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News&Views

Enhanced oxygen reduction through axial chlorine engineering of p-block antimony atomic sites

The oxygen reduction reaction (ORR) is a fundamental electrochemical process in fuel cells and metal-air batteries, playing a crucial role in energy storage and conversion. Although Pt catalysts perform well, their scarcity and high-cost limit large-scale application. Therefore, the development of non-precious metal catalysts has become a major research focus [1,2]. Atomically dispersed 3d transition metals (such as Fe, Co, Mn, and Cu) coordinated with nitrogen-doped carbon (M–N–C structures) exhibit high catalytic activity and excellent atomic utilization. However, M–N–C single-atom catalysts (SACs) with d-electron-rich metal centers often undergo Fenton reactions, which may corrode the carbon substrate, ionomers, and polymer membranes during practical operation [3]. Therefore, designing novel SACs that can suppress Fenton reactions while enhancing reaction stability is urgently needed. Unlike 3d transition metals, main-group metals possess closed d-electron shells, and their negligible interaction with hydrogen peroxide makes them intrinsically Fenton-inactive. Nevertheless, due to the lack of open d orbitals for effective interaction with reaction intermediates, main-group metal centers generally exhibit poor surface catalytic activity for electrochemical reactions such as ORR. In fact, the intrinsic activity of single-atom catalytic sites is closely related to their electronic structure, which can be precisely tuned by manipulating the coordination environment of the metal center [4]. Therefore, rational regulation of the coordination structure in main-group metal SACs to improve ORR performance, along with elucidating the atomic-scale catalytic mechanisms, has emerged as a critical scientific challenge.

In a recent study published in the *Journal of the American Chemical Society*, Li, Chen, Yang and co-workers reported an Sb SAC with an SbN_4–Cl configuration synthesized *via* a molten chloride salt-assisted pyrolysis strategy, which markedly enhanced the ORR performance of main-group metals [5]. In this study, ZIF-8 was employed as a sacrificial template, into which Sb source was introduced *via* electrostatic adsorption. Meanwhile, Cl atoms were incorporated through molten chloride salt-assisted pyrolysis to enable axial coordination, thereby yielding the SbN_4Cl/NC catalyst (Fig. 1(a)). Transmission electron microscopy and high-angle annular darkfield scanning images revealed that the catalyst retained the rhombic dodecahedral morphology of ZIF-8, exhibited a porous surface, and contained atomically dispersed Sb species (Fig. 1(b)). X-ray diffraction patterns exhibited only the (002) and (100) peaks attributed to graphitic carbon at 24° and 43°, with no observable Sb-related crystalline peaks, thereby confirming the atomic dispersion of Sb species (Fig. 1(c)). X-ray photoelectron spectroscopy confirmed the existence of Sb–N and Sb–Cl bonds. Moreover, the observed shift in Sb 3d binding energy indicated that the valence state of Sb ranged from 0 to +3, with the axial Cl coordination leading to an increased oxidation state relative to SbN_4Cl/NC. In addition, X-ray absorption near-edge structure spectroscopy and extended X-ray absorption fine structure analyses elucidated the local coordination environment at the atomic scale, confirming that the introduction of axial Cl preserved the Sb–N_4 framework and resulted in the formation of a five-coordinated SbN_4Cl configuration.

Electrochemical data provide clear and compelling evidence for elucidating the structure-activity relationship of the catalyst. Firstly, the ORR performance of SbN_4Cl/NC was systematically evaluated under alkaline conditions. Compared with SbN_4/NC and commercial Pt/C catalysts, SbN_4Cl/NC exhibited remarkable catalytic activity, with onset and half-wave potentials ($E_{1/2}$) of 1.03 and 0.921 V, respectively, a high kinetic current density of 16.95 mA cm^{-2}, and a low Tafel slope of 56 mV dec^{-1} (Fig. 1(d)). Koutecky-Levich and rotating ring-disk electrode measurements confirmed a near four-electron transfer pathway ($n \approx 3.98$) and a low H_2O_2 yield ($< 4\%$), indicating excellent selectivity. The catalyst also demonstrated the lowest charge transfer resistance and a relatively high electrochemical active surface area ($C_{dl} = 10.25$ mF cm^{-2}), along with outstanding methanol tolerance and durability, with only a loss of 4 mV in $E_{1/2}$ after 10,000 cycles. Using 3,3′,5,5′-tetramethylbenzidine as a probe for reactive oxygen species, the absorbance of SbN_4Cl/NC at 652 nm was significantly lower than that of the Fe SAC, indicating that SbN_4Cl/NC exhibited negligible Fenton reaction activity. The high stability of SbN_4Cl/NC was attributed to the synergistic effect of the efficient four-electron reduction pathway and the suppressed Fenton reaction activity. *In situ* Raman spectroscopy showed that SbN_4Cl/NC could detect key ORR intermediates at higher potentials and more efficiently reduce/desorb OH species. Additionally, SbN_4Cl/NC also exhibited excellent ORR activity in 0.1 M $HClO_4$, delivering an $E_{1/2}$ of 0.780 V, which was higher than that of SbN_4/NC (0.688 V). However, compared with Pt/C ($E_{1/2} = 0.837$ V), the $E_{1/2}$ of SbN_4Cl/NC still showed a certain gap. Furthermore, it exhibited a lower Tafel slope (57 mV dec^{-1}) and an electron transfer number of approximately 3.96, confirming a highly efficient four-electron pathway. Moreover, SbN_4Cl/NC exhibited excellent stability in acidic electrolytes, with only an 11 mV $E_{1/2}$ decrease after 5000 cycles.

The superior performance is attributed to electronic structure modulation induced by the axial chlorine ligand, which effectively weakens the adsorption energy of HO* intermediates, thereby significantly enhancing catalytic activity and durability. The practical performance of SbN_4Cl/NC as the air cathode catalyst in zinc-air batteries was further evaluated. The assembled battery exhibited a high open-circuit voltage (1.49 V), a peak power density of 193 mW cm^{-2}, a specific capacity of 793 mAh g_{Zn}^{-1}, and an energy density of 1052 Wh kg_{Zn}^{-1} (Fig. 1(e)). Additionally, the battery based on SbN_4Cl/NC demonstrated long-term cycling stability exceeding 200 h, significantly outperforming the Pt/C-based battery.

Density functional theory calculations revealed the regulatory mechanism of axial Cl on the ORR performance of SbN_4Cl/NC catalyst. The axial Cl induces significant changes in the electronic distribution of

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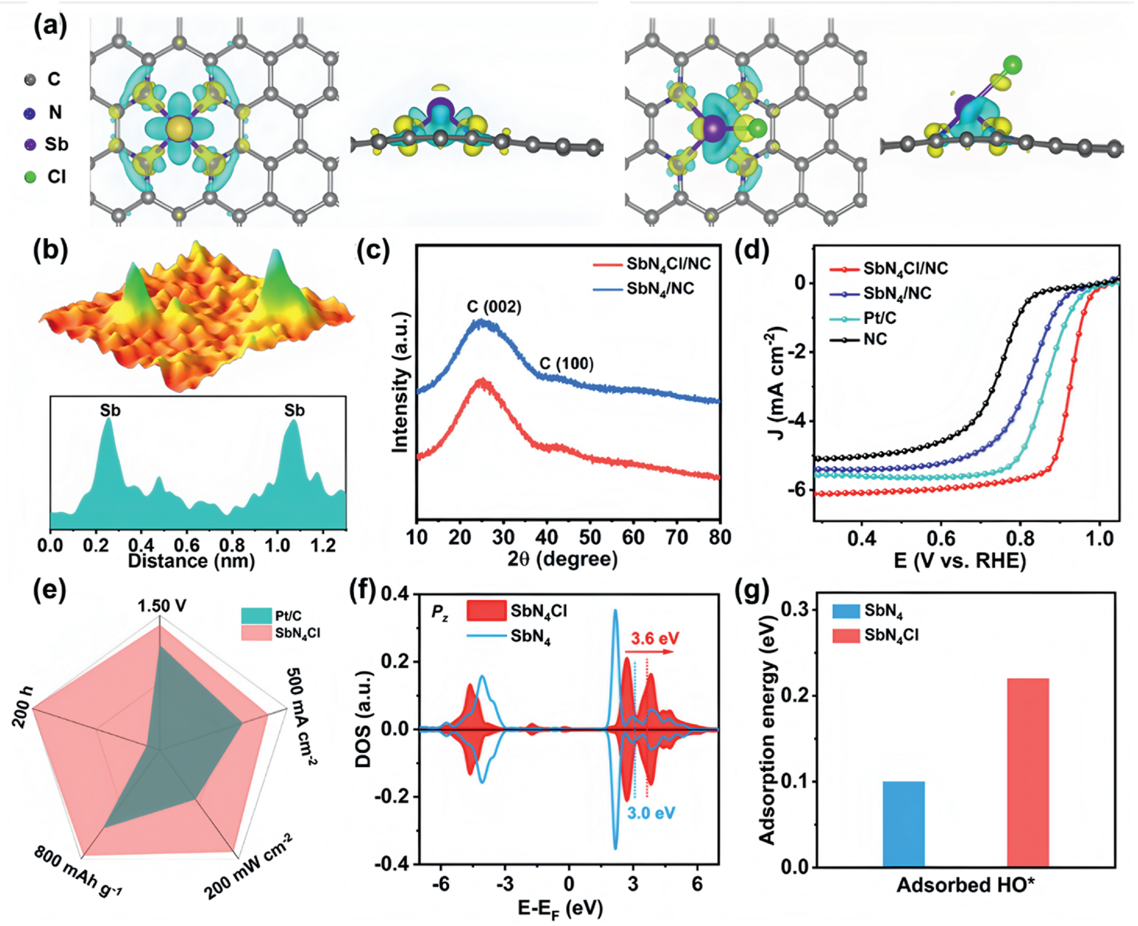

Fig. 1. (a) Charge density difference of SbN_4 and SbN_4Cl. (b) Intensity surface profile and intensity line profile taken from the HAADF-STEM image. (c) XRD patterns of SbN_4Cl/NC and SbN_4/NC. (d) ORR polarization curves of SbN_4Cl/NC, SbN_4, commercial Pt/C, and NC. (e) Comparison of the performance metrics of the Zn-air battery based on SbN_4Cl/NC and Pt/C. (f) PDOS plot of Sb in SbN_4 and SbN_4Cl as well as the corresponding P_z-band center. (g) Adsorption energy of HO* on SbN_4 and SbN_4Cl. Adapted with permission from Ref. [5]. Copyright©2025, American Chemical Society.

Sb atoms, enhancing the electronic density at the Fermi level and facilitating electron transfer (Fig. 1(f)). Meanwhile, the introduction of Cl increases the adsorption energy of Sb toward the HO* intermediate, weakening their interaction. This reduces the ORR overpotential from 0.86 to 0.73 eV, thereby improving catalytic activity and efficiency (Fig. 1(g)). These results demonstrate that axial Cl effectively modulates the electronic structure of the catalyst, promoting the ORR process.

In summary, Li, Chen, Yang and co-workers successfully constructed atomically dispersed Sb active sites on the hierarchical mesoporous carbon framework *via* a molten chloride salt-assisted pyrolysis strategy, forming a unique SbN_4–Cl coordination structure. This innovative design effectively regulated the electronic structure of the Sb center through the introduction of an axial chlorine ligand, optimizing the p-band distribution and significantly reducing the adsorption energy of key intermediates such as HO*, thereby enhancing the kinetic rate and overall catalytic efficiency of the ORR. This study not only overcomes the inherent limitation of low catalytic activity commonly observed in main-group metal catalysts but also greatly expands their application prospects in energy conversion systems such as fuel cells and metal-air batteries. Moreover, it provides new theoretical guidance and design strategies for tuning the p-band structure of main-group metal SACs through precise coordination engineering. However, the air electrode in zinc-air batteries is simultaneously governed by the oxygen evolution reaction (OER) and ORR during charge-discharge cycling. Therefore, the development of main-group metal catalysts with bifunctional ORR and OER activity in both acidic and alkaline environments is essential. In addition, from a practical perspective, substantial improvements in the long-term cycling stability and overall durability of electrode materials in zinc-air batteries are imperative.

CRediT authorship contribution statement

Wenjie Zhang: Writing – original draft. **Jiong Zhou:** Writing – review & editing.

Declaration of competing interest

The authors declare no competing interests.

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Wenjie Zhang[a], Jiong Zhou[a,b,*]
[a] *Department of Chemistry, College of Sciences, Northeastern University, Shenyang, 110819, China*
[b] *Key Laboratory of Functional Molecular Solids, Ministry of Education, and School of Chemistry and Materials Science, Anhui Normal University, Wuhu, 241002, China*

[*] Corresponding author. Department of Chemistry, College of Sciences, Northeastern University, Shenyang, 110819, China.
E-mail address: zhoujiong@mail.neu.edu.cn (J. Zhou).