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COMMENTARY

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Curved supports unlock activity-stability trade-off in Fe/N–C single-atom catalysts for acidic oxygen reduction

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Proton exchange membrane fuel cells (PEMFCs) have garnered considerable interest as one of the most promising clean power sources for next-generation transportation and distributed energy systems.[1] Notably, PEMFCs distinguish themselves from internal combustion engines through their higher energy efficiency, zero carbon emissions, and noiseless operation, while surpassing other electrochemical devices by virtue of their rapid start-up, modular scalability, and compatibility with renewable hydrogen. These advantages underscore the role of PEMFCs as a cornerstone technology in the clean energy landscape. Despite decades of progress, their large-scale deployment remains constrained by the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode and the reliance on platinum–group metals (PGMs).[2] The scarcity, high cost, and limited durability of PGMs–based catalysts constitute a critical bottleneck, highlighting the urgent need for low-cost and robust alternatives to enable practical commercialization.

Among PGM-free catalysts, Fe/N–C single-atom catalysts (SACs) have emerged as promising candidates, with atomically dispersed Fe–N_4 motifs providing favorable ORR kinetics and low material cost ensuring economic viability.[3] However, their practical implementation is limited by several key factors. First, current synthesis methods anchor Fe atoms on bulk carbon or stacked graphene, restricting active site density and thus limiting current output and device–level power. Second, the intrinsic performance of Fe–N_4 sites is constrained by linear scaling relationships among the adsorption free energies of key ORR intermediates (*OH, *O, and *OOH), imposing a thermodynamic ceiling on the simultaneous optimization of all reaction steps. Additionally, surface–exposed Fe sites are prone to Fenton–type degradation from peroxide and hydroxyl radicals, compromising stability. Strategies such as coordination environment modulation have improved performance but often at the cost of activity, leaving the inherent activity–stability trade–off as

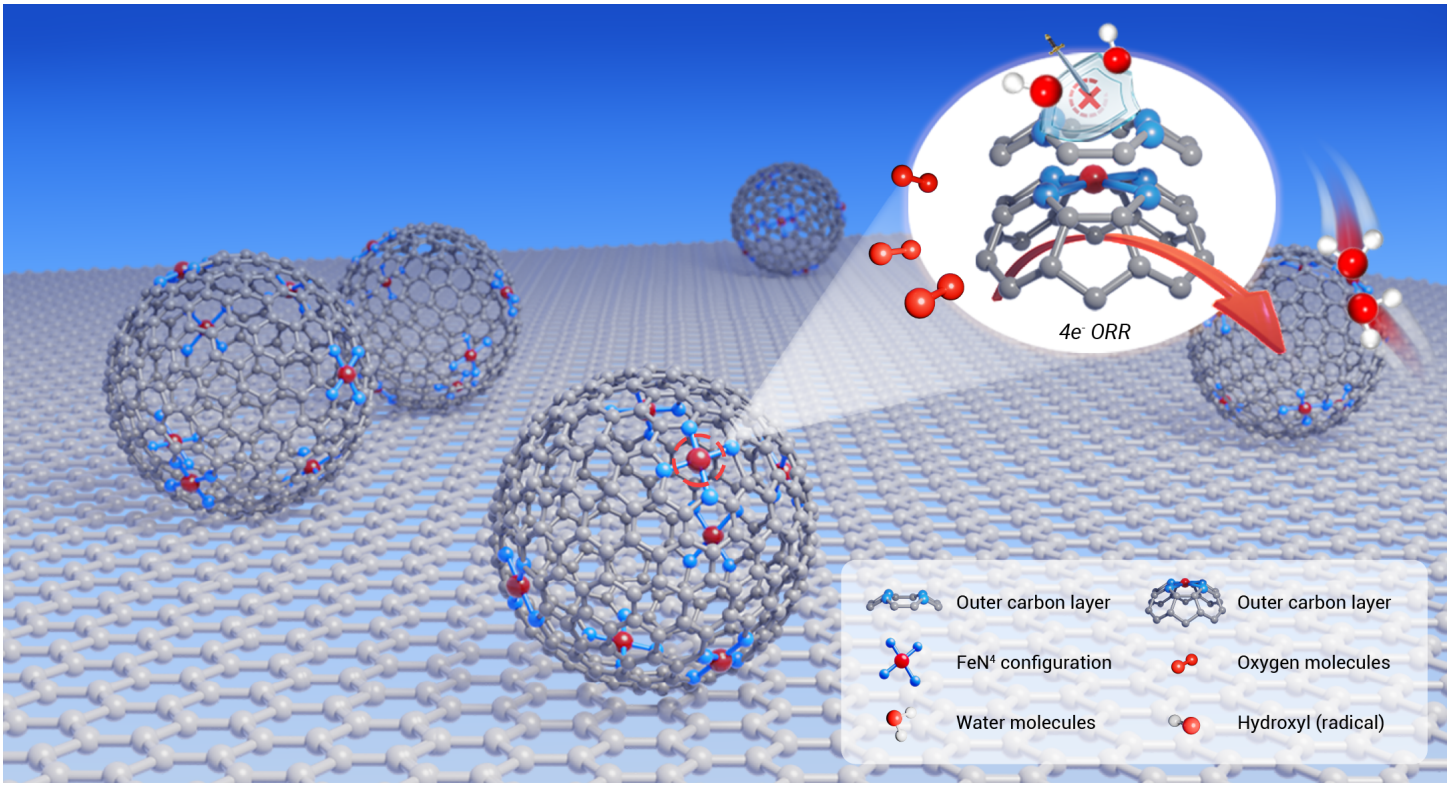

Figure 1. Schematic diagram of ORR reaction mechanism catalyzed by CS Fe/N–C.

a major obstacle to durable, high–performance Fe/N–C cathodes under practical PEMFCs conditions.[4]

In a recent study published in *Nature*, Wang et al. reported a new type curved-surface Fe/N–C catalyst (CS Fe/N–C, Figure 1) that offers a promising solution to the aforementioned challenges, in which single Fe atoms with Fe–N_4 motif are dispersed within a graphitized multilayered carbon with high-curvature surfaces by controlled pyrolysis C_3N_4/ tannic acid–Fe(III) followed by acid etching.[5] The control catalyst 2D Fe/N–C was synthesized using the same overall protocol, except for the amount of $FeCl_3$ used in the precursor, which was identified as the key parameter steering the formation of hollow multilayered nanoprotrusions versus planar morphology. The morphology during pyrolysis is significantly influenced by the precursor ratio and heating profile; however, the authors did not provide inter-batch statistical data in the article. Providing data from multiple experimental batches is essential for evaluating the robustness of curvature engineering in practical production. Multiple characterization techniques corroborated the structural and electronic features of the CS Fe/N–C catalyst. Aberration–corrected scanning transmission electron microscopy directly visualized that the atomically

dispersed Fe sites embedded in the curved region were mainly located in deep fourth layer of the graphitized multilayered carbon layer (97.6%), with only 2.4% of the Fe atoms found in the outermost carbon layer. Although most atomically dispersed Fe atoms reside in the inner curved layers, these sites remain catalytically accessible due to the presence of porous channels and electronic coupling within the conductive carbon framework. The curved nanoprotrusions create triple-phase boundaries that facilitate O_2 transport and charge transfer, ensuring effective utilization of the inner Fe–N_4 sites. X–ray absorption near-edge structure (XANES) and extended X–ray absorption fine structure analyses identified that CS Fe/N–C catalyst exhibits the Fe–N_4 coordination environment with an elongated Fe–N bond length of relative to the control two–dimensional Fe/N–C (denoted as 2D Fe/N–C) catalyst. Furthermore, Mössbauer spectroscopy revealed a higher proportion of low-spin Fe(II)–N_4 sites, commonly regarded as ORR–active, alongside a markedly increased Fe site density in the curved region (~1.6 No. nm^{-2} versus ~1.0–1.2 No. nm^{-2} in 2D planar counterparts, where No. mm^{-2} denotes the number of Fe atoms per square nanometre), together highlighting the structural and electronic advantages imparted by curvature engineering.

To elucidate the catalytic mechanism of the multilayered carbon structure toward ORR, the authors employed density functional theory (DFT) calculations and crystal orbital Hamiltonian population (COHP) analyses. The results show that the curvature of the inner carbon layer induces structural modifications at the Fe–N_4 sites, weakening the adsorption of *OH and *OOH and disrupting the linear scaling relationship. Although the curvature of the carbon support introduces local strain to the carbon matrix, the authors demonstrated that the graphitized outer carbon layer effectively protects the Fe–N_4 sites from acidic degradation, inhibits Fenton-type demetallation and hydroxyl radical formation, and balances the trade-off between apparent activity and stability. Additionally, electrostatic repulsion between the nitrogen atoms in the outer carbon layer and the ORR intermediates in the inner layers further modulates the adsorption energies. These combined effects significantly reduce the calculated overpotential to 0.34 V, enhancing ORR activity. It is well known that *OOH is the key ORR intermediate governing ORR selectivity, with the O–O and O–Fe bond strengths determining the reaction pathway. COHP analysis reveal that the bond–length ratio of O–O to O–Fe influences the selectivity, with the curved surface catalyst favoring the $2e^-$ pathway to H_2O_2 and the low H_2O adsorption energy improving stability by facilitating easy desorption of H_2O.

Electrochemical evaluations reveal that the CS Fe/N–C catalyst exhibits remarkable activity and durability in 0.1 M $HClO_4$ electrolyte. The CS Fe/N–C demonstrated an onset potential of 0.94 V versus RHE and a half–wave potential of 0.82 V, significantly outperforming the control 2D Fe/N–C catalyst. The catalyst achieved a high current density of 5.8 $mA{\cdot}cm^{-2}$ with four-electron selectivity (n = 3.96), highlighting its superior ORR activity. Furthermore, under practical H_2–air conditions in a PEMFCs, the CS Fe/N–C cathode delivered a peak power density of 0.78 $W{\cdot}cm^{-2}$, with only 17.5% loss in power density after 30,000 cycles in an accelerated stress test (AST). After 303 hours of continuous operation at 0.6 V, the catalyst retained 86% of its initial current density, indicating excellent stability. The CS Fe/N–C catalyst also showed a significantly lower Fe loss (24.5%) compared to the 2D Fe/N–C counterpart (58.9%), demonstrating superior metal retention and enhanced long–term durability. These results underscore the significant improvements in catalytic performance and stability enabled by the unique hollow multilayered carbon layer structure.

In situ characterizations, including X-ray absorption spectroscopy (XAS) and electron paramagnetic resonance (EPR), were employed to investigate the dynamic structural evolution of the CS Fe/N–C catalyst during ORR. XAS measurements revealed a pronounced blue shift in the XANES white line of CS Fe/N–C, indicating greater Fe valence reduction and faster structural kinetics compared to 2D Fe/N–C. The k^3–weighted FT-EXAFS spectra further showed that the Fe–N bond length in CS Fe/N–C increased with decreasing cathodic potential, suggesting structural adjustments during oxygen adsorption. In situ electrochemical impedance spectroscopy (EIS) and dynamic resistance spectra demonstrated superior O_2 diffusion and ORR kinetics for CS Fe/N–C, highlighting its enhanced reaction and transport dynamics. Moreover, EPR measurements confirmed that CS Fe/N–C produced significantly fewer OH• radicals than 2D Fe/N–C, thanks to its protective outer carbon layer that mitigates the Fenton reaction. The catalyst also favors a more selective $4e^-$ ORR pathway, reducing radical formation and enhancing stability. These results underscore the structural and electrochemical advantages of CS Fe/N–C for efficient and durable ORR catalysis.

In summary, Wang et al. introduced a groundbreaking approach that successfully overcomes the long-standing activity–stability trade–off in Fe/N–C SACs. By leveraging the curvature effect and shell confinement, they developed CS Fe/N–C catalyst that demonstrates both high catalytic activity and exceptional long-term durability under PEMFCs operating conditions. This work emphasizes the synergistic coupling between curvature-induced strain and the encapsulating carbon shell as a conceptual framework for balancing electronic activation and structural protection. This perspective extends the impact of the study beyond Fe–N–C systems, suggesting that curvature modulation could guide the rational design of other single-atom catalysts for reactions such as CO_2 reduction and oxygen evolution. The work also highlights key experimental challenges for technological translation, such as ensuring reproducible curvature control, achieving scalable synthesis, and effectively integrating such catalysts into membrane–electrode assemblies for practical fuel-cell operation. By articulating these mechanistic insights and practical considerations, this Commentary aims to provide a broader and forward-looking perspective on curvature-engineered single-atom catalysis.

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AUTHOR CONTRIBUTIONS

All authors contributed to and approved the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.