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Durability Challenges and Mitigation of Fe–N–C Single-Atom Catalysts in Acidic PEMFCs: Mechanisms, Strategies, and Perspectives

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Abstract. Proton exchange membrane fuel cells (PEMFCs) face critical challenges of high cost and limited operational lifespan, primarily due to the insufficient stability of conventional platinum-based catalysts. Fe–N–C single-atom catalysts have attracted extensive attention for their Pt-comparable activity; however, their durability remains a major limitation. This review systematically analyzes the trade-off between cost and durability in PEMFCs, with particular emphasis on the "deactivation chain" and associated engineering strategies. Four dominant deactivation mechanisms are summarized—demetalization, carbon/nitrogen framework corrosion, Fenton-type self-amplification, and interfacial mass-transfer imbalance—along with five representative mitigation strategies: heteroatom co-doping, secondary coordination engineering, protective shell construction, interface and water management, and self-healing approaches. Key performance indicators such as electrochemical surface area loss, voltage decay rate, and Fe dissolution rate are comparatively synthesized from the literature. The findings reveal that catalyst deactivation involves strong coupling and amplification effects, while multi-strategy integration can significantly alleviate early-stage performance degradation. Finally, the review highlights the urgent need for unified durability evaluation protocols, advanced multi-physics coupling characterizations, and scalable self-healing architectures to bridge current research gaps and accelerate the practical deployment of Fe–N–C catalysts in PEMFCs.

Keywords: Durability Challenges, Mitigation, Acidic PEMFCs

1. Introduction

The commercialization of polymer electrolyte membrane fuel cells (PEMFCs) has long been constrained by the cost and durability bottlenecks arising from the reliance of the cathodic oxygen reduction reaction (ORR) on platinum group metals (PGMs). In the PGM-free approach, Fe–N–C catalysts with single-atom coordination sites have demonstrated intrinsic activity and stack-level power densities approaching those of Pt under acidic conditions, positioning them as promising candidates for overcoming cost limitations [1,2].

Nevertheless, most Fe–N–C catalysts suffer from rapid voltage decay in the early stages of operation, which is driven not by a single factor but by a coupled "deactivation chain." This

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includes: (i) demetalization of Fe–N_4 sites [3-5]; (ii) corrosion of carbon/nitrogen frameworks; (iii) Fenton-type self-amplification reactions; and (iv) interfacial mass-transfer imbalance and water flooding, which mutually accelerate performance degradation [6–8].

Currently, durability evaluations lack sufficient cross-study comparability. Variations in accelerated stress test (AST) windows, electrode structures, and operating conditions hinder direct alignment between degradation mechanisms and performance outcomes. Recent advances have proposed in-situ characterization paradigms to deconvolute degradation pathways under operating conditions, alongside the publication of standardized AST protocols for heavy-duty fuel cells and catalyst layers by agencies such as DOE/M2FCT [7,9].

Building on this foundation, this review adopts the framework of "deactivation chains + engineering countermeasures" to systematically categorize the four dominant degradation mechanisms of Fe–N–C catalysts in PEMFCs—demetalization, carbon/nitrogen framework corrosion, Fenton-type self-amplification, and interfacial mass-transfer imbalance—and to synthesize five major mitigation strategies. Representative studies demonstrate the potential of multi-strategy synergies to significantly suppress early decay. However, substantial gaps remain in the establishment of unified durability indicators, multi-physics coupling characterization, and scalable self-healing architectures [10–12].

2. Literature review

2.1. Overview of existing research: site structure – characterization – MEA durability

From 2019 to 2025, the design of Fe–N–C catalysts has largely focused on electronic and coordination tuning of Fe–N_4 sites as well as stabilization of the carbon framework. Introducing a moderate amount of H_2 during thermal activation was shown to increase the density of active sites and promote the formation of the more stable S2 configuration, thereby mitigating early-stage decay [13]. Similarly, atomically dispersed Fe sites encapsulated by an N–C shell achieved near-Pt activity and slower initial degradation in MEAs [10].

Significant progress has also been made in characterization paradigms and mechanism identification. Operando techniques allow the deconvolution of voltage losses into contributions from site degradation, pore transport, and ionic-flux limitations [7]. Moreover, ICP-MS and gas-diffusion electrode studies have highlighted the critical role of local pH in governing Fe–N_4 stability and dissolution kinetics [11].

At the MEA level, practical durability has been enhanced through outer graphitization and thin N–C shell construction [10]. At the same time, the release of AST protocols for heavy-duty fuel cells by M2FCT [9], along with DOE/HFTO roadmap updates, has laid the foundation for standardized evaluation.

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Table 1. Representative progress (2019–2025)

Year	Focus	Key finding	MEA durability takeaway	Representative reference(s)
2019	Cost/roadmap for PGM-free	PGM-free catalysts identified as key cost lever	Sets cost/durability targets for vehicles	Thompson & Papageorgopoulos, 2019; US DRIVE, 2017 [1,2]
2020	H_2O_2 / pH effects	Acidic H_2O_2 induces rapid deactivation; strong pH dependence	Points to the need for ROS control/buffering	Bae et al., 2020 [5]
2021	AEM/bipolar interface transport	Flooding and mass-transport limits dominate polarization	Elevates interface/water management to an engineering priority	Seeberger et al., 2021 [8]
2022	N–C shell shielding	Operando evidence that shells suppress demetallation/early decay	Much slower initial voltage decay in MEAs	Myers et al., 2022 [10]
2023	Operando deconvolution; H_2 atmosphere	Parallel mechanisms resolved under operation; H_2 activation breaks trade-off	Calls for standardized operando protocols; boosts site density & stability	Liu et al., 2023; Zeng et al., 2023 [6,12]
2024 – 2025	Fe dissolution / local pH; AST norms	Local pH controls dissolution kinetics; heavy-duty AST online	Provides unified baselines for comparison and lifetime prediction	Pedersen et al., 2024; M2FCT, 2025; DOE/HFTO 2024–2025 [11,7]

2.2. Key gaps in the literature

Multiple mechanisms with insufficient quantitative apportionment: Many studies provide fragmented evidence in half-cells or short windows, with limited quantification of contribution ratios under MEA/AST conditions [7,11].

Numerous strategies but limited standardized comparison: Strategies vary widely in AST windows, ionomer loading/thickness, and gas/humidity settings, hindering comparability [9].

Limitations of existing reviews: Many reviews emphasize synthesis/characterization inventories but lack a causal closed loop and cross-scale coupling perspective [12].

2.3. Relevance to the present study (contribution positioning)

This review aligns mechanisms, engineering countermeasures, and evaluation metrics to form a causal closed loop:

Demetallation → electronic/coordination tuning, secondary coordination, shell shielding [10,13];

Carbon/N-framework corrosion and ROS → interface and water management, shell confinement [5];

Mass-transfer imbalance/flooding → pore hierarchy and membrane/electrode coupling [8].

Metrics such as voltage-decay rate, Fe dissolution rate, and active-site loss are compared under unified AST conditions [7,9].

2.4. Theoretical framework (expanded)

This research propose a two-domain framework coupling electronic structure and interfacial mass transfer:

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Electronic-structure domain: coordination and spin states modulate Fe–N_4 activity and stability; H_2-atmosphere activation and shell shielding stabilize sites [10,13].

Interfacial mass-transfer domain: local pH, water content, and fluxes govern H_2O_2 generation and Fenton-type self-amplification; ionomer distribution and pore hierarchy control flooding and O_2/proton transport [5,8,11].).

3. Result

Under acidic operation, catalyst degradation follows a coupled amplification pathway in which demetalation, carbon/nitrogen corrosion, Fenton-type self-amplification, and interfacial mass-transfer imbalance act in series and parallel. Local pH rise, together with H_2O_2 and radical species, accelerates Fe–N_4 demetalation and carbon oxidation. Operando ICP-MS studies confirm these effects [14–16].

Co-doping: P/F-modified catalysts in alkaline media achieve higher half-wave potentials, while acidic systems typically show lower values [13,17,18].

Shell/encapsulation: Thin N–C shells substantially slow early voltage decay; dissolution signals are significantly reduced [10,11].

Interface/water management: Optimization of pore hierarchy and ionomer distribution can restrict degradation during AST [8,16,19].

Self-healing architectures: In acidic half-cells, self-renewal systems show promising stability, though long-term MEA demonstrations remain lacking [18].

4. Discussion

Multi-strategy collaboration—combining coordination regulation, shell encapsulation, and interfacial management—consistently suppresses early-stage decay [7,11]. Shells slow the initial voltage drop [10], while activation atmospheres shift activity–stability balances [13].

Compared with Pt/C, which shows gradual quasi-linear loss, Fe–N–C catalysts display a two-stage profile with sharp early decay followed by slower degradation. This behavior is linked to Fe dissolution, local pH excursions, and ROS amplification [2,12]. These contrasts explain why stabilization and water management provide outsized benefits for Fe–N–C, while Pt/C relies on alloying and support engineering.

At the material scale, stabilizing Fe–N_4 sites through coordination tuning and shells raises thresholds; at the electrode scale, engineered pore hierarchies mitigate flooding; at the operation scale, optimized humidity and pressure limit ROS accumulation [1,2].

Limitations remain: protocol heterogeneity and batch effects complicate reproducibility, and many mechanistic claims rely on half-cell studies with insufficient MEA validation. Future research should converge on unified AST protocols, multimodal operando frameworks, and scalable self-healing designs [9,7,13,18].

5. Conclusion

This review reframes the durability challenge of Fe–N–C catalysts through the coupled “deactivation chain” framework, highlighting how demetalation, carbon/nitrogen corrosion, radical self-amplification, and interfacial mass-transfer imbalance are intrinsically coupled and require systematic understanding.

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Multi-strategy integration—including coordination/electronic tuning, protective shell encapsulation, and interfacial water management—has been shown to effectively suppress early-stage decay, and compared with Pt/C systems, the distinctive ROS-driven degradation of Fe–N–C underscores the disproportionate importance of transport-aware and ROS-regulating designs.

Looking ahead, achieving milestones such as <30 mV voltage loss after 30,000 cycles and >90% retention beyond 3,000 h in acidic MEAs will establish Fe–N–C as a practical, cost-effective PGM-free cathode platform, provided that unified AST protocols, multimodal operando quantification, and scalable self-healing architectures are further advanced.

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