

## 中性锌空气电池催化剂的理论设计

孙中贤, 张 宝, 孙 威

(电子科技大学材料与能源学院, 成都 611731)

**摘 要:** 中性锌空气电池因其高比能、高安全性和长寿命受到广泛关注, 但其空气正极动力学迟滞问题限制了其实际应用。通过第一性原理计算方法, 研究了中性锌空气电池的催化路径, 并提出了其催化剂设计的描述符。结果表明: 4 电子路径倾向于发生在氧吸附强度较强的催化剂上, 而 2 电子路径更易出现在吸附强度较弱的催化剂表面。此外, 吸附强度与过电势遵循 Sabatier 原理, 适中吸附强度具有最佳性能。研究发现 Pt 和 Ag 表现出适中的氧吸附特性, 是中性锌空气电池正极催化剂的潜在候选材料。

**关键词:** 中性锌空气电池; 催化剂; 描述符; 第一性原理计算; 线性标度关系

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在“双碳”战略背景下, 发展用于发电的风电、太阳能等为代表的可再生能源势在必行。然而, 由于可再生能源的波动性和间歇性特征, 其并网运行面临着巨大挑战。新型储能技术成为间歇性可再生能源并网不可或缺的部分<sup>[1-3]</sup>。当前, 新型储能技术市场以电化学储能, 尤其是锂离子储能, 占据主导地位。然而, 锂离子电池存在安全性和资源问题, 难以满足大规模储能的诉求<sup>[4]</sup>。因此, 开发新型储能电池迫在眉睫。

锌空气电池具有高的理论能量密度、本征安全、低成本以及原材料资源丰富等优势, 是下一代储能电池的潜在候选<sup>[5-6]</sup>。传统的锌空气电池以碱性电解液为主, 使用高浓度 KOH<sup>[7]</sup>。然而, 碱性电解液导致的锌负极腐蚀、枝晶、析氢、钝化以及电解液碳酸盐化等问题<sup>[8-9]</sup>, 严重制约了二次碱性锌空气电池的发展。得益于近年来中性锌金属电池电解液的发展<sup>[10-12]</sup>, 中性锌空气电池也得到了蓬勃发展<sup>[13-16]</sup>。在前期的工作中, 首次在中性三氟甲基磺酸锌电解液中报道了全新的 2 电子锌空气电池反应机制<sup>[17]</sup>。相比于碱性锌空气电池, 这种全新的中性锌空气电

池具有更高的可逆性和稳定性, 是二次锌空气电池更加有力的候选。与碱性锌空气电池相同的是, 中性锌空气电池能量效率依旧受制于空气正极反应。能量效率受限同样存在于其他非质子参与的金属空气/氧气电池中<sup>[18]</sup>。针对此问题, 大量金属催化剂<sup>[19-20]</sup>及氧化物催化剂<sup>[21-22]</sup>被用于加速正极反应动力学。但是, 目前中性锌空气电池正极催化剂系统研究存在空白, 其正极材料依旧以碳材料为主<sup>[23]</sup>。如何理性设计中性锌空气电池的正极催化剂仍是亟待解决的问题。

在本工作中, 通过第一性原理计算方法, 系统地探究了多种催化剂材料表面中性锌空气电池(以下简称“中性锌空”)反应路径。计算结果表明, 不同反应中间体吸附能之间的线性标度关系在中性锌空气电池中仍然成立。这种线性标度关系赋予氧吸附强度作为中性锌空气电池催化的描述符能力, 同时也限制了最大理论催化活性。此外, 计算结果还表明反应路径也与和氧吸附强度有很好的关联。4 电子过程更倾向于发生在具有强氧吸附作用强度的催化剂表面, 而在弱氧吸附作用强度的催化剂表面更多地

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第一作者: 孙中贤(2002—), 男, 硕士研究生。

通信作者: 张 宝(1993—), 男, 博士, 特聘研究员;

孙 威(1989—), 男, 博士, 教授。

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First author: SUN Zhongxian (2002—), male, Master candidate.

E-mail: szx1341119206@163.com

Correspondent author: ZHANG Bao (1993—), male, Ph.D., Senior Research Fellow.

SUN Wei (1989—), male, Ph.D., Professor.

E-mail: zhangbao@uestc.edu.cn; weisun@uestc.edu.cn

进行 2 电子放电路径。这些理论计算结果为中性锌空气电池的机理认识和正极设计提供了理论基础。

## 1 方法

采用基于 VASP<sup>[24]</sup> 的密度泛函理论(DFT)计算, 使用 PAW 基组<sup>[25]</sup>和 PBE 泛函<sup>[26]</sup>。同时, 对弱相互作用进行 Grimme D3 校正<sup>[27]</sup>。 $K$  点网格采用 Monkhorst-Pack 方法<sup>[28]</sup>, 使用 Pymatgen 生成<sup>[29]</sup>, 采用 MPRelaxSet 设置。截断能为 520 eV, 自洽计算能量收敛标准为  $10^{-5}$  eV。离子弛豫收敛标准为 0.02 eV/Å。计算采用平板模型, 材料厚度约 10 Å, 真空层大于 15 Å。自由能计算采用式(1):

$$G = E + \text{ZPE} - \text{TS} \quad (1)$$

式中:  $G$ 、 $E$ 、ZPE 和 TS 分别是吉布斯自由能、DFT 总能、零点能和熵贡献能量(温度均采用 300 K)。ZPE 可以通过声子频率计算:

$$\text{ZPE} = \frac{1}{2} \sum_K \hbar \nu_K \quad (2)$$

吸附物种的 TS 只考虑振动的贡献<sup>[30]</sup>:

TS =

$$k_B T \left[ \sum_K \ln \left( \frac{1}{1 - e^{-\hbar \nu_K / k_B T}} \right) + \sum_K \frac{\hbar \nu_K}{k_B T} \frac{1}{(e^{\hbar \nu_K / k_B T} - 1)} + 1 \right] \quad (3)$$

计算模型可视化采用 VESTA 软件<sup>[31]</sup>。

## 2 结果与讨论

### 2.1 中性锌空反应中间体的线性标度关系

如图 1a 所示, 借鉴锂氧电池和碱性锌空气电池反应路径, 考虑中性锌空正极 4 电子( $\text{ZnO}$  产物)和 2 电子( $\text{ZnO}_2$ )反应路径。选取了贵金属、非贵金属、碳材料、氧化物和单原子这几类典型材料作为研究对象(见图 1b), 重点分析其表面中性锌空反应路径、机制以及作为催化剂的潜力。具体地, 金属催化剂包括 Ag (111)、Au (111)、Co (001)、Pt (111)和 Ru (001), 碳材料采用石墨烯结构, 单原子催化剂包括 Co-N<sub>4</sub>、Fe-N<sub>4</sub>, Mn-N<sub>4</sub> 和 Ni-N<sub>4</sub>, 而氧化物材料包括 CoO (111)和  $\delta$ -MnO<sub>2</sub> (001)。在反应中间体选择上, 以单电子转移为基元反应步骤<sup>[17, 32]</sup>, 忽略了最终固相产物前的吸附状态( $\text{ZnO}_2^*$ 和  $\text{ZnO}$ )。

根据 Sabatier 原理, 每一种中间体都应适中的强度时, 催化剂具有最佳的催化活性。然而在大部分电催化反应中, 由于线性标度关系(LSRs)的存在, 导致催化剂的理论催化活性往往难以达到最佳<sup>[33]</sup>。因此, 首先探究多种中间体吸附之间的关联。如图 2

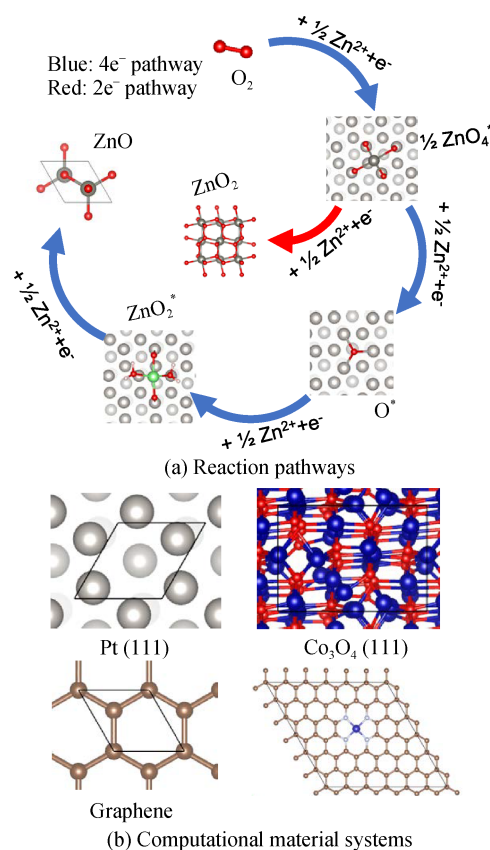


图 1 反应路径和计算材料体系示意图

Fig. 1 Schematic diagram of reaction pathways and computational material systems

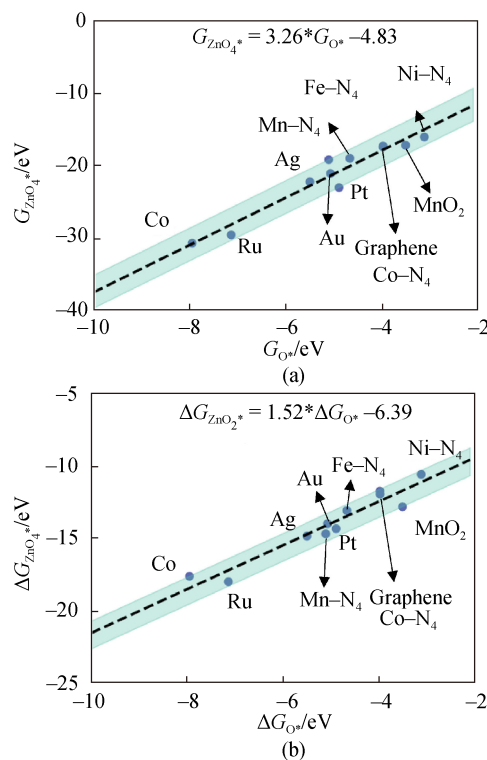


图 2 不同反应中间体吸附自由能之间的线性标度关系

Fig. 2 Linear scaling relationships between adsorption free energies of different reaction intermediates

所示,在中性锌空反应中, $O^*$ 、 $ZnO_2^*$ 和 $ZnO_4^*$ 吸附强度之间也存在明显的线性标度关系。这种线性标度关系在碱金属氧气电池中同样存在<sup>[32]</sup>,它限制了催化剂设计的自由度。线性标度关系导致多种中间体的吸附强度相互关联,从而难以同时优化所有中间体的吸附强度。如何打破这种线性标度关系将是后续研究的重点。

## 2.2 催化剂的理论设计

进一步地,探讨不同电位对2电子与4电子反应路径的影响。图3展示了Ag(111)在0.6、0.9、1.2、1.4 V (vs.  $Zn/Zn^{2+}$ )下的自由能路径。可以看出,4电子和2电子反应限速步骤均为第1个电子转移。较弱的 $ZnO_4^*$ 吸附使得第一步反应能垒在1.2 V下高达0.78 eV。该计算结果表明,由于受限于线性标度关系,即使采用金属催化剂,中性锌空气电池的放电电压依旧难以与碱性锌空气电池匹敌。此外,由于4电子路径在 $O^*$ 到 $ZnO_2^*$ 的反应,在低极化条件下(即高放电电位)下依旧存在明显势垒。这也意味着4电子路径更容易出现在即在高极化放电条件下,此时 $O^*$ 到 $ZnO_2^*$ 的反应无明显台阶,更有利于4电子转移反应。

接着,对比了不同金属表面的反应自由能路径,这里选取1.0 V作为基准。如图4所示,Pt(111)和Au(111)的限速步骤与Ag(111)催化剂一致,主要为较弱的 $ZnO_4^*$ 吸附使得第一步反应能垒较为困难。其中,Pt(111)具有更低反应能垒。这也意

味Pt作为优异的常规氧化还原反应(ORR)催化剂,在锌离子参与的ORR过程中依旧保持了高催化活性。相反地,Ru(001)和Co(001)催化剂表面反应性明显高于Ag(111),过强的 $ZnO_4^*$ 吸附使得第2个电子转移反应成为限速步骤。同时,4电子转移势垒明显低于2电子转移势垒。这意味着在Ru(001)和Co(001)催化剂表面反应极化更大,且更加倾向于发生4电子转移,生成全新的ZnO放电产物。在碳材料以及单原子M-N<sub>4</sub>材料表面,其反应路径均与Ag(111)催化剂一致。过弱的 $ZnO_4^*$ 吸附使得第一步反应能垒较大,反应动力学更加迟滞。单原子M-N<sub>4</sub>材料的催化活性从高到低遵从如下顺序:Mn-N<sub>4</sub>、Fe-N<sub>4</sub>、Co-N<sub>4</sub>、Ni-N<sub>4</sub>。MnO<sub>2</sub>表面也具有较为的反应性,导致其第一步电子转移反应极为困难。

利用线性标度关系,绘制了不同电压下,2电子转移和4电子转移路径的限速步骤能垒与 $O^*$ 吸附自由能的关联。从图5可以看出,最佳的 $O^*$ 吸附自由能为-6 eV左右。此外,反应路径选择性在最佳 $O^*$ 吸附能附近与反应极化密切相关,低极化工况不利于4电子路径。在所计算的催化材料体系中,Ag(111)和Pt(111)具有较为合适的 $O^*$ 吸附强度。进一步提高Ag(111)和Pt(111)的 $O^*$ 吸附强度,可以更加接近最佳理论催化活性。通过合金化、应变工程等修饰策略Ag和Pt,提高其d带中心,增强表面反应性,可以进一步提升中性锌空催化活性。

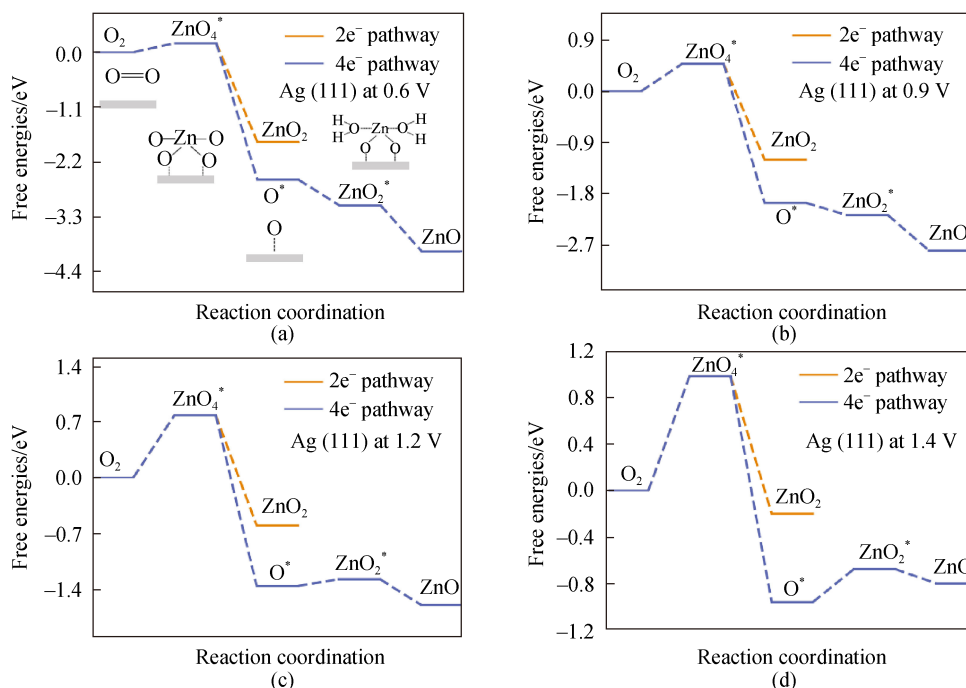


图3 Ag(111)表面不同电位下的反应自由能路径

Fig. 3 Reaction free energy pathways at different potentials on the Ag(111) surface

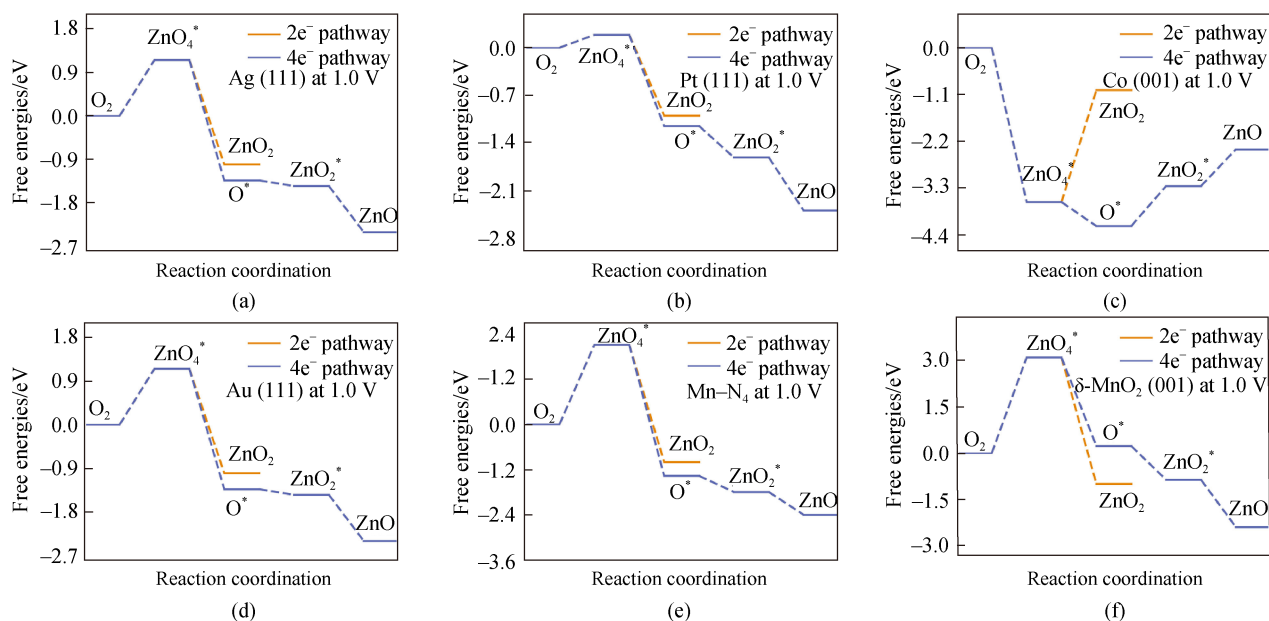
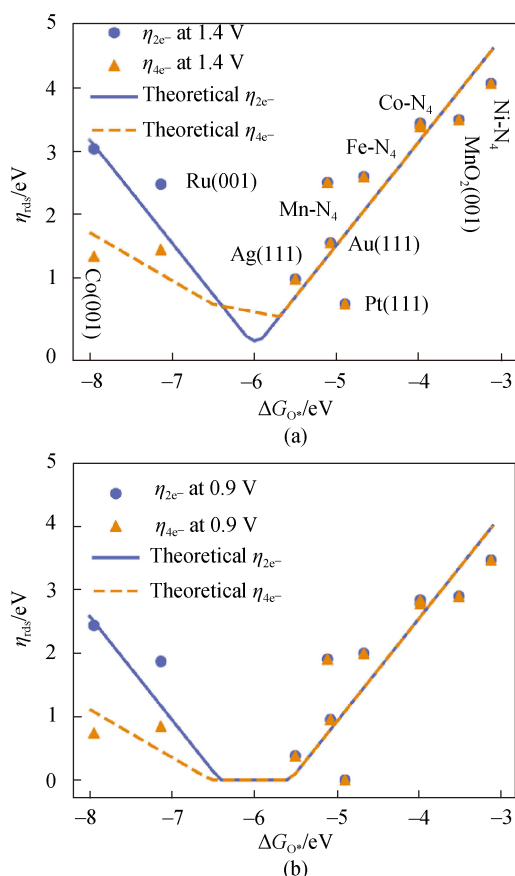
图 4 不同材料在 1.0 V(vs. Zn/Zn<sup>2+</sup>)下的反应自由能路径Fig. 4 Reaction free energy paths for different materials at 1.0 V (vs. Zn/Zn<sup>2+</sup>)

图 5 限速步骤能垒与 O\* 吸附自由能的关联

Fig. 5 Correlation of energy barrier of the rate-determined step with the O\* adsorption free energy

此外,如图 6 所示,对比 2 电子转移和 4 电子转移路径可以看出,2 电子路径发生在具有弱反应

性表面的正极材料上,如碳材料及 M-N<sub>4</sub> 型单原子催化剂,这与相关实验报道结果一致<sup>[14,17]</sup>。4 电子路径则倾向于发生在具有强反应活性的材料表面(如 Pt、Ru)。相关中性锌空 4 电子路径目前无直接实验报道,但是已有少量报道在金属催化剂表面可以放电生成 4 电子 ZnO 产物<sup>[13,34]</sup>,这对发展新型非质子参与的 4 电子锌空气电池机制具有一定理论指导意义。

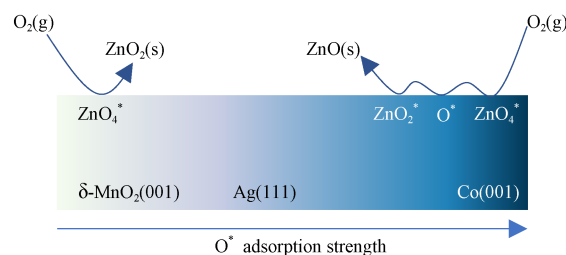


图 6 中性锌空反应路径调控示意图

Fig. 6 Schematic diagram of reaction path regulation in neutral zinc-air batteries

### 3 结论

理论计算结果表明,线性标度关系在中性锌空反应的多种吸附中间体中依旧成立。并且氧吸附作用强度与过电势之间遵循 Sabatier 原理,即适中的强度( $\Delta G_{O^*} \sim -6$  eV)具有最佳的催化活性。在众多催化剂中,Ag 和 Pt 具有较为适中的表面反应性,其理论催化活性较高,可能表现出更快速的反应动力学。通过合金化、应变工程等手段提高 Ag 和 Pt 表

面反应性, 是进一步提升其中性锌空气电池催化活性的有效手段。此外, 低氧吸附自由能有利于锌离子参与的 4 电子 ORR 过程。因此, 采用具有较强表面反应性的金属催化剂, 是实现新型非质子 4 电子锌空气电池的潜在手段。

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# Theoretical Design of Catalysts for Neutral Zinc-Air Batteries

SUN Zhongxian, ZHANG Bao, SUN Wei

(School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 610054, China)

## Extended Abstract

**Introduction** Zinc-air batteries have a significant promise for next-generation energy storage due to their low cost, high safety, high theoretical capacity, and abundant availability. Recently, we reported a new rechargeable zinc-air battery based on zinc peroxide chemistry. Compared to conventional zinc-air batteries, this neutral zinc-air battery exhibits higher reversibility and stability, making it a more promising candidate for secondary zinc-air batteries. However, the low energy efficiency of neutral zinc-air batteries remains a challenge. And the mechanism of these neutral zinc-air battery reactions is still unclear. In this work, we systematically investigated the reaction pathways of neutral zinc-air reaction by first-principles calculations.

**Methods** Density Functional Theory calculations based on a software package named VASP was employed with PAW potentials and the PBE functional. The vdW interactions were corrected by the Grimme's D3 method. The  $k$ -point mesh was generated by the Monkhorst-Pack scheme *via* Pymatgen with MPRelaxSet settings. A cutoff energy of 520 eV was utilized within a convergence criterion of  $10^{-5}$  eV for self-consistent calculations. The convergence criterion for ionic relaxation was set to be 0.02 eV/Å. The calculations were performed by a slab model with a thickness of approximately 10 Å and a vacuum layer of greater than 15 Å.

**Results and discussion** There is a clear linear scaling relationship among the adsorption strengths of O\*, ZnO<sub>2</sub>\*, and ZnO<sub>4</sub>\* in neutral zinc-air reactions. This relationship constrains the freedom in catalyst design, making it difficult to optimize all intermediate adsorption strengths simultaneously. Breaking this linear scaling relationship will be a focus of future research. The rate-determined step for both the four-electron and two-electron reactions in Ag (111) is the first electron transfer. A weaker ZnO<sub>4</sub>\* adsorption makes the first reaction barrier as high as 0.78 eV at 1.2 V (*vs.* Zn/Zn<sup>2+</sup>). This result indicates that even with this metal catalyst, the discharge voltage of neutral zinc-air batteries remains smaller than that of alkaline batteries due to the limitation of linear scaling relationships.

Among various catalysts, Pt (111) exhibits a lowest reaction barrier, indicating that Pt maintains a high catalytic activity in Zn<sup>2+</sup>-involved ORR processes. Conversely, the surface reactivity of Ru (111) and Co (001) catalyst surfaces is significantly greater than that of Ag (111), where over-strong ZnO<sub>4</sub>\* adsorption makes the second electron transfer the rate-determined step. Meanwhile, the energy barrier of four-electron pathway is notably lower than that of two-electron transfer pathway, showing that the Ru (111) and Co (001) catalyst can favor a four-electron transfer reaction and form ZnO discharge products.

The optimal O\* adsorption free energy is found to be around -6 eV based on the linear scaling relationships. And Ag (111) and Pt (111) have relatively appropriate O\* adsorption strengths. The neutral zinc-air catalytic activity of Ag and Pt can be further improved *via* increasing the  $d$ -band center. In addition, the calculations also reveal that catalysts with a strong reactivity favor a four-electron transfer pathway.

**Conclusions** The theoretical calculation results showed that linear scaling relationships still had true among various adsorption intermediates in neutral zinc-air reactions. Oxygen adsorption strength and overpotential followed the Sabatier principle, indicating that a moderate strength (*i.e.*,  $\Delta G_{O^*} \sim -6$  eV) yielded an optimal catalytic activity. Among numerous catalysts, Ag and Pt exhibited an optimal surface reactivity with a high theoretical catalytic activity. Furthermore, employing catalysts with a strong surface reactivity, such as Co and Ru, represented a potential approach to achieve non-protonic four-electron zinc-air batteries.

**Keywords** neutral zinc-air batteries; catalysts; descriptors; first-principles calculations; linear scaling relationship