The Role of Nitrogen and Sulfur Dual Coordination of Cobalt in Co-N$_{4-x}$S$_x$/C Single Atom Aatalysts in the Oxygen Reduction Reaction

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Introduction

Single-atom catalysts (SACs) have been considered as a potential candidate for fuel cell application due to the fact that they exhibit good oxygen reduction reaction (ORR) activity. In this study, the ORR catalytic activity of sulfur-doped Co-N$_4$/C catalysts, denoted as Co-N$_{4-x}$S$_x$/C ($x = 0–4$), is systematically studied via density functional theory calculations. The interaction of the ORR intermediates (*OOH, *O and *OH) with catalysts and the thermodynamics of the ORR process are also taken into account. In addition, electronic structure analysis is employed to investigate the source of the ORR activity, which will help to design promising ORR catalysts with high efficiency at a reasonable price.

Computational methods

Spin-polarized DFT calculations are performed using the Vienna ab initio simulation package (VASP)[1] coupled with the atomic simulation environment (ASE)[2]. All calculations are done with the BEEF-vdW exchange correlation-functional[3] in which vdW-DF2 non-local correlation is used to account for non-local van der Waals interactions.

The d-band center of the catalyst can be calculated:

$$\varepsilon_d = \frac{\int_{-\infty}^{\infty} E \cdot D(E) dE}{\int_{-\infty}^{\infty} D(E) dE}$$

where D(E) is the total d states of the metal atom in Co-N$_{4-x}$S$_x$/C.

The binding energy of Co (ΔE_b) in these catalysts can be calculated:

$$\Delta E_b = E_{Co-N_{4-x}S_x/C} - E_{N_{4-x}S_x/C} - E_{Co}$$

The Gibbs free energy of the intermediates can be calculated as:

$$\Delta G(U = 0V) = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S$$

Figure 1: Top and side view of the structures: (a) Co-N$_4$/C, (b) Co-N$_3$S/C, (c) Co-N$_2$S$_2$/C, (d) Co-NS$_3$/C, and (e) Co-S$_4$/C.

- two C atoms in pristine graphene were removed to create di-vacancy defective graphene.
- then C atoms around the di-vacancy are replaced by 4-x (x = 0-4) nitrogen atoms and x sulfur atoms.
- Co atom is incorporated at the center of the di-vacancy, as illustrated in the above Fig. 1(a–e).

Electronic properties and stability of the structures

Table 1: The average bond length of adjacent C-N and Co-N (d_{Co-N} and d_{Co-S}/Å), binding energy (ΔE_b / eV), Co d-band center (Co(d) / eV), the charge of the Co atom, the S, and the N atom around the double vacancies in Co-N$_{4-x}$S$_x$/C systems.

Systems	d_{C-N}	d_{Co-N}	ΔE_b	Q(Co)	Q(S)	Q(N)	Co d-band center
Co-N$_4$/C	1.376	1.879	-9.38	1.06	-	-1.21	-0.71
Co-N$_3$S/C	1.375	1.889	-7.96	0.72	0.16	-1.21	-0.91
Co-N$_2$S$_2$/C	1.375	1.890	-7.45	0.63	0.14	-1.21	-0.96
Co-NS$_3$/C	1.385	1.940	-5.97	0.47	0.14	-1.18	-1.06
Co-S$_4$/C	-	-	-5.97	0.37	0.12	-	-1.24

- Few electrons are distrebuted around the Co atom as shown in Fig. (2).
- Because the coordinated N and S atoms (3.05 and 2.58) are more electronegative than the Co atom (1.88).
- The binding energy of Co in all systems is negative indicating good stability of the structures.
- d-band center used to discribe the activity of catalyst.
- There is a decreasing trend in the d-band center from Co-N$_4$ /C to Co-S$_4$/C.
- clear correlation between decreasing the number of N atoms and the d-band center.
- suggesting that the catalytic activity of Co-N 4 /C can be tailored through changing the number of N atoms by sulfur atoms
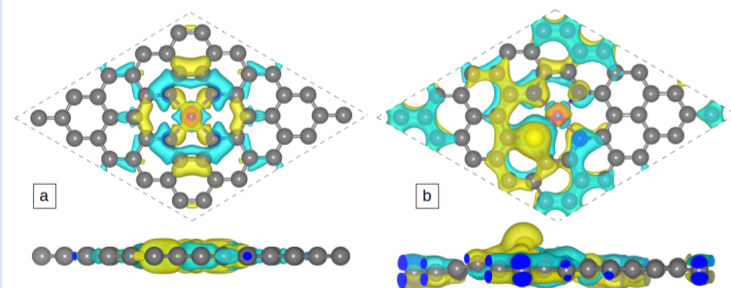
Figure 2: Charge density distributions of a) Co-N$_4$/C and b) Co-N$_3$S/C.
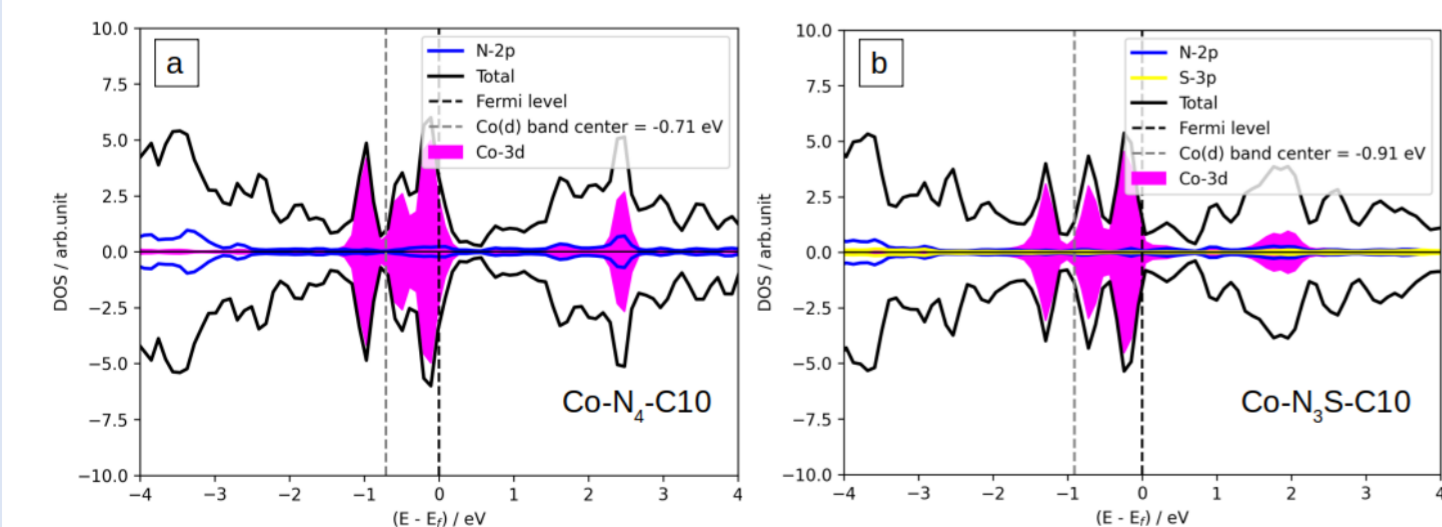
Figure 3: Density of states (DOS) of; a) Co-N$_4$/C and b) Co-N$_3$S/C system.

References

1. Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. Physical Review B 1993, 47, 558–561.

2. Larsen, A. H.; Mortensen, J. J.; Blomqvist, J.; Castelli, I. E.; Christensen, R.; Dułak, M.; Friis, J.; Groves, M. N.; Hammer, B.; Hargus, C., et al. The atomic sim- ulation environment— a Python library for working with atoms. Journal of Physics: Condensed Matter 2017, 29, 273002.

3. Wellendorff, J.; Lundgaard, K. T.; Møgelhøj, A.; Petzold, V.; Landis, D. D.; Nørskov, J. K.; Bligaard, T.; Jacobsen, K. W. Density functionals for surface science: Exchange-correlation model development with Bayesian error estimation. Phys. Rev. B 2012, 85, 235149.

Adsorption energy of the ORR intermediates on model catalysts

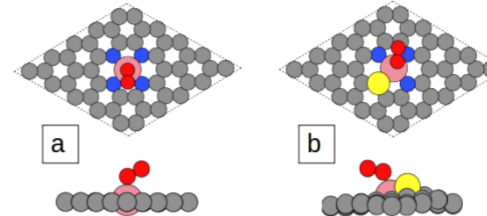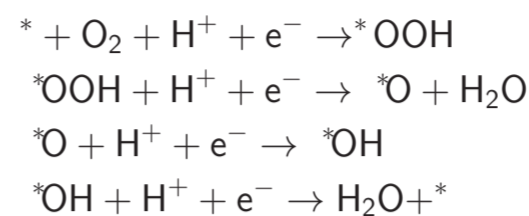The associative 4 e$^-$ pathway is considered to study the ORR mechanism.

$$* + O_2 + H^+ + e^- \rightarrow *OOH$$
$$*OOH + H^+ + e^- \rightarrow *O + H_2O$$
$$*O + H^+ + e^- \rightarrow *OH$$
$$*OH + H^+ + e^- \rightarrow H_2O + *$$

Figure 4: Optimized adsorption structures of O$_2$ adsorbed on: a) Co-N$_4$S/C and b) Co-N$_3$S/C

Figure 5: Optimized adsorption structures of ORR intermediates; a) Co-N$_4$/C, and Co-N$_3$S/C. Pink, cobalt (Co); blue, nitrogen (N); yellow, sulfur (S); gray, carbon (C); red, oxygen (O), and white, hydrogen (H).

Table 2: Adsorption energy (E_{ads}) of ORR intermediates on model catalysts (eV).

System	*OOH	*O	*OH
Co-N$_4$/C	3.12	2.17	0.32
Co-N$_3$S/C	3.39	2.05	0.52
Co-N$_2$S$_2$/C	3.42	1.84	0.51
Co-NS$_3$/C	3.43	1.94	0.57
Co-S$_4$/C	3.50	2.01	0.63

- The Co atom is the most active site to adsorb the ORR intermediates.
- The adsorbtion energy of *OH is weakened.
- The decreased d-band center is attributed to the weaker adsorption energy.

Thermodynamics of the ORR

The Gibbs free energy of the intermediates can be calculated as:

$$\Delta G(U = 0V) = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S$$

The ΔG_{ads} can be calculated by the equations of:

$$\Delta G(*OOH) = \Delta E_{ads}(*OOH) + 0.67$$
$$\Delta G(*O) = \Delta G_{ads}(*O) + 0.11$$
$$\Delta G_{ads}(*OH) = \Delta E_{ads}(*OH) + 0.34$$

limiting potential (U_{lim}):

$$U_{lim} = -\max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}/e$$

limiting overpotential:

$$\eta_{lim} = 1.23 - U_{lim} = 1.23 + U_{lim}$$

Figure 6: Volcano plot for the ORR limiting potential (U_L) against the Gibbs free energy of $\Delta_{ads}G(*OH)$.

Table 3: ORR intermediates adsorption Gibbs free energies at $U = 0$ V$_{RHE}$ and the calculated ORR overpotential (η_{ORR}) on the considered surfaces.

Systems	OOH*	O*	OH*	η_{ORR} / V
		$\Delta_{ads}G$ / eV		
Co-N$_4$/C	3.79	2.28	0.66	0.57
Co-N$_3$S/C	4.05	2.16	0.86	0.37
Co-N$_2$S$_2$/C	4.07	1.93	0.82	0.41
Co-NS$_3$/C10	4.09	2.05	0.91	0.40
Co-S$_4$/C10	4.16	2.28	0.97	0.47
Co-N$_4$S/C10	3.86	2.23	0.72	0.51

Figure 7: The Gibbs free energy diagram of ORR; a) Co-N$_4$/C and b) Co-N$_3$S/C catalysts.
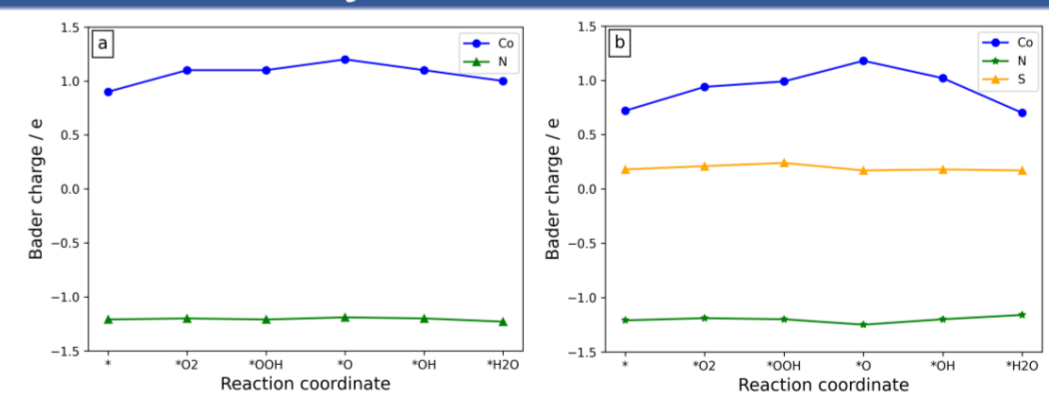
Origin of the ORR activity

Figure 8: The Bader charge of the atoms at the active sites of (a) Co-N$_4$/C and (b) Co-N$_3$S/C catalysts. The charge of N is the average charge of the existing N atoms.

- for Co-N$_4$/C and Co-N$_3$S/C, during the whole ORR process, the charge fluctuation of the Co atom is obvious (Fig. 8)
- the charge on N atoms remains almost constant.
- This suggests that the ORR activity is mainly due to the Co atom.

Conclusion

In summary, the ORR activities of Co-N$_{4-x}$S$_x$/C systems were investigated using density functional theory. Among the studied systems, Co-N$_3$S/C possesses enhanced ORR activity. The overpotential of Co-N$_3$S/C is 0.37 V which is smaller than that of the Co-N$_4$/C (0.57 V) catalyst. Therefore, we can conclude that modifying the electronic structure of the central metal atom could enhance the ORR catalytic activity of the Co-N$_4$/C system.

Acknowledgment