fourfold-coordinated, are considered, corresponding to carbon mono-vacancy and double-vacancy structures, denoted as MnN<sub>3</sub>, MnN<sub>4</sub>, CoN<sub>3</sub>,  $CoN_4$ , NiN<sub>3</sub>, and NiN<sub>4</sub>. The MN<sub>3</sub> catalysts (M = Mn, Co, and Ni) exhibit a high spin state compared to the MN<sub>4</sub> catalysts. We observe that the high spin state induces the side-on adsorption mode of oxygen, with the strong oxygen adsorption strength in MN<sub>3</sub> catalysts. This oxygen adsorption mode causes formation of composite intermediates during oxygen activation. We elucidate the formation mechanism of composite intermediates and the influence on the active center. Furthermore, oxygen adsorption energy is observed to be a desirable descriptor of the overpotential of Na-O<sub>2</sub> batteries. Through this exploration, the evolution mechanism of SACs induced by the high spin state and corresponding impact on the active center is clarified, which enriches the comprehension of spin SACs in the catalytic reactions involving oxygen adsorption-activation.

## **Methods**

The geometry optimizations and energy calculations are approached by the Vienna Ab initio Simulation Package (VASP).17 The generalized gradient approximation (GGA) functional externalized by Perdew, Burke, and Ernzerhof (PBE)18 is incorporated to describe the exchange-correlation energy within the Projector Augmented Wave (PAW) form.<sup>19</sup> To ensure the calculation accuracy, a cutoff energy of 500 eV is adopted. The spin-polarized calculations are conducted until the selfconsistent electronic energies and the ionic relaxation converged within  $1 \times 10^{-5}$  eV and 0.02 eV Å<sup>-1</sup>, respectively. In all calculations, the van der Waals (vdW) interactions are estimated through the DFT-D3 method interpreted by Grimme.<sup>20</sup> The Brillouin zone is sampled using a Monkhorst–Pack 3  $\times$  3  $\times$ 1 k-point grid. A 7  $\times$  8 supercell carbon substrate is set. The threefold-coordinated catalyst model includes 108 carbon atoms, 3 nitrogen atoms, and 1 metal atom, while the fourfoldcoordinated catalyst model comprises 106 carbon atoms, 4 nitrogen atoms, and 1 metal atom. The GGA +  $U_{eff}$  method is applied to account for the strongly localized d orbitals of Mn, Co, and Ni in the selected structures. The Hubbard  $U_{\rm eff}$  values for Mn, Co, and Ni are chosen to be 3.9,<sup>21</sup> 5.3,<sup>22</sup> and 5.3,<sup>23,24</sup> respectively. The vacuum layer is set to be 25 Å for all the simulations to eliminate the interaction between adjacent molecular layers. The transition states of the O2 activation and Na migration are implemented by the climbing image nudged elastic band (CI-NEB) method<sup>25,26</sup> at a reduced force criterion of 0.05 eV  $Å^{-1}$ . The obtained transition state is further verified by vibrational frequency calculation, and only one imaginary frequency is obtained for each transition state.

The formation energy  $(E_f)$  of metal atoms with the MN<sub>x</sub> is defined as:

$$E_{\rm f} = E_{\rm MNx} - E_{\rm NC} - E_{\rm M} ({\rm M} = {\rm Mn, Co, and Ni})$$
(1)

where  $E_{MNx}$  is the total energy of catalysts  $MN_x$ .  $E_{NC}$  is the energy of N-doped graphene with vacancies.  $E_M$  is the energy of the metal atom in the most stable bulk phase.

To evaluate the adsorption strength of Na, O<sub>2</sub>, and the reaction intermediates  $Na_yO_2$  (y = 1, 2, 3, and 4) on the substrate MN<sub>x</sub>, their adsorption energies ( $E_{ads}$ ) are calculated as

$$E_{\rm ads}(\rm Na) = E_{\rm Na@sub} - E_{\rm sub} - E_{\rm Na}$$
(2)

$$E_{\rm ads}(O_2) = E_{O_2@{\rm sub}} - E_{\rm sub} - E_{O_2}$$
(3)

$$E_{ads}(Na_yO_2) = E_{Na_yO_2@sub} - E_{sub} - E_{Na_yO_2}$$
(4)

where  $E_{\text{Na}@\text{sub}}$ ,  $E_{\text{O}_2@\text{sub}}$ , and  $E_{\text{Na}_y\text{O}_2@\text{sub}}$  stand for the total energy of Na, O<sub>2</sub>, and Na<sub>y</sub>O<sub>2</sub> adsorbed on the MN<sub>x</sub>, respectively.  $E_{\text{sub}}$  is the energy of the MN<sub>x</sub> substrate.  $E_{\text{Na}}$ ,  $E_{\text{O}_2}$ , and  $E_{\text{Na}_y\text{O}_2}$  denote the energy of the Na atom in the bulk phase structure, a free O<sub>2</sub> gas and Na<sub>y</sub>O<sub>2</sub>, respectively.

The reaction Gibbs free energy ( $\Delta G$ ) can be expressed as

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S + ne U \tag{5}$$

where  $\Delta E$  is the electronic energy difference of the reaction.  $\Delta ZPE$  and  $\Delta S$  denote the variations in zero-point energy and entropy, respectively. *neU* is the free energy contribution of the applied electrode potential.

The overpotential  $(\eta)$  is used to estimate the catalytic properties of doped SACs:

$$\eta_{\rm ORR} = U_0 - U_{\rm dc} \tag{6}$$

$$\eta_{\rm OER} = U_{\rm c} - U_0 \tag{7}$$

$$\eta_{\rm TOT} = \eta_{\rm ORR} + \eta_{\rm OER} \tag{8}$$

where  $U_0$ ,  $U_{dc}$ , and  $U_c$  are the equilibrium, discharging, and charging potentials, respectively.  $U_{dc}$  is the maximum prerequisite voltage where all discharging steps are exothermic, while  $U_c$  indicates that the minimum prerequisite voltage for all charging steps is exothermic. The total overpotential,  $\eta_{TOT}$ , is the sum of the overpotentials in the ORR and OER processes.

The occupied d-band center  $(\epsilon_d)$  of the metal atom was calculated by

$$\varepsilon_{\rm d} = \frac{\int_{-\infty}^{E_F} \rho(E) E dE}{\int_{-\infty}^{E_F} \rho(E) dE}$$
(9)

where  $\rho(E)$  represents the projected density of states of the specified orbital.  $E_{\rm f}$  is the Fermi energy.

#### **Results and discussion**

#### Geometries, spin properties, and stabilities of catalysts MN<sub>x</sub>

Two types of SAC models, i.e., threefold-coordinated and fourfold-coordinated configurations, are taken into account to regulate the spin state of the active atoms based on the motifs determined via experimental characterization and related theoretical studies.<sup>27-31</sup> Mn, Co, and Ni atoms are anchored on N-doped graphene with single and double carbon vacancies, denoted as MnN<sub>3</sub>, MnN<sub>4</sub>, CoN<sub>3</sub>, CoN<sub>4</sub>, NiN<sub>3</sub>, and NiN<sub>4</sub>, respectively (Fig. 1a and S1<sup>†</sup>). The optimized geometric structures of  $MN_x$  (M = Mn, Co, and Ni, x = 3 and 4) are shown in Fig. S2.<sup>†</sup> Fig. 1b shows the M–N bond length  $(l_{M-N})$  of MN<sub>3</sub> and MN<sub>4</sub> catalysts. The trend of  $l_{M-N}$  is consistent with the atomic radius order: Mn > Co > Ni. The calculated  $l_{\rm Co-N}$  of CoN<sub>4</sub> is 1.89 Å, which is close to the experimental data (1.90 Å (ref. 32)), showing the accuracy of our study. The spin magnetic moments of Mn, Co, and Ni in the threefold-coordinated catalysts are 4.00, 2.01, and 0.83  $\mu_{\rm B}$ , respectively, exceeding those of fourfoldcoordinated catalysts, which are 3.31, 1.00, and 0  $\mu_{\rm B}$  for Mn, Co, and Ni, respectively (Table 1). In particular, we find that the spin magnetic moment disappears in NiN4 which is consistent with a previous study.<sup>33</sup> The stability of the metal atoms in the MN<sub>x</sub> catalysts is evaluated by calculating the formation energy (Fig. 1c). The negative formation energies of  $MN_x$  imply exothermicity during their formation, elucidating the thermodynamic stability of these catalysts. The  $E_{\rm f}$  of MnN<sub>3</sub>, CoN<sub>3</sub> and NiN<sub>3</sub> is -1.14, -2.82 and -2.88 eV, respectively, which indicates the NiN<sub>3</sub> catalyst is the most stable structure. The  $E_{\rm f}$  of MnN<sub>4</sub>, CoN<sub>4</sub> and NiN<sub>4</sub> is -6.44, -7.37 and -7.02 eV, respectively,



**Fig. 1** (a) Top (upper) and side (lower) view diagrams of the  $MN_x$  structures. (b) The M–N bond length ( $l_{M-N}$ ) in the different optimized  $MN_x$  structures. (c) The formation energy ( $E_f$ ) of MnN<sub>3</sub>, CoN<sub>3</sub>, NiN<sub>3</sub>, MnN<sub>4</sub>, CoN<sub>4</sub>, and NiN<sub>4</sub>.

Table 1 The spin magnetic moments (M) of the metal atoms in the six spin catalysts in units of  $\mu_{\rm B}$ 

Catalysts	$M_{ m Mn}$	$M_{ m Co}$	$M_{ m Ni}$
MN <sub>3</sub>	4.00	2.01	0.83
$MN_4$	3.31	1.00	0

which indicates the  $CoN_4$  catalyst is the most stable. Comparing the formation energies of  $MN_3$  and  $MN_4$ , the fourfoldcoordinated catalysts have more negative  $E_f$ , denoting their higher structural stability than the threefold-coordinated catalysts.

#### Reaction mechanism catalyzed by spin-induced SACs

To delve into the impact of spin states on battery reactions, it is imperative to elucidate the precise reaction mechanism of the Na–O<sub>2</sub> batteries catalyzed by MnN<sub>3</sub>, CoN<sub>3</sub>, NiN<sub>3</sub>, MnN<sub>4</sub>, CoN<sub>4</sub>, and NiN<sub>4</sub>. In aprotic solvents, the main reaction in the battery is the formation and decomposition of sodium oxides corresponding to the discharging oxygen reduction reaction and the charging oxygen evolution reaction. There exist two main sodium oxides in the reaction mechanism, *i.e.* NaO<sub>2</sub> and Na<sub>2</sub>O<sub>2</sub> (eqn (10) and eqn (11)).<sup>6</sup> The detailed schematic diagram of the reaction pathway is illustrated in Fig. 2a. The activation of battery reactions involves two divergent paths,

$$Na + O_2 \rightleftharpoons NaO_2, E^o = 2.27 V$$
 (10)

$$2Na + O_2 \rightleftharpoons Na_2O_2, E^o = 2.33 V$$
(11)

characterized by the distinction in adsorption preference between the substrate and the Na and  $O_2$ . Thus, the adsorption



Fig. 2 (a) The reaction pathway schematic diagram. (b) The side (upper) schematic diagram of the adsorption modes of  $O_2$  and the top (lower) schematic diagram of the adsorption modes of Na on MN<sub>x</sub> structures. (c) The adsorption energy of  $O_2$  ( $E_{ads}(O_2)$ ) and Na ( $E_{ads}(Na)$ ) on MnN<sub>3</sub>, CoN<sub>3</sub>, NiN<sub>3</sub>, MnN<sub>4</sub>, CoN<sub>4</sub>, and NiN<sub>4</sub>. (d) The relationship between the adsorption energy of  $O_2$  ( $E_{ads}(O_2)$ ) and the O–O bond length ( $l_{O-O}$ ).

behavior of  $O_2$  and Na on catalysts plays a critical role in determining the initial nucleation of  $NaO_2$ .

In order to investigate the nucleation mechanism of  $NaO_{2}$ , the adsorption energies of O<sub>2</sub> and Na on the six substrates are calculated. In threefold-coordinated catalysts, the adsorption energies of O<sub>2</sub> are -6.75, -4.80, and -3.99 eV for MnN<sub>3</sub>, CoN<sub>3</sub> and NiN<sub>3</sub>, respectively. The most negative oxygen adsorption energy on MnN<sub>3</sub> shows that O<sub>2</sub> promises the strongest adsorption strength. Moreover, the O2 interacts with MN3 via the sideon adsorption mode, characterized by the slight distortion of the N-doped graphene monolayer and the obvious protrusion of the metal atom out of the plane, leading to shorter M-O bond lengths  $(l_{M-O})$  (Fig. 2b and S3 and S4<sup>†</sup>). In the fourfoldcoordinated catalysts, the adsorption energies of  $O_2$  are -1.58, -1.00, and -0.72 eV for MnN<sub>4</sub>, CoN<sub>4</sub>, and NiN<sub>4</sub>, respectively, indicating that the adsorption of O2 on MnN4 is the most beneficial. Unlike MN<sub>3</sub> catalysts, the O<sub>2</sub> is adsorbed and activated on the MN<sub>4</sub> catalysts through the end-on adsorption mode, with the Ni and Co atoms located in the plane. Nevertheless, in the case of MnN<sub>4</sub>, the slightly protruding plane of the Mn atom may be attributed to the larger atomic radius of Mn. The side-on mode for O<sub>2</sub>@MN<sub>3</sub> and end-on mode for O<sub>2</sub>@MN<sub>4</sub> are also supported by literature data, as shown in Table S1.† Comparing the adsorption energy of oxygen on MN<sub>3</sub> and MN<sub>4</sub>, the more negative adsorption energy of oxygen on MN<sub>3</sub> indicates a stronger adsorption capability. For the adsorption of Na on MN<sub>3</sub>, the adsorption energies are -3.98, -2.29, and -0.76 eV for MnN<sub>3</sub>, CoN<sub>3</sub>, and NiN<sub>3</sub>, respectively, indicating that the adsorption of Na on MnN<sub>3</sub> is energetically the most favorable. Na atoms tend to be captured with the top-on site via the formation of three Na-N bonds (Fig. 2b and S5<sup>†</sup>). In terms of the

Na adsorbed on  $MN_4$ , the adsorption energies are 0.40, 0.52, and 0.17 eV for  $MnN_4$ ,  $CoN_4$ , and  $NiN_4$ , respectively. The hole-on site of  $MN_4$  facilitates the adsorption of Na. The top-on mode for Na@MN<sub>3</sub> and hole-on mode for Na@MN<sub>4</sub> are also supported by literature data, as shown in Table S2.† More importantly, the adsorption energy of oxygen on the six substrates is observed to be consistently lower than that of Na on these substrates, implying that path I has a thermodynamic advantage over path II. This is due to the nucleophilic nature of  $O_2^-$ , which makes it more predisposed to acquiring electrons from the substrate compared to the electrophilic nature of  $Na^+$ . The adsorption state of the reactant impacts the reaction mechanism,<sup>34</sup> and thus it is necessary to figure out the reason why there are two distinct oxygen adsorption modes.

To further explore the adsorption modes of O<sub>2</sub>, the O–O bond length ( $l_{O-O}$ ) after adsorption is investigated. For threefoldcoordinated catalysts, the  $l_{O-O}$  of O<sub>2</sub>@MnN<sub>3</sub>, O<sub>2</sub>@CoN<sub>3</sub>, and O<sub>2</sub>@NiN<sub>3</sub> is 1.42, 1.39, and 1.35 Å, respectively. And the  $l_{O-O}$  of 1.42 Å in O<sub>2</sub>@MnN<sub>3</sub> can be verified by AIMD simulation (Fig. S6–S8†). For fourfold-coordinated catalysts, the  $l_{O-O}$  of O<sub>2</sub>@MnN<sub>4</sub>, O<sub>2</sub>@CoN<sub>4</sub>, and O<sub>2</sub>@NiN<sub>4</sub> is 1.31, 1.27, and 1.25 Å, respectively. The O–O bond lengths of O<sub>2</sub>@MN<sub>3</sub> and O<sub>2</sub>@MN<sub>4</sub> are incremental for Ni, Co, and Mn catalysts, which is consistent with the change of the adsorption energy (Fig. 2d). The O–O bond length of the adsorbed O<sub>2</sub> exhibits a significant degree of elongation compared with the bond length (1.23 Å) of a single O<sub>2</sub> molecule, reflecting the activation of O<sub>2</sub>.

To clarify the differences in the  $O_2$  activation process, we take Mn catalysts as an example due to their longest  $l_{O-O}$ . During the initial activation of  $O_2$  on MnN<sub>3</sub>, one oxygen atom deviates around another oxygen atom. The entire oxygen molecule

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experiences a slight shift and rotation around the Mn atom. There exists a continuous transfer of electrons between Mn and  $O_2$ , leading to corresponding changes in the spin distribution during this process (Fig. 3a). The transitioning from the initial state (IS) to state II (reaction coordination II in Fig. 3b) represents an oxygen adsorption and activation process, as evidenced by reaching an activation bond length of oxygen (1.3 Å (ref. 35)) with a value of 1.4 Å in state II. During the transition from state II to the final state (FS), the slight change in the O–O bond length indicates an adjustment to maximize the overlap between the active oxygen and the substrate electron, leading to increased system stability with a 9.85 eV release. In addition to the continuous stretching of O–O bond length during the whole activation process, the Mn center also moves outward from the graphene plane. A continuous decrease in the total energy of the process (Fig. 3b) manifests a thermodynamic self-regulation behavior, which can be attributed to the formation of a composite intermediate, namely (OMnO)N<sub>3</sub>. The energy released during the formation process of (OMnO)N<sub>3</sub> primarily consists of two factors: the energy generated by O<sub>2</sub> activation and the energy generated by the evolution of the Mn center. For MnN<sub>4</sub>, the activation process of O<sub>2</sub> requires an energy barrier of 0.63 eV to be overcome, which closely resembles the O<sub>2</sub> activation energy barrier on FeN<sub>4</sub> of about 0.45 eV (ref. 36) (Fig. 3d and e). The O–O bond length is maintained around 1.3 Å. The rotation of O<sub>2</sub> around the *z*-axis mainly involves the adjustment of spatial overlap between the O<sub>2</sub> molecular orbital and the Mn d<sub>z</sub><sup>2</sup> orbital (Fig. 3d side view). It can also be observed that the



**Fig. 3** (a) The schematic diagram of the configuration change of oxygen activation on  $MnN_3$  and corresponding spin-charge density. (b) The height of Mn displacement ( $h_{Mn}$ ) and energy change during the activation of oxygen. (c) The charge density difference of  $O_2(@MnN_3)$ , where the yellow and cyan regions denote the electron accumulation and depletion zones, respectively. The isosurface value is  $0.0015 \text{ e bohr}^{-3}$ . (d) The schematic diagram of the configuration change of oxygen activation on  $MnN_4$  and corresponding spin-charge density. (e) The energy change during activation of oxygen. (f) The charge density difference of  $O_2(@MnN_4)$ , where the yellow and cyan regions denote the electron accumulation and depletion zones, respectively. The isosurface value is  $0.0015 \text{ e bohr}^{-3}$ . (g) The projected density of states (PDOS) of the metal in  $MnN_3$ ,  $CoN_3$ ,  $NiN_3$ ,  $MnN_4$ ,  $CoN_4$ , and  $NiN_4$ . The Fermi level is set to zero.

spin magnetic moment of Mn in the O<sub>2</sub>@MnN<sub>3</sub> is larger than that in the O<sub>2</sub>@MnN<sub>4</sub>. Moreover, Mn undergoes a subtle displacement compared with O<sub>2</sub>@MnN<sub>3</sub>. This observation suggests that the composite intermediate (*i.e.*, (OMnO)N<sub>3</sub>) is formed during the activation process of O<sub>2</sub> on MnN<sub>3</sub>, whereas no composite intermediate is formed on MnN<sub>4</sub>. Applying the aforementioned analytical approach, the formation of composite intermediates (*i.e.*, (OCoO)N<sub>3</sub> and (ONiO)N<sub>3</sub>) is also observed during the activation process of O<sub>2</sub> on CoN<sub>3</sub> and NiN<sub>3</sub>, and the detailed information is provided in the ESI (Fig. S9 and S10<sup>†</sup>).

To further prove the formation of  $(OMO)N_3$ , the charge analysis is depicted in Fig. 3c and f. The Bader charge transferred by the metal for O<sub>2</sub>@MnN<sub>3</sub>, O<sub>2</sub>@CoN<sub>3</sub>, O<sub>2</sub>@NiN<sub>3</sub>, O<sub>2</sub>@MnN<sub>4</sub>, O<sub>2</sub>@CoN<sub>4</sub>, and O<sub>2</sub>@NiN<sub>4</sub> is 1.54, 1.18, 1.03, 1.41, 0.98 and 0.81, respectively. The number of electrons lost by the metal follows the order: Mn > Co > Ni, can be explained by the declining innate attribute of electronegativity: Mn < Co < Ni. The threefold-coordinated system possesses a greater number of metal transfer electrons than its fourfold-coordinated counterpart, which is related to the oxygen adsorption mode. A similar charge distribution of the two O atoms on (OMO)N<sub>3</sub> is formed through the side-on adsorption mode. For the O<sub>2</sub>@MN<sub>4</sub>, the end-on adsorption mode results in an uneven charge distribution of the two O atoms. Bader charge analysis further quantitatively confirms this finding, with 0.39 and 0.51 e<sup>-</sup> transferring to  $O_2$  on MnN<sub>3</sub>, and 0.17 and 0.24 e<sup>-</sup> transferring to  $O_2$  on MnN<sub>4</sub> (Fig. 3c and f). Furthermore, the higher charge depletion between the two O atoms on  $O_2$ @MnN<sub>3</sub> implies a greater degree of activation of the adsorbed oxygen on MnN<sub>3</sub> compared to MnN<sub>4</sub>. The results also confirm the formation of intermediates (OMO)N<sub>3</sub> for Mn, Co, and Ni (*i.e.*, (OMnO)N<sub>3</sub>, (OCoO)N<sub>3</sub>, and (ONiO)N<sub>3</sub>). Overall, the variation in oxygen adsorption modes alters the spatial charge distribution, leading to a discrepancy in the oxygen activation process under two distinct coordination modes.

To elucidate the spin-coupling mechanism during the oxygen adsorption–activation process, the d-orbital projected densities of states (PDOS) of metal atoms are systematically analyzed. As shown in Fig. 3g, there is an asymmetric arrangement of d electron states in the spin channels, signifying the spin polarization apart from NiN<sub>4</sub>. After the formation of the M– N coordination structure, according to the crystal field theory, the five 3d orbitals in the metal atom with the same energy undergo a splitting into four groups:  $d_z^2$ ,  $d_{xz/yz}$  (two-fold degenerate),  $d_{xy}$ , and  $d_{x^2-y^2}$ . For MN<sub>4</sub>, all three metals have empty  $d_{x^2-y^2}$  anti-bonding orbitals with energy above the Fermi energy level (*E*<sub>F</sub>) and occupied  $d_{xy}$  bonding orbitals with energy



Fig. 4 The Gibbs free energy profiles of the most appropriate intermediate state for  $NaO_2$ ,  $Na_2O_2$ ,  $Na_3O_2$ , and  $Na_4O_2$  at diverse voltages on (a) MnN<sub>3</sub>, (b) CoN<sub>3</sub>, (c) NiN<sub>3</sub>, (d) MnN<sub>4</sub>, (e) CoN<sub>4</sub>, (f) NiN<sub>4</sub>, (g) (OMnO)N<sub>3</sub>, (h) (OCoO)N<sub>3</sub>, and (i) (ONiO)N<sub>3</sub> catalysts, respectively.

below  $E_{\rm F}$ . This means  $d_{x^2-y^2}$  and  $d_{xy}$  are not active compared to the  $d_z^2$  and  $d_{xz/yz}$ , which is consistent with previous research.<sup>37-39</sup> We find that  $d_z^2$  is the main active orbital according to the degree of orbital overlap (Fig. S11 and S12†). Unlike MN<sub>4</sub>, the  $d_{xy}$  orbital electron states on MN<sub>3</sub> occur within the energy range of -2 to 0 eV, which implies that the  $d_{xy}$  orbital electrons of the metal in MN<sub>3</sub> are more active than those of MN<sub>4</sub>. MN<sub>3</sub> with a higher spin magnetic moment exhibits an increased exposed charge density due to its prominent metal atoms, leading to an intensified coupling between the  $d_{xy}$  orbital electrons of metals and the  $\pi_{2p}$  anti-bonding electrons of oxygen. The differences in the spin-coupling mechanism can be accounted for by changes in the coordination environment, which result in different spin charge distributions of MN<sub>3</sub> and MN<sub>4</sub>.

To shed light on the impact of the aforementioned spincoupling mechanism on catalytic performance, the Gibbs free energy profiles during the ORR and OER processes of Na–O<sub>2</sub> batteries on MN<sub>x</sub> under various potentials are illustrated in Fig. 4. In addition to NaO<sub>2</sub> and Na<sub>2</sub>O<sub>2</sub> as the main products, the deep reduction products (*i.e.*, Na<sub>3</sub>O<sub>2</sub> and Na<sub>4</sub>O<sub>2</sub>) are also considered which can also be formed to improve the energy density of the battery.<sup>21</sup> The stable structures of \*NaO<sub>2</sub>, \*Na<sub>2</sub>O<sub>2</sub>, \*Na<sub>3</sub>O<sub>2</sub>, and \*Na<sub>4</sub>O<sub>2</sub> are presented in Fig. S13–S16.† All reaction steps are exothermic under  $U_0$  during the discharge process, decoding that the reactions are thermodynamically preferable and deep reductions are feasible. The  $\eta_{ORR}$  values for MnN<sub>3</sub>, CoN<sub>3</sub>, NiN<sub>3</sub>, MnN<sub>4</sub>, CoN<sub>4</sub>, and NiN<sub>4</sub> are 1.80, 1.12, 0.93, 0.54, 0.86, and 0.24 V, respectively (Fig. 4a–f). The  $\eta_{OER}$  values for MnN<sub>3</sub>, CoN<sub>3</sub>, NiN<sub>3</sub>, MnN<sub>4</sub>, CoN<sub>4</sub>, and NiN<sub>4</sub> are 4.77, 2.92, 2.61, 1.06, 0.38, and 0.25 V, respectively. Compared to the  $\eta_{OBR}$ ,  $\eta_{OER}$ is higher particularly in the case of threefold-coordinated catalysts (e.g. for MnN<sub>3</sub>, the value of  $\eta_{OER}$  is 4.77 V, greater than the value of  $\eta_{\text{ORR}}$  of 1.80 V). This can be interpreted by the challenging dissociation of the stable intermediate (OMO)N<sub>3</sub> in the OER process. However, if we set the composite intermediates as the catalytic center (*i.e.*, the center is stable and may not decompose in the OER catalysis process), the average overpotential of (OMO)N<sub>3</sub> is 0.64 V which is significantly lower than that of the pristine single atom center (*i.e.*, MN<sub>3</sub>) (Fig. 4g-i). These results reflect that the formed (OMO)N<sub>3</sub> could lower the overpotential and exhibit high activity as the active center. The kinetic stability of the composite intermediates is illustrated through Ab initio molecular dynamics (AIMD) simulation; all three (OMO)N<sub>3</sub> structures are not dissociated, reflecting their excellent kinetic stability (Fig. S17–S19†).

In order to explore the correlation between the adsorption and activation of  $O_2$  and battery performance, the difference between the spin and electronic properties of catalysts before and after  $O_2$  adsorption is investigated, as well as correlations between the adsorption energy and corresponding overpotential. As depicted in Fig. 5a, the spin magnetic moment of the metal is positively correlated with the total overpotential of the battery for catalysts of the same coordination type. A low spin state is beneficial to the catalytic reaction. Therefore, the regulation of the spin state is an effective strategy to design highly active catalysts.



Fig. 5 (a) The relations between the magnetic moment (*M*) of metal and the total overpotential ( $\eta_{TOT}$ ). (b) The schematic diagram of the shift of the occupied d-band center ( $\varepsilon_d$ ) before and after O<sub>2</sub> adsorption. (c) The relations between the adsorption energy of O<sub>2</sub> ( $E_{ads}(O_2)$ ) and the occupied d-band center ( $\varepsilon_d$ ). (d) The linear relations between the integrated COHP (iCOHP) and the total overpotential ( $\eta_{TOT}$ ). (e) The scaling relationship between the adsorption energy of Na<sub>y</sub>O<sub>2</sub> ( $E_{ads}(Na_yO_2)$ ) and the adsorption energy of O<sub>2</sub> ( $E_{ads}(O_2)$ ) on MnN<sub>3</sub>. CoN<sub>3</sub>, NiN<sub>3</sub>, MnN<sub>4</sub>, CoN<sub>4</sub>, and NiN<sub>4</sub>. (f) The contour plot between the adsorption energy of O<sub>2</sub> ( $E_{ads}(O_2)$ ), the adsorption energy of Na ( $E_{ads}(Na)$ ) and the total overpotential ( $\eta_{TOT}$ ).

After the adsorption of oxygen, the occupied d-band center of the metal shifted upward (Fig. 5b). According to the classical dband center theory, the higher the d-band center value, the stronger the adsorption strength of adsorbates due to the decrease of anti-bonding filling.<sup>40,41</sup> Nevertheless, in our work, it is observed that for the more negative occupied d-band center value systems (such as O<sub>2</sub>@MnN<sub>3</sub>), their adsorption is stronger (Fig. 5c). This tendency seems to be contrary to the classical dband center theory, which can be attributed to the fact that the adsorption strength is influenced by both the filling of antibonding and the extent of energy level alignment.42,43 The extent of energy level alignment can be understood as the gap between the d-band of the metal and p-band center of the adsorbate (e.g., O<sub>2</sub>). The smaller the gap value, the stronger the strength of interaction according to molecular orbital theory and relevant literature.44,45 The downshift of the d-band center results in an enhanced alignment of energy levels between the d-band and p-band, thereby decreasing the gap due to the lowlying p-band center (*i.e.* more negative values) in the adsorbate compared to the high-lying d-band center. Therefore, the adsorption strength of O2 increases. We also find that the O2 adsorption strength is correlated with the M-O bond, which can be quantitatively characterized utilizing the projected Crystal Orbital Hamilton Population (pCOHP) analysis. The more negative the value of the integrated COHP (iCOHP), the stronger the bond strength between metal and oxygen. As plotted in Fig. S20,<sup>†</sup> the strength of the two M–O bonds in the side-on adsorption mode of MN<sub>3</sub> is similar (e.g. for MnN<sub>3</sub>, the iCOHP of the two Mn-O bonds is 0.43 and 0.55, respectively), unlike the end-on adsorption mode of MN4 where the M-O bond strengths are different (e.g. the -iCOHP of the two Mn-O bonds are 0.34 and 0.09, respectively). Moreover, it can be found that a strong bonding strength between metal and oxygen can lead to an increase in overpotential (Fig. 5d). The adsorption energy of NaO<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>, Na<sub>3</sub>O<sub>2</sub>, and Na<sub>4</sub>O<sub>2</sub> on the same catalyst is linked to the adsorption energy of O<sub>2</sub>, as shown in Fig. 5e. The adsorption energy of sodium oxides  $(E_{ads}(Na_{\nu}O_2))$  is linear to the  $E_{ads}(O_2)$ , with correlation coefficients above 0.91. Furthermore, it can be demonstrated from Fig. 5f that the catalytic performance is associated with both  $E_{ads}(O_2)$  and Na. The correlation coefficient between  $E_{ads}(O_2)$  and  $\eta_{TOT}$  is 0.98, indicating that the O2 adsorption energy can be a practical descriptor of overpotential of the Na–O<sub>2</sub> battery:  $\eta_{\text{TOT}} = -0.92E_{\text{ads}}(O_2) + 0.02$ . The noticeable negative correlation can be imputed to the fact that the stronger the oxygen-affinity nature of MN<sub>x</sub> catalysts, the less favorable the oxygen desorption during the OER. The oxygenaffinity can be divided into three types. When the metal atom in the catalyst displaces outward from the graphene plane, forming a side-on adsorption mode with oxygen, we describe the catalyst as being oxyphilic. The value of adsorption energy is greater than  $-3 \text{ eV}(i.e., MN_3)$ . If the metal atom remains within the graphene plane and engages in end-on adsorption with  $O_{2}$ , it is categorized as oxyphobic with the adsorption energy smaller than -1 eV (*i.e.*, CoN<sub>4</sub> and NiN<sub>4</sub>). Between oxyphilic and oxyphobic, there is an oxy-amphiphilic zone when the metal atom resides within the graphene plane and interacts with oxygen in an end-on adsorption mode. The value of adsorption

energy is between -3 and -2 eV (*i.e.*, MnN<sub>4</sub>). In conclusion, oxyphilic catalysts play a decisive role in inducing the formation of oxygen-containing active centers, namely (OMO)N<sub>3</sub>. Our findings indicate that regulating the oxygen-affinity of a catalyst is paramount in modifying the catalytic performance of reactions involving oxygen.

#### Adsorption and migration of Na ions on spin-state MN<sub>x</sub>

In the battery reaction, Na atoms react with the adsorbed O<sub>2</sub> to form a series of sodium oxides (*i.e.*, NaO<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>, Na<sub>3</sub>O<sub>2</sub>, and Na<sub>4</sub>O<sub>2</sub>), which involves the migration of Na atoms. Considering the size effect of Na, the migration degree determines the rate performance of Na-O<sub>2</sub> batteries. During the migration process, the appropriate energy barrier is vital in enabling a faster migration rate. The super-high energy barrier to Na migration suggests that the substrate has a strong trapping effect on Na, which further blocks the activity of the catalyst; meanwhile, the too low energy barrier to Na migration indicates that the substrate has a weak adsorption effect on Na, which cannot provide a large enough driving force to combine with oxygen and other discharge products for a deep reduction reaction, resulting in a lower catalytic efficiency.46 Hence, we further investigated the migration of Na on the catalyst substrate. Considering the symmetry of the substrate structure and the stable adsorption sites of MN<sub>x</sub>, two different pathways are constructed, namely the proximal path and the distal path (Fig. 6 and S18 and S19<sup>†</sup>). The proximal path represents the migration of Na near the active structure, and the distal path represents the migration of Na from near the active structure to far away from the site.

For the proximal path of Na on MnN<sub>3</sub>, it is intriguing that an energy well appears when the Na traverses the site above the Mn atom (Fig. 6a). It can be observed that the Mn shifts outward towards the graphene, which is attributed to the repulsive effect of the Mn atom on the Na atom. Meanwhile, Na is captured due to the Coulomb interaction force between the three N atoms and Na atom. The formed intermediate structure (*i.e.*, Na–N<sub>3</sub>) is similar to a very stable substance, NaN<sub>3</sub>. Therefore, the transition from the IS to the energy well involves the formation of two Na-N bonds and tends towards stability, resulting in an energy change exceeding 5 eV. The energy well can be explained by the strong capture effect generated by the unsaturated coordination mono-vacancy doped structures (*i.e.*, MnN<sub>3</sub>). For the distal path, Na needs to overcome an energy barrier of 2.24 eV to get rid of the MnN<sub>3</sub> center (Fig. 6b). Compared with MnN<sub>3</sub>, there is a barrier of 1.46 eV for the proximal migration of Na on MnN<sub>4</sub>, indicating a weaker trapping capability of MnN<sub>4</sub> (Fig. 6c). As for the distal migration of Na on MnN<sub>4</sub>, it is necessary to absorb 0.46 eV energy to break the balance between the Coulomb interaction force of MnN<sub>4</sub>-Na and C-Na (Fig. 6d). Furthermore, the order of the energy barrier of Na distal migration on the  $MnN_x$  is the same as the trend of Na adsorption energy on the  $MnN_x$  (*i.e.*,  $MnN_3 > MnN_4$ ), which also underscores the strong capture ability of the threefold-coordinated catalysts. Using the same method, we analyze the migration of Na on  $CoN_x$  and NiN<sub>r</sub>. We observe that there exists a potential well when Na





Fig. 6 The relative energy profiles of (a) the proximal path and (b) the distal path of the Na atom migration on  $MnN_3$ ; (c) the proximal path and (d) the distal path of the Na atom migration on  $MnN_4$ .

migrates proximally on  $CoN_3$  and  $NiN_3$ , while there exists an energy barrier on  $CoN_4$  and  $NiN_4$  (Fig. S21 and S22<sup>†</sup>).

## Conclusion

In this research, the catalytic mechanism of two coordination modalities' spin SACs has been thoroughly investigated for Na-O<sub>2</sub> battery applications. Compared with fourfold-coordinated catalysts with carbon double-vacancies (i.e., MN<sub>4</sub>), threefoldcoordinated catalysts with a carbon mono-vacancy (*i.e.*,  $MN_3$ ) exhibits high spin states. Such disparity in spin states leads to an oxygen side-on adsorption mode and end-on adsorption mode of O2. The side-on adsorption mode on MN3 can induce the formation of composite intermediates (*i.e.*,  $(OMO)N_3$ ), which can serve as an active center to reduce the overpotential (e.g. for MnN<sub>3</sub>, reduced from 4.77 to 0.65 V). The end-on adsorption mode on MN<sub>4</sub> cannot facilitate the transformation of the active center. We further find that the oxygen adsorption energy can be a descriptor of the overpotential of the Na-O<sub>2</sub> battery. The established scaling relationship has a correlation coefficient of 0.98. We elucidate the spin-coupling mechanism and the evolution mechanism of the active center of spin SACs in Na-O2 batteries at the atomic level. We hope our work will promote the rational design of superior oxygen adsorption-activation involving catalysts over conventional trial and error methods.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

J. L and A. M. contributed equally to this work.

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

This work was supported by the National Key R&D Program of China (No. 2022YFB4602101), the Fundamental Research Funds for the Central Universities (No. 2022ZFJH004), the National Natural Science Foundation of China (No. 22308096, 22278127, and 22378112), and Shanghai Pilot Program for Basic Research (22T01400100-18).

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