

Perovskite oxide electrocatalysts for selective NO_x reduction to ammonia: Material design, reaction mechanisms, and beyond

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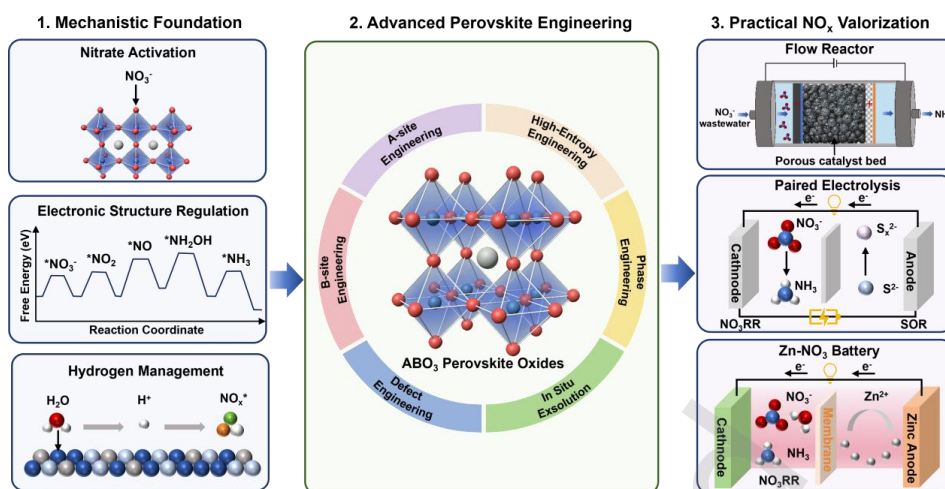
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This review links NO_x reduction mechanisms to rational perovskite design, highlighting how symmetry polarization, electronic structure, and hydrogen management control nitrate activation and selective NH_3 formation. We discuss perovskite engineering strategies, including cation/defect tuning, phase/spatial decoupling, and exsolution, for sustainable NO_x -to- NH_3 conversion.

Review Article

Perovskite oxide electrocatalysts for selective NO_x reduction to ammonia: Material design, reaction mechanisms, and beyond

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Abstract: Electrocatalytic NO_x reduction, particularly nitrate reduction (NO₃RR), has emerged as a promising waste-to-value strategy that simultaneously mitigates nitrogen pollution and enables sustainable ammonia (NH₃) synthesis under ambient conditions. Among the various catalyst families, perovskite oxides (ABO₃) have attracted considerable attention because their structural flexibility and compositional tunability enable precise regulation of surface electronic structure, defect chemistry, and reaction pathways. In this review, we establish a unified mechanistic framework that links the elementary processes of NO_x reduction with rational perovskite design. This framework highlights how symmetry polarization, electronic structure regulation, and hydrogen management collectively govern nitrate activation, intermediate evolution, and selective NH₃ formation, and discusses how these mechanistic principles are translated into advanced materials-design strategies, including cation and defect engineering, phase and spatial decoupling, and in situ exsolution of catalytically active nanoparticles. We further emphasize that practical NO_x valorization depends not only on catalyst optimization but also on integrating catalyst design with reactor engineering and emerging waste-to-energy electrochemical systems. Finally, we discuss key opportunities for advancing the field through

operando characterization, predictive design descriptors, standardized catalyst evaluation, and data-driven materials discovery. This review provides a unified perspective for the rational development of next-generation perovskite electrocatalysts for efficient NO_x -to- NH_3 conversion, with particular emphasis on nitrate reduction.

Keywords: perovskite oxides; nitrate reduction; mechanistic framework: ammonia synthesis

1. Introduction

The accelerating disruption of the global nitrogen cycle has increased the environmental burden of reactive nitrogen species while highlighting their potential as chemical resources.^[1-5] Nitrate (NO_3^-), in particular, accumulates in agricultural runoff, industrial effluents, and municipal wastewater, where excessive concentrations contribute to eutrophication, groundwater contamination, and ecosystem degradation.^[6-8] At the same time, ammonia (NH_3) remains indispensable for fertilizer production, chemical manufacturing, and emerging energy applications.^[9,10] However, its industrial production remains dominated by the Haber-Bosch process, which requires high temperatures and pressures and is associated with substantial energy consumption and CO_2 emissions.^[11] These challenges have motivated electrochemical strategies that convert nitrogen-containing pollutants into value-added ammonia, coupling environmental remediation with decentralized chemical production.

Among these approaches, electrochemical reduction of nitrogen oxyanions has attracted particular interest because nitrate and related NO_x species can serve as feedstocks for ambient ammonia synthesis.^[12] NO_3RR has emerged as the most extensively investigated route because nitrate is highly soluble, widely present in contaminated water, and considerably more reactive toward electrochemical reduction than molecular N_2 .^[13-15] Nevertheless, NO_x reduction involves complex proton-coupled electron-transfer processes accompanied by sequential N-O bond cleavage and hydrogenation of nitrogen-containing intermediates.^[16-18] The reaction pathway therefore depends on the catalyst's ability to simultaneously promote reactant activation, regulate the adsorption and conversion of nitrogen-containing intermediates, and provide an appropriate hydrogen supply while suppressing the competing hydrogen evolution reaction (HER).^[19-22] These interconnected requirements govern activity, NH_3 selectivity, and energy efficiency and provide a common mechanistic basis for understanding the electrochemical conversion of nitrogen oxyanions to ammonia.

Addressing these challenges requires catalyst platforms capable of regulating multiple physicochemical properties simultaneously rather than optimizing a single catalytic descriptor. In this context, perovskite oxides with the general formula ABO_3 have emerged as versatile platforms for electrocatalyst design.^[23, 24] Their crystal structures contain larger A-site cations and transition-metal B-site cations coordinated within corner-sharing BO_6 octahedral frameworks. The resulting lattice can accommodate extensive compositional substitution and structural modification while retaining a well-defined oxide framework, enabling systematic regulation of electronic structure, metal-oxygen covalency, oxygen-vacancy concentration, lattice distortion, crystal symmetry, and surface structure.^[25] These characteristics provide multiple, potentially coupled design parameters for regulating reactant adsorption, intermediate stabilization, water activation, hydrogen transfer, and interfacial charge transport. Perovskite oxides therefore offer a useful platform for examining how structural and electronic descriptors can be translated into selective NO_x -to- NH_3 conversion.

Recent advances have substantially expanded the structural-design space of perovskite electrocatalysts. Strategies including A- and B-site engineering, defect and oxygen-vacancy regulation, crystal-phase control, high-entropy composition, dynamic surface reconstruction, phase and spatial decoupling, and in situ exsolution have provided increasingly diverse approaches for tailoring catalytic environments across multiple length scales. Meanwhile, operando characterization and density functional theory (DFT) calculations have improved understanding of catalyst evolution and reaction intermediates under electrochemical conditions. These developments have shifted perovskite electrocatalyst research from empirical composition optimization toward mechanism-guided structural engineering, creating an opportunity to establish design principles that connect the elementary chemistry of NO_x reduction with controllable structural features.

Although several reviews have summarized NO_3RR catalysts, catalytic performance, and reaction mechanisms, the connections between elementary reaction requirements and advanced perovskite structural engineering remain fragmented.^[26-29] In particular, a unified framework linking reactant activation, intermediate regulation, and hydrogen management with emerging structural-design strategies has not yet been sufficiently established for perovskite-based NO_x reduction. To address this gap, this review adopts a mechanistically guided framework based on three fundamental

catalytic requirements: nitrate activation, intermediate regulation, and hydrogen management (**Figure 1**). Building on this framework, we examine how intra-lattice engineering, phase and spatial decoupling, and in situ exsolution regulate these catalytic requirements and influence activity, selectivity, and stability. We further extend the discussion beyond catalyst-level optimization to practical NO_x valorization, including reactor engineering, operation under demanding feed conditions, and emerging waste-to-energy electrochemical systems. Finally, we discuss opportunities associated with operando characterization, predictive descriptors, standardized evaluation, and data-driven materials discovery. By connecting NO_x reduction chemistry with perovskite structural engineering and practical electrochemical systems, this review provides a unified perspective on the development of perovskite electrocatalysts for NO_x-to-NH₃ conversion, with particular emphasis on nitrate reduction.

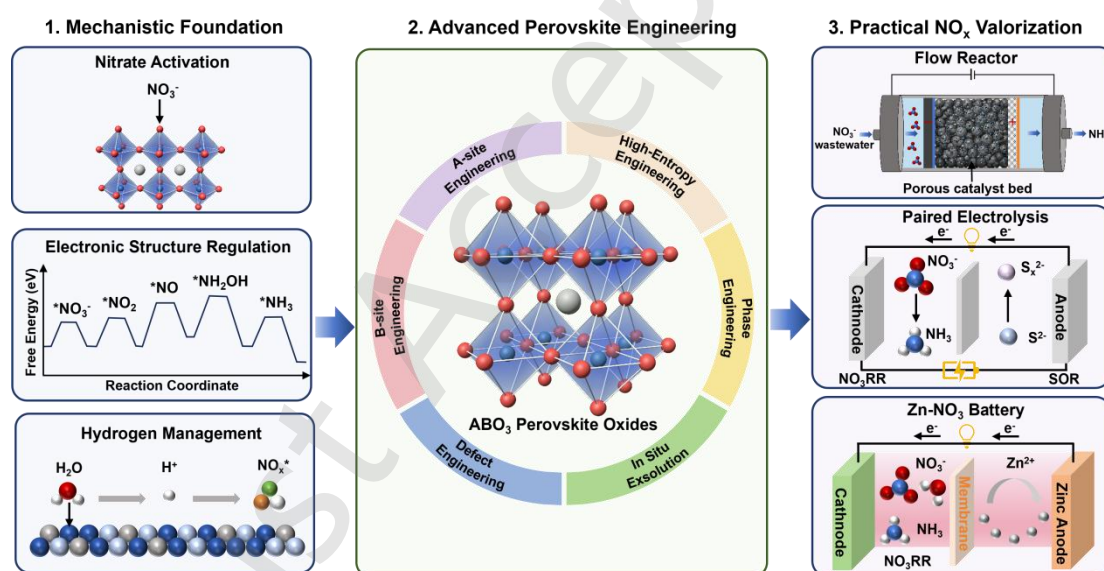


Figure 1. Conceptual mechanism-guided framework for the rational design of perovskite electrocatalysts, linking the three fundamental catalytic requirements of NO_x reduction with advanced perovskite engineering strategies and practical NO_x valorization systems.

2. Decoding the Electronic Coordinates of NO_x Reduction

Despite the complexity of electrocatalytic NO_x reduction, its activity and NH₃ selectivity are ultimately governed by three fundamental catalytic requirements: nitrate activation, intermediate regulation, and hydrogen management. These interconnected processes are rooted in the catalyst electronic structure, which controls charge redistribution, adsorption energetics, and proton-electron transfer throughout the reaction pathway. Here, electronic structure regulation represents the broader

physical basis governing charge redistribution, adsorption energetics, and interfacial interactions, whereas the three catalytic requirements describe the functional demands associated with different stages of NO_x reduction. Symmetry polarization is treated as a specific mode of electronic regulation in which local structural or coordination asymmetry generates a spatially nonuniform electronic environment. These principles provide the mechanistic framework for understanding how perovskite composition, defects, phase structure, and exsolution strategies influence NO_x reduction, as discussed in the following sections.

This framework should also account for the fact that the perovskite surface may evolve under the cathodic conditions required for NO_3RR . Electrochemical reduction can induce changes in surface composition, coordination, and defect chemistry, thereby modifying the nature of the sites exposed to the electrolyte. Yang and colleagues demonstrated this behavior for ABO_3 -type BiFeO_3 , where cathodic polarization during NO_3^- RR induced surface reconstruction accompanied by the formation of metallic Bi^0 clusters and additional oxygen vacancies.^[30] The reconstructed BiFeO_3 exhibited markedly enhanced NO_3RR activity relative to the pristine material, demonstrating that the surface present during operation can differ substantially from the initially characterized perovskite structure. Accordingly, the mechanistic relationships discussed below should be considered in the context of an evolving catalyst-electrolyte interface, with the pristine perovskite structure serving as the initial structural reference.

2.1 Breaking Symmetry: Symmetry Polarization via Local Fields

Nitrate activation represents a key kinetic challenge in electrocatalytic NO_3RR because the trigonal planar NO_3^- ion possesses strong N-O bonds and a highly delocalized electronic structure, making selective electron transfer and subsequent deoxygenation energetically demanding.^[31, 32] Consequently, catalytic performance depends not only on the availability of active sites but also on the local electronic environment that governs charge transfer at the catalyst-electrolyte interface. Symmetry polarization provides a specific approach to this problem by introducing local electronic asymmetry around catalytic centers, thereby creating an uneven electronic environment that can redistribute electron density, modify nitrate adsorption, and facilitate interfacial charge transfer. The emphasis here is therefore on

how spatially asymmetric electronic environments promote the initial activation of nitrate.

Although symmetry polarization can arise from different structural modifications, perovskite oxides offer several routes for creating such local electronic heterogeneity, including defect engineering, multication compositional regulation, and targeted cation substitution. Defect engineering provides a representative strategy for modifying the local electronic environment of perovskite surfaces. Yang et al. developed a polarity-inversion strategy to introduce La and O vacancies in LaFeO_3 , which modified the surface potential and strengthened the interaction between the perovskite surface and NO_3^- .^[33] The resulting enhancement in nitrate adsorption and interfacial charge transfer facilitated the initial activation of NO_3^- , illustrating how defect-induced modification of the local electronic environment can favor nitrate activation.

Compositional complexity provides another route for generating heterogeneous electronic environments within perovskite lattices. High-entropy perovskites represent one such strategy, in which the incorporation of multiple transition-metal cations creates chemically diverse local environments and promotes charge redistribution. Chen et al. reported that high-entropy LaSrNiCoMnFeCuO_3 porous nanotubes exhibited enhanced NO_3RR performance owing to multisite electronic interactions.^[34] Kelvin probe force microscopy revealed distinct surface potential distributions compared with LaNiO_3 (**Figure 2a**), indicating modified interfacial electrostatic environments, while shifts in the La 3d and Ni 2p XPS spectra (**Figures 2b and 2c**) confirmed electronic interactions among neighboring metal centers. These results suggest that high-entropy engineering can generate spatially heterogeneous electronic environments that promote nitrate activation through cooperative interactions among multiple metal sites.

Targeted lattice substitution provides a more localized route for tuning the electronic environment. Chu et al. introduced Cu into the B-site of $\text{LaFeO}_{3-\delta}$ to construct oxygen-vacancy-rich $\text{LaFe}_{0.9}\text{Cu}_{0.1}\text{O}_{3-\delta}$, thereby modifying the electronic structure of the Fe active centers.^[35] The altered Fe oxidation-state distribution observed in the Fe 2p XPS spectra (**Figure 2d**) indicated charge redistribution associated with Cu substitution, while the more positive surface potential relative to pristine $\text{LaFeO}_{3-\delta}$ (**Figure 2e**) was associated with enhanced nitrate enrichment at the catalyst interface. DFT calculations further revealed pronounced charge transfer

between the modified catalyst surface and adsorbed nitrate (**Figure 2f**), supporting the role of substitution-induced electronic redistribution in facilitating NO_3^- activation through stronger interfacial electronic coupling.

Taken together, these studies indicate that local electronic asymmetry relevant to symmetry polarization can be introduced through distinct structural routes, including defect engineering, high-entropy multication regulation, and targeted lattice substitution. Despite their different structural origins, these approaches modify the local electronic environment of the catalyst and thereby influence nitrate accumulation, adsorption, and initial charge transfer. Future efforts should focus on quantitatively correlating local electronic environments with nitrate adsorption energetics and interfacial charge-transfer kinetics using operando characterization and theoretical modeling, thereby enabling symmetry polarization to evolve from a qualitative concept into a predictive design descriptor for next-generation perovskite NO_3RR electrocatalysts.

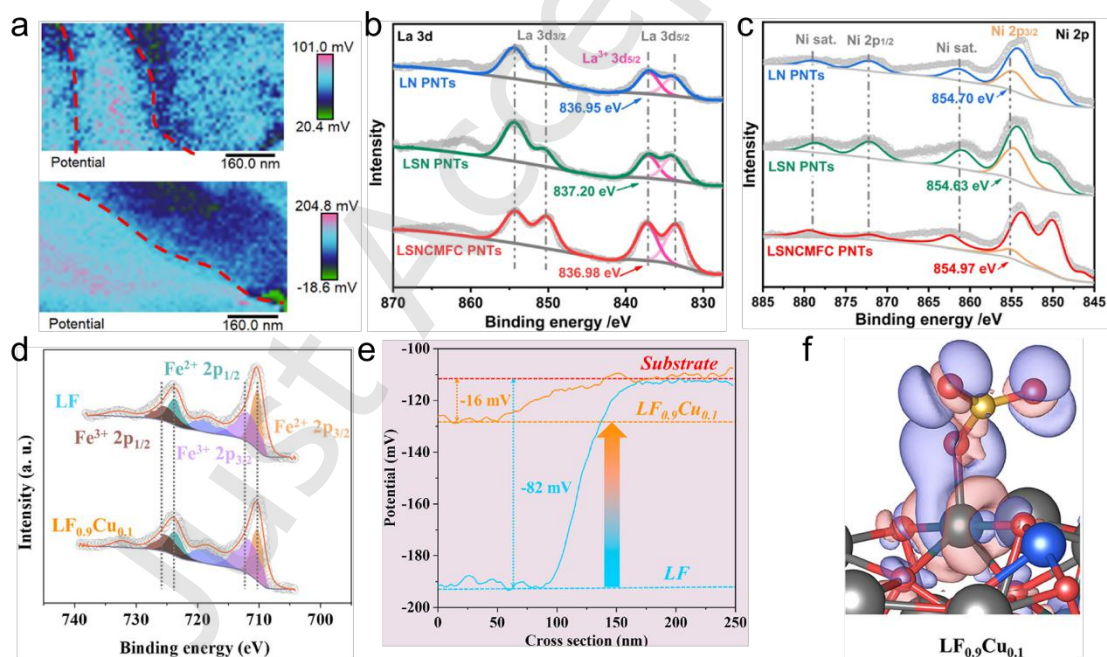


Figure 2. Symmetry polarization through local electronic structure engineering for enhanced nitrate activation. (a) KPFM surface potential mapping and (b, c) XPS spectra of high-entropy LaSrNiCoMnFeCuO_3 , revealing multisite-induced charge redistribution. Reproduced with permission.^[34] Copyright 2024, American Chemical Society. (d) Fe 2p XPS spectra, (e) surface potential measurements, and (f) DFT charge-density difference of Cu-substituted $\text{LaFe}_{0.9}\text{Cu}_{0.1}\text{O}_{3-\delta}$, illustrating substitution-induced electronic polarization and enhanced catalyst NO_3^- interfacial charge transfer. Reproduced with permission.^[35] Copyright 2023, American Chemical Society.

2.2 Balancing the Reaction Landscape: Site and Interface Regulation

Once nitrate is activated, the catalytic challenge shifts from initial reactant activation to controlling the adsorption and conversion of downstream nitrogen-containing intermediates. During NO₃RR, sequential proton-coupled electron-transfer steps generate intermediates such as *NO₃, *NO₂, *NO, and *NH₂OH, each requiring appropriate adsorption and conversion energetics for subsequent hydrogenation without becoming kinetically trapped on the catalyst surface.^[36, 37] Consequently, catalytic activity and NH₃ selectivity depend not on maximizing adsorption strength at a single site, but on providing suitable catalytic environments for the successive reaction steps. Site differentiation and interfacial coupling offer two complementary approaches to this challenge by distributing catalytic functions among distinct sites or phases.

One effective strategy is the creation of electronically differentiated active sites that distribute catalytic functions across the crystal lattice. Zuo et al. demonstrated this concept using Co-substituted Sr₂CuWO₆ double perovskites, where Cu and Co sites perform complementary roles during NO₃RR.^[38] Open-circuit potential measurements revealed preferential NO₃⁻ adsorption and activation on Cu sites, whereas Co sites exhibited stronger affinity toward NO₂⁻ intermediates (**Figure 3a**). Operando FTIR spectroscopy further tracked the sequential evolution of *NO₃, *NO₂, *NOH, and *NH₂OH before NH₃ formation (**Figure 3b**), supporting the involvement of distinct catalytic environments in successive reaction steps. DFT calculations further showed that Cu sites preferentially facilitate nitrate adsorption, whereas Co sites more strongly stabilize downstream intermediates, particularly *NO₂ (**Figure 3c**). Importantly, the reported free-energy difference of -2.02 eV between *NO₂ adsorption on Co and Cu provides thermodynamic support for the proposed *NO₂ spillover from Cu to Co. However, direct experimental tracking of *NO₂ migration between the two sites under operating conditions has not been established. The Cu-Co cooperation should therefore be regarded as a theoretically supported mechanistic interpretation rather than a directly observed intersite transfer process. This spatial separation of catalytic functions allows different sites to favor different stages of the reaction pathway, avoiding the need for a single site to simultaneously optimize the adsorption and conversion of structurally distinct intermediates.

A complementary strategy is to couple different catalytic functions through a heterointerface. Xu et al. demonstrated that exsolved PdNi alloy nanocrystals

anchored on defective $\text{La}_{0.52}\text{Ca}_{0.28}\text{Ni}_{0.06}\text{Ti}_{0.94}\text{O}_3$ optimize NO_3RR through the synergistic effects of oxygen vacancies and alloy-perovskite electronic interactions.^[39] Pd 3d XPS confirmed electronic interaction between the exsolved PdNi alloy and the perovskite support (**Figure 3d**), while DFT calculations showed that the Pd-Ni alloy/perovskite configuration modifies the free-energy landscape of the NO_3RR hydrogenation pathway (**Figure 3e**). In addition, the calculated hydrogen adsorption free energy (ΔG_{H}) suggests weaker HER propensity, consistent with preferential utilization of reactive hydrogen for nitrate reduction (**Figure 3f**).

Collectively, these results show that coupling a defective perovskite with an exsolved alloy can provide complementary reaction environments, while their electronic interaction further modifies the energetics of intermediate hydrogenation and HER competition. Thus, site differentiation and interfacial coupling provide complementary means of regulating the reaction landscape after nitrate activation. Site differentiation assigns different intermediate-conversion functions to distinct catalytic centers, whereas interfacial coupling combines complementary functions across different phases. In both cases, the resulting local electronic environments influence intermediate adsorption and conversion energetics, linking structural differentiation to the sequential chemistry of NO_3RR . Rather than maximizing nitrate adsorption alone, efficient perovskite electrocatalysts should therefore coordinate successive intermediate transformations by designing complementary catalytic sites and interfaces. Future research should establish quantitative relationships between site/interface structure, intermediate adsorption energetics, and catalytic performance through operando characterization and theoretical modeling, thereby advancing site and interface regulation from an empirical strategy toward a quantitative framework for the rational design of next-generation NO_x -to- NH_3 electrocatalysts.

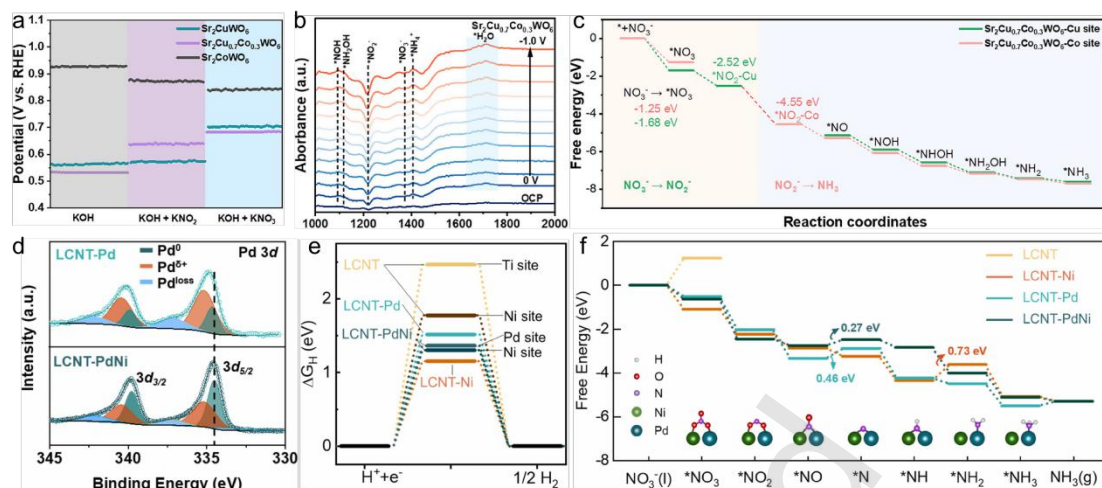


Figure 3. Electronic structure regulation balances intermediate evolution during NO₃RR. (a) Open-circuit potential measurements of Co-substituted Sr₂CuWO₆. (b) Operando FTIR spectra of reaction intermediates from OCP to -1.0 V (vs. RHE) in 0.1 M KOH with 0.1 m KNO₃. (c) DFT free-energy pathway for NO₃RR. Reproduced with permission.^[38] Copyright 2026, Wiley-VCH. (d) Pd 3d XPS spectra of exsolved PdNi/La_{0.52}Ca_{0.28}Ni_{0.06}Ti_{0.94}O₃. (e) Calculated free-energy profiles of the NO₃RR elementary steps. (f) Calculated Gibbs free energy (ΔG_H) for the hydrogen evolution reaction. Reproduced with permission.^[39] Copyright 2025, Elsevier.

2.3 The Hydrogen Supply Line

Beyond nitrate activation and intermediate regulation, efficient NO_x electroreduction ultimately depends on how hydrogen is generated, transported, and consumed at the catalyst interface. Because nitrate-to-ammonia conversion proceeds through multiple proton-coupled electron-transfer steps, the availability of reactive hydrogen (*H) must remain synchronized with the sequential hydrogenation of nitrogen-containing intermediates.^[40] The hydrogen supply pathway is also pH-dependent because proton availability changes with the reaction environment. Under acidic conditions, nitrate-reduction kinetics can be sensitive to hydronium availability, whereas under strongly alkaline conditions, limited proton availability places greater reliance on water-derived hydrogen species.^[41, 42] The structure and dynamics of interfacial water therefore become particularly important for maintaining hydrogen supply under conditions where proton availability is limited. Insufficient hydrogen supply can slow intermediate hydrogenation, whereas excessive hydrogen availability can increase the propensity for the competing HER. Consequently, high NO₃RR performance requires not simply efficient water activation, but precise control over the entire hydrogen supply line from *H generation to its selective delivery toward nitrogen intermediates.

One strategy focuses on regulating hydrogen generation by tailoring the electronic structure of the catalyst-electrolyte interface. Zuo et al. demonstrated that Co incorporation into Sr_2CuWO_6 reconstructs the interfacial water environment, increasing the proportion of water species with enhanced dissociation capability, as revealed by operando FTIR spectroscopy (**Figure 4a**).^[38] Electrochemical kinetic analysis further indicated improved interfacial charge transfer while maintaining a balance between *H generation and consumption (**Figure 4b**). DFT calculations showed that Co-associated sites lower the energy barrier for water dissociation relative to Cu sites (**Figure 4c**), establishing that cation engineering can regulate hydrogen availability by promoting water activation while maintaining selective hydrogen utilization during NO_3RR . Hydrogen generation alone, however, does not guarantee efficient ammonia synthesis if the resulting *H cannot be effectively delivered to adsorbed nitrogen intermediates.

A complementary strategy therefore engineers the hydrogen transport pathway. Xu et al. constructed hydroxyl-rich nanocavity-confined hydrogenation reactors on $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_{3-\delta}$ (SNC-LSF) for nitrite reduction to ammonia (NITRR), providing a complementary example of hydrogen management in nitrogen oxyanion reduction.^[43] Under cathodic polarization, the confined nanocavities increased the proportion of dissociated water species, indicating enhanced water activation and *H generation (**Figure 4d**). FTIR spectroscopy further revealed a broad O-H stretching band centered at approximately 3411 cm^{-1} , assigned to hydrogen-bonded O-H species (**Figure 4e**), consistent with the formation of hydrogen-bond networks within the hydroxyl-rich nanocavities. Rather than serving solely as surface species, these hydroxyl groups provide a hydrogen-bonded pathway for hydrogen transfer. Correspondingly, DFT calculations revealed an intramolecular hydrogen-transfer pathway analogous to a Grotthuss-like process, with an energy barrier of only 0.10 eV (**Figure 4f**), supporting rapid hydrogen migration toward nitrogen-containing intermediates. Although this study concerns NITRR rather than NO_3RR , it illustrates a hydrogen-transfer mechanism that is relevant to the broader reduction of nitrogen oxyanions and complements the NO_3RR -specific evidence discussed above.

Collectively, these studies demonstrate that hydrogen management extends beyond increasing *H generation. Efficient reduction of nitrogen oxyanions requires coordinated control of hydrogen production, transfer, and utilization at the catalyst-electrolyte interface. Future research should establish quantitative relationships

between interfacial water structure, hydrogen-transfer kinetics, and NH_3 selectivity through operando characterization and multiscale theoretical modeling, thereby providing a basis for developing predictive hydrogen-management descriptors for next-generation perovskite NO_x electrocatalysts.

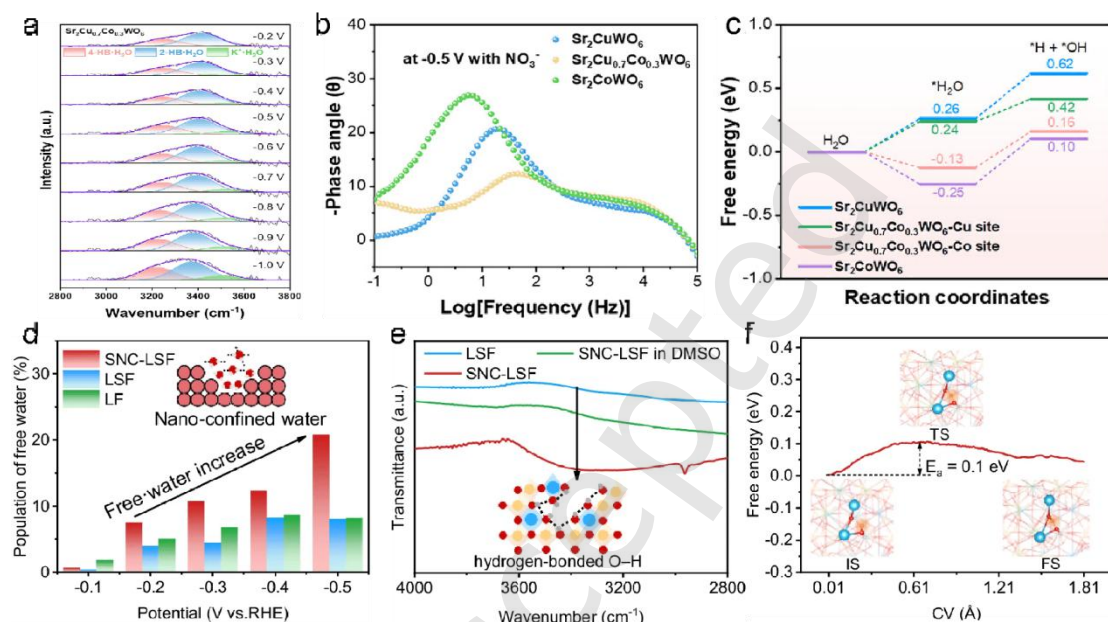


Figure 4. Hydrogen supply regulation in nitrogen oxyanion reduction over perovskite electrocatalysts. (a) Operando FTIR spectra of interfacial water on Co-substituted Sr_2CuWO_6 from OCP to -1.0 V (vs. RHE) in 0.1 M KOH with 0.1 M KNO_3 . (b) Electrochemical kinetic analysis of Co-substituted Sr_2CuWO_6 . (c) DFT-calculated water dissociation on Co-substituted Sr_2CuWO_6 . Reproduced with permission.^[38] Copyright 2026, Wiley-VCH. (d) Potential-dependent relative proportions of interfacial water on SNC-LSF from -0.1 to -0.5 V (vs. RHE) during NITRR. (e) FTIR spectra of LSF, SNC-LSF, and SNC-LSF treated by DMSO, highlighting the hydrogen-bonded O-H vibration centered at approximately 3411 cm^{-1} . (f) DFT-calculated hydrogen-transfer pathway through the intramolecular hydrogen-bond network on SNC-LSF. Reproduced with permission.^[43] Copyright 2026, Springer Nature.

3. Engineering Perovskite Oxides Beyond Conventional Design

The mechanistic principles discussed in Section 2 establish three fundamental requirements for efficient NO_x reduction: effective nitrate activation, balanced intermediate conversion, and regulated hydrogen supply. The challenge therefore, shifts from understanding the reaction mechanism to designing perovskite structures capable of fulfilling these requirements. Owing to their compositional and structural flexibility, ABO_3 perovskites provide a versatile platform in which composition, lattice defects, crystal phases, and interfacial architectures can be systematically tailored to regulate the electronic environment of catalytically active sites. Rather than

independently modifying individual material properties, these structural engineering strategies provide different routes for regulating the elementary processes governing NO_x reduction. The following sections discuss how advanced perovskite engineering translates mechanistic design principles into high-performance electrocatalysts.

3.1 Intra-Lattice Engineering

Intra-lattice engineering represents a fundamental strategy for tailoring perovskite oxide electrocatalysts because it directly modifies the crystal framework that governs the local catalytic environment. By regulating the composition and defect chemistry of the ABO₃ lattice, this approach enables systematic control over electronic structure, metal-oxygen interactions, and active-site coordination, thereby influencing the elementary processes governing NO_x reduction.^[44] Rather than relying on a single modification strategy, intra-lattice engineering can be implemented through three complementary levels of structural regulation: global lattice modulation via A-site substitution, localized active-site tuning through B-site substitution, and multisite electronic regulation using high-entropy compositions.

A-site substitution provides a global approach to regulating lattice properties without directly replacing the catalytically active transition-metal center. Instead, altering the A-site composition modifies the electronic interaction between the B-site cation and surrounding oxygen framework, thereby influencing metal-oxygen covalency and defect energetics. Wu et al. demonstrated that replacing La³⁺ with Sr²⁺ in La_{1-x}Sr_xCoO₃ systematically modifies the Co 3d and O 2p electronic states and Co-O covalency (**Figure 5a**).^[45] Electronic-structure analysis further showed that Sr incorporation alters Co-O bonding and lowers the oxygen-vacancy formation energy (**Figures 5b and 5c**). These results establish A-site substitution as an effective means of coupling lattice composition with electronic structure and defect chemistry. Rather than treating oxygen-vacancy concentration as an independent optimization target, this relationship suggests that catalytic design should consider the coupled effects of metal-oxygen covalency and defect formation on the surface reaction environment. Thus, A-site substitution primarily provides global regulation of the electronic and defect landscape of the perovskite lattice.

In contrast, B-site substitution directly modifies the local coordination environment of the transition-metal center, providing more localized control over reaction-relevant electronic and structural properties. Chu et al. demonstrated that

partial Cu substitution in $\text{LaFeO}_{3-\delta}$ shortens the Fe-O bond distance, as evidenced by Fe K-edge FT-EXAFS analysis (**Figure 5d**), indicating modification of the Fe coordination environment and Fe-O interactions.^[35] These changes were accompanied by enhanced oxygen-vacancy formation, consistent with the increased oxygen-vacancy contribution observed in the O 1s XPS spectra of $\text{LaFe}_{0.9}\text{Cu}_{0.1}\text{O}_{3-\delta}$ relative to pristine $\text{LaFeO}_{3-\delta}$ (**Figure 5e**). Unlike A-site regulation, which modifies the broader lattice environment, B-site substitution directly tailors the local catalytic center through coupled changes in coordination and defect chemistry, providing a localized route for regulating nitrate activation and intermediate adsorption.

High-entropy engineering extends intra-lattice regulation beyond localized compositional modification by introducing multiple cations into a single crystallographic site, thereby generating a distribution of chemically distinct local environments throughout the lattice. Lee et al. demonstrated that incorporating Co, Mn, and Ni into LaFeO_3 preserves the single-phase perovskite structure of $\text{La}(\text{FeCoMnNi})\text{O}_3$ (**Figure 5f**), illustrating the ability of configurational entropy to stabilize chemically complex lattices.^[46] DFT calculations further showed that multication interactions induce local lattice distortion while lowering the energy barrier for proton-assisted oxygen-vacancy formation (**Figure 5g**), providing a route to generating catalytically accessible defect sites. Compared with conventional single-element substitution, high-entropy engineering introduces multiple coupled compositional variables that can simultaneously influence lattice stability, electronic structure, and defect formation, thereby expanding the design space for catalytic optimization.

Overall, these strategies show that the effectiveness of intra-lattice engineering arises not from increasing compositional complexity or defect concentration alone, but from precisely regulating the electronic landscape of the perovskite lattice. While A-site substitution tunes the global lattice environment, B-site substitution directly tailors the local catalytic center, and high-entropy engineering introduces cooperative multisite interactions. These distinct levels of structural regulation establish a hierarchical design framework for tuning perovskite architectures toward enhanced NO_x reduction activity and NH_3 selectivity.

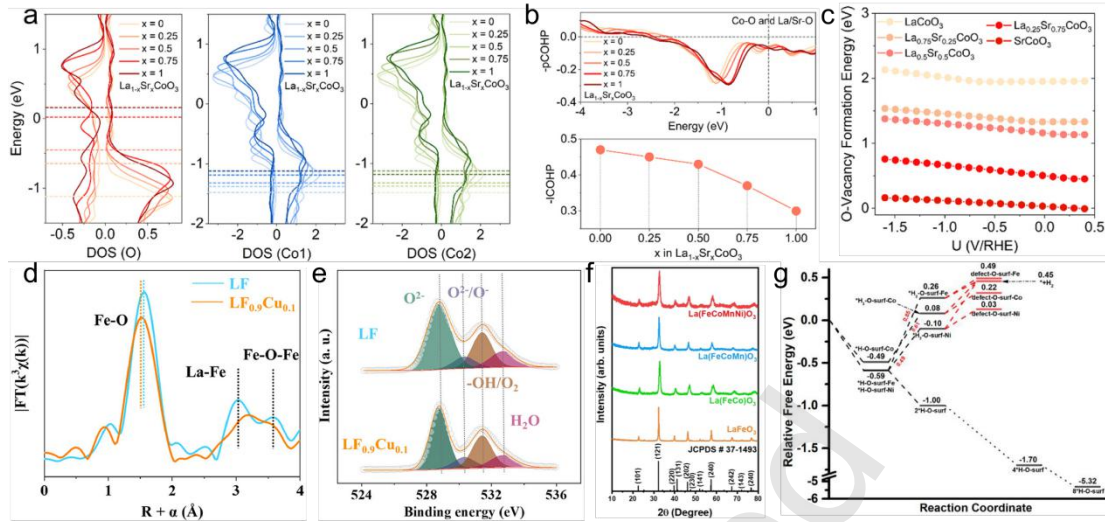


Figure 5. Intra-lattice engineering strategies for regulating the electronic structure and defect chemistry of perovskite oxides. (a) Co 3d and O 2p band centers of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. (b) COHP analysis of Co-O bonding. (c) Oxygen-vacancy formation energies of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ under NO_3RR conditions. Reproduced with permission.^[45] Copyright 2025, American Chemical Society. (d) Fe K-edge FT-EXAFS spectra of $\text{LaFe}_{0.9}\text{Cu}_{0.1}\text{O}_{3-\delta}$. (e) O 1s XPS spectra. Reproduced with permission.^[35] Copyright 2023, American Chemical Society. (f) XRD patterns of LaFeO_3 , La(FeCo)O_3 , La(FeCoMn)O_3 , and La(FeCoMnNi)O_3 . (g) DFT-calculated proton-assisted oxygen-vacancy formation. Reproduced with permission.^[46] Copyright 2026, Elsevier.

3.2 Phase and Spatial Decoupling

Although intra-lattice engineering effectively tailors the electronic structure of perovskite oxides through cation substitution and defect regulation, the multistep nature of NO_3RR means that nitrate adsorption, intermediate hydrogenation, and NH_3 desorption may require different catalytic environments.^[47-49] Consequently, optimizing all elementary steps at a single active site is intrinsically challenging. Phase and spatial decoupling therefore represent a further stage of perovskite catalyst design by redistributing catalytic functions across distinct structural domains. Depending on the level of structural organization, this concept can be realized through crystal phase engineering, layered oxide architectures, and multiphase heterointerfaces, providing increasing opportunities for catalytic functional differentiation while maintaining cooperative interactions between structural domains.

Crystal phase engineering provides a direct approach to phase decoupling by modifying crystallographic symmetry and the associated electronic structure without fundamentally changing the perovskite framework. Zhou et al. investigated a series of La-based high-entropy perovskites (LaB_5O_3 ; B = Fe, Cu, Co, Cr, and Ni), where increasing compositional complexity induced a structural evolution from

orthorhombic (Pnma) to cubic (Pm-3m) symmetry.^[50] XRD confirmed the phase transformation through systematic peak evolution and shifts (**Figures 6a, 6b, and 6c**). The cubic phase exhibited higher NH₃ Faradaic efficiency and lower operating potentials than the orthorhombic counterparts, indicating that crystallographic symmetry can influence reaction energetics through changes in the local electronic environment. Because both crystal phase and elemental composition evolve across the LaB₅O₃ series, the individual contribution of phase transformation cannot be completely isolated. Nevertheless, this work demonstrates that crystal phase can serve not merely as a structural descriptor, but also as a design parameter for tuning phase-dependent catalytic behavior.

Layered Ruddlesden-Popper (RP) oxides further extend phase engineering by introducing structural anisotropy within a single oxide framework. Unlike conventional three-dimensional ABO₃ perovskites, RP oxides consist of corner-sharing BO₆ octahedral layers separated by rock-salt AO layers, thereby creating chemically distinct regions within the same crystal structure.^[51, 52] This layered architecture can introduce anisotropic ion-transport pathways while retaining distinct transition-metal-oxygen environments within the perovskite-like layers. For example, studies of La₂NiO_{4+δ} have shown that interstitial oxygen within the rock-salt layers can provide additional pathways for oxygen transport, illustrating how the distinct structural layers can contribute differently to ion transport.^[53] Such structural differentiation provides a basis for spatially differentiating transport-related and catalytic functions rather than requiring a single structural environment to accommodate both. Gong et al. investigated La₂CuO₄-based RP oxides (**Figure 6d**) and showed that B-site substitution further modulates metal-oxygen electronic interactions within the layered structure.^[54] Among the investigated compositions, Co substitution strengthened metal-oxygen hybridization and enhanced nitrate-reduction activity, whereas other dopants produced different catalytic responses. These findings suggest that RP architectures provide an additional structural degree of freedom for regulating catalytic environments while retaining distinct layered transport characteristics. However, because transport behavior and catalytic activity depend strongly on composition, defects, and local coordination, the extent to which these functions can be independently decoupled in NO₃RR remains to be established.

While phase engineering regulates catalytic behavior within a continuous oxide lattice, spatial decoupling physically separates catalytic functions into coupled

reaction domains. In situ exsolution has emerged as an effective strategy for constructing robust metal-oxide heterointerfaces. Hao et al. reported a high-entropy LaSrAgFeCoO_x perovskite in which Ag species exsolved from the parent lattice during thermal treatment to form metallic Ag nano-islands.^[55] XRD confirmed the coexistence of metallic Ag and the perovskite oxide phase (**Figure 6e**), while atomic-resolution HAADF-STEM imaging revealed that the Ag nanoparticles remained partially embedded within the oxide matrix (**Figure 6f**). This socketed architecture strengthens metal-support interactions, which can suppress nanoparticle agglomeration while maintaining intimate electronic coupling at the interface. Rather than functioning as isolated particles, the metallic Ag domains and surrounding oxide matrix create spatially differentiated catalytic environments that can support cooperative catalytic processes. Compared with lattice-level phase engineering, exsolution therefore provides a higher degree of structural differentiation by integrating distinct phases within a stable multiphase architecture.

Collectively, these strategies illustrate how perovskite catalyst design can progress from modifying crystallographic symmetry to engineering structurally differentiated catalytic domains. Crystal phase engineering regulates catalytic behavior through phase-dependent structural and electronic changes, layered RP structures introduce anisotropic environments within a single lattice, and exsolution creates physically distinct yet electronically coupled phases. These approaches provide different routes for spatially differentiating catalytic functions and expanding the structural design space for perovskite-based NO_x -to- NH_3 conversion.

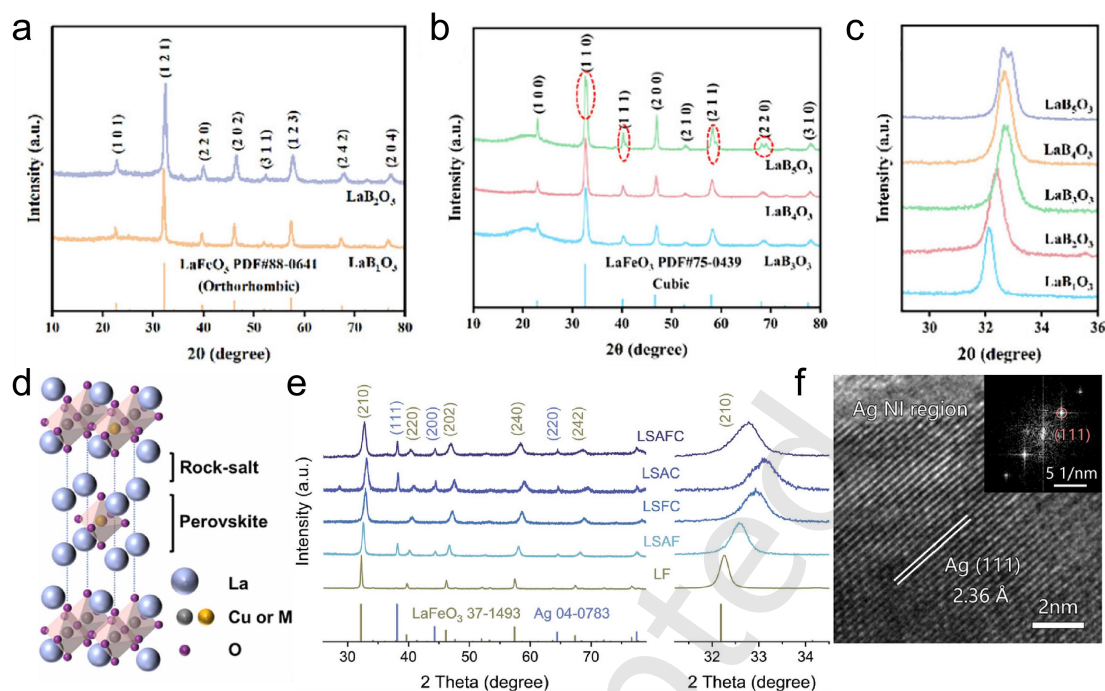


Figure 6. Phase and spatial decoupling strategies for perovskite NO₃RR electrocatalysts. (a, b) XRD patterns of La-based high-entropy perovskites with increasing compositional complexity. (c) Enlarged XRD patterns showing phase evolution near the main diffraction peaks. Reproduced with permission.^[50] Copyright 2025, Wiley-VCH. (d) Crystal structure of the layered Ruddlesden-Popper oxide La₂Cu_{0.8}M_{0.2}O₄. Reproduced with permission.^[54] Copyright 2022, Elsevier. (e) XRD patterns of the exsolved Ag-LaSrAgFeCoO_x catalyst and control samples. (f) Atomic-resolution HAADF-STEM image of Ag nanoparticles embedded in the LaSrAgFeCoO_x perovskite. Reproduced with permission.^[55] Copyright 2026, Wiley-VCH.

4. From Catalyst Design to Practical NO_x Valorization

The structural strategies discussed in Section 3 primarily address catalyst-level control of NO_x reduction. Their translation into practical technologies, however, requires consideration of the reactor and operating environment in which these catalysts function.^[56-58] Accordingly, this section moves from material design toward device-level implementation, examining reactor engineering, flow-cell operation, durability, and emerging self-powered waste-to-energy systems for practical NO_x valorization.

4.1 Translating Perovskite Oxides toward Practical NO_x Valorization

At the reactor level, high intrinsic catalytic activity does not necessarily translate into efficient nitrate conversion because catalyst utilization, mass transport, and operational stability depend strongly on reactor configuration and operating conditions.^[59-62] One of the major limitations of conventional electrochemical reactors is the incomplete utilization of catalyst active sites. Li et al. demonstrated that

although mesoporous LaCoO_3 possesses a substantially higher surface area than its bulk counterpart, these structural advantages cannot be fully exploited in conventional flow-by reactors because electrolyte transport is largely confined to the outer catalyst surface.^[63] To address this limitation, the authors developed an electrocatalytic flow-through filtration reactor in which the electrolyte is forced through the porous catalyst layer (**Figure 7a**). Compared with the conventional configuration, the flow-through reactor achieved markedly higher nitrate removal rates (**Figure 7b**), demonstrating that reactor architecture can determine whether intrinsic catalyst properties are effectively translated into practical electrochemical performance. This study highlights an important design principle: increasing catalytic activity alone is insufficient if reactor configurations cannot efficiently access the available active sites.

Improving catalyst utilization, however, addresses only part of the practical challenge. Under high-current operation, rapid reactant delivery and product removal become equally important for sustaining efficient NO_3RR . Wang et al. addressed these transport limitations by integrating a $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_3$ perovskite into a flow electrolyzer (**Figure 7c**).^[64] Relative to a conventional H-type cell, the flow configuration achieved higher NH_3 production rates (**Figure 7d**) together with improved energy efficiency (**Figure 7e**), demonstrating that enhanced electrolyte circulation and interfacial mass transport can improve overall device performance.

Beyond reactor configuration, the practical operating envelope must also be considered. Guo et al. demonstrated nitrate reduction over $\text{La}_{1.5}\text{Sr}_{0.5}\text{Ni}_{0.5}\text{Fe}_{0.5}\text{O}_4$ at nitrate concentrations up to 0.5 M, substantially exceeding the concentration range commonly employed in laboratory NO_3RR studies.^[65] In an acidic membrane-electrode assembly, the same perovskite-based system reached 200 mA cm^{-2} and was operated at current densities up to 1 A cm^{-2} , demonstrating the feasibility of high-current nitrate reduction in membrane-electrode devices. Together with the 150 mA cm^{-2} flow-cell operation reported by Wang et al., these results indicate progress toward more demanding operating regimes, although sustained operation above 200 mA cm^{-2} in perovskite flow electrolyzers remains insufficiently demonstrated.^[64]

Practical deployment further requires catalysts to maintain their activity and structural integrity during prolonged operation. Yang et al. evaluated electrochemically activated $\text{La}_{0.9}\text{FeO}_{3-\delta}$ under continuous nitrate reduction and observed stable nitrate conversion over 240 h (**Figure 7f**).^[66] Post-reaction XRD analysis confirmed that the perovskite framework remained largely unchanged after

extended electrolysis (**Figure 7g**), indicating strong structural robustness under continuous operation. Importantly, this work illustrates that long-term durability depends not only on the intrinsic stability of the catalyst but also on maintaining structural integrity under sustained electrochemical operation, an aspect that remains underexplored for many emerging perovskite electrocatalysts.

However, reactor optimization and catalyst durability alone do not address another major barrier to practical NO_x valorization: the chemical complexity of real wastewater. Unlike the simplified nitrate electrolytes commonly used in laboratory studies, wastewater contains competing ions, organic matter, and variable pH, which can alter nitrate adsorption and interfacial reaction conditions.^[67, 68] Systematic electrochemical denitrification studies have shown that these effects are strongly species- and concentration-dependent. Importantly, most of these studies have been conducted using non-perovskite electrodes and therefore provide general evidence for wastewater-matrix effects rather than direct evidence of anion tolerance in perovskite NO₃RR catalysts. For example, phosphate can substantially inhibit nitrate reduction through competitive adsorption, while chloride and sulfate can also influence nitrate-reduction performance and NH₃ selectivity.^[68, 69] Goyal et al. reported a slight decrease in NH₃ Faradaic efficiency in the presence of Cl⁻ and SO₄²⁻, indicating that these common wastewater anions should be considered when evaluating NO₃RR under realistic feed conditions.^[69] Organic matter can also suppress nitrate-reduction performance, with stronger inhibition observed at higher organic loadings.^[68] These results demonstrate that performance measured in simplified nitrate electrolytes cannot be directly extrapolated to complex wastewater matrices. Importantly, systematic evaluation of Cl⁻ and SO₄²⁻ tolerance in perovskite NO₃RR catalysts remains limited.

Coexisting multivalent cations, particularly Mg²⁺ under locally alkaline conditions, can introduce additional challenges through interfacial accumulation and precipitation, potentially blocking active sites and altering local ion distributions.^[67] Recent work by Fan et al. demonstrated that pulsed electrolysis can mitigate Mg²⁺ interference by suppressing local pH elevation and dynamically redistributing interfacial ions, thereby recovering nitrate conversion and NH₃ production.^[70] Meanwhile, pH variations can alter interfacial speciation, proton availability, and the competition between NO₃RR and HER, while high current densities can generate substantial local pH gradients.^[67, 71] Accordingly, practical mitigation should combine feed pretreatment when

necessary with reactor-level control of mass transport, current density, buffering, and interfacial pH. For perovskite NO_3RR systems, however, systematic evaluation under realistic combinations of competing ions, organic matter, and pH remains limited. Long-term testing in authentic wastewater will therefore be essential to establish catalyst-matrix compatibility and determine whether the structure-activity relationships identified in model electrolytes remain valid under practical conditions.

Overall, these considerations demonstrate that practical NO_x valorization requires moving beyond the traditional objective of maximizing intrinsic catalytic activity. Efficient electrocatalytic systems must simultaneously maximize catalyst utilization, facilitate mass transport, withstand complex wastewater matrices, minimize energy consumption, and maintain long-term structural stability. Future development should therefore integrate catalyst engineering, reactor design, wastewater compatibility, and device optimization into a unified design framework, enabling perovskite oxides to progress from high-performance laboratory catalysts toward scalable systems for NO_x remediation and NH_3 production.

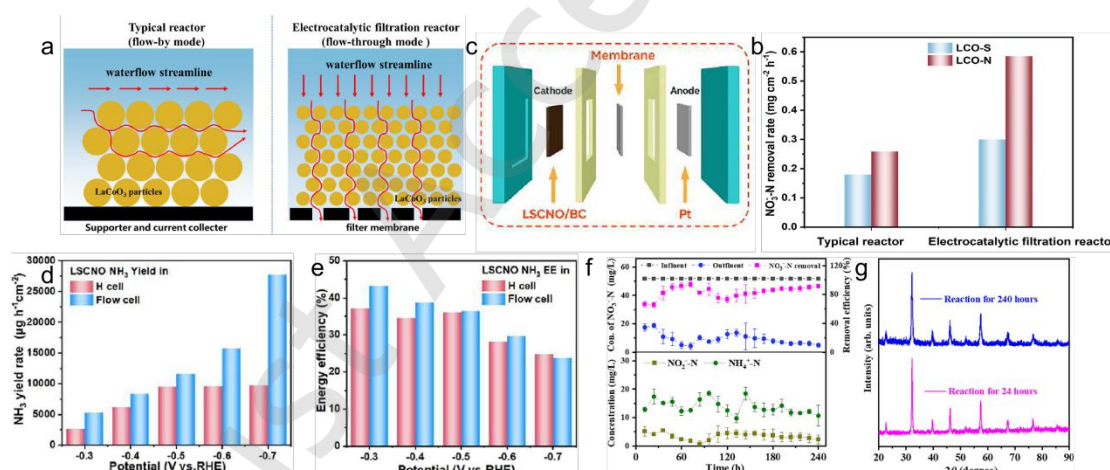


Figure 7. Translation of perovskite electrocatalysts toward practical NO_3RR systems. (a) Schematic comparison of conventional and electrocatalytic flow-through reactors. (b) Nitrate removal rates in conventional and flow-through reactors. Reproduced with permission.^[63] Copyright 2025, American Chemical Society. (c) Schematic of the flow electrolyzer. (d) NH_3 production performance in flow and H-type cells. (e) Energy efficiency of flow and H-type cells. Reproduced with permission.^[64] Copyright 2026, American Chemical Society. (f) Continuous nitrate reduction performance during prolonged operation. (g) XRD patterns of $\text{La}_{0.9}\text{FeO}_{3-\delta}$ after extended electrolysis. Reproduced with permission.^[66] Copyright 2023, Elsevier.

4.2 Self-Powered Waste-to-Energy Systems

Although advances in catalyst and reactor engineering have improved the performance of electrocatalytic NO_3RR , the broader sustainability of nitrate valorization also depends on reducing the external energy input required to drive the

process.^[72-74] Conventional electrolyzers typically pair NO₃RR with the anodic OER, whose sluggish kinetics impose a high cell voltage while producing no value-added product.^[75, 76] Consequently, recent efforts have shifted from optimizing individual half-reactions toward engineering integrated electrochemical systems in which both anodic and cathodic processes contribute to pollutant remediation, resource recovery, or energy generation. This systems-level perspective extends the role of perovskite oxides beyond electrocatalysis to their integration into waste-to-energy technologies.

Replacing the anodic OER with more favorable oxidation reactions represents a systems-level strategy that complements catalyst engineering by reducing the electrical demand of electrolysis while enabling co-valorization of waste streams.^[77-79] Two recent studies independently demonstrated that coupling NO₃RR with sulfide oxidation (SOR) can substantially reduce the cell voltage required for nitrate electrolysis. Zhou et al. constructed a bifunctional high-entropy perovskite-based NO₃ RR||SOR electrolyzer that simultaneously converted nitrate and sulfide within a single device (**Figure 8a**).^[50] Replacing OER with SOR substantially reduced the operating cell voltage (**Figure 8b**), and the integrated electrolyzer was successfully powered by a commercial photovoltaic cell (**Figure 8c**), demonstrating the feasibility of renewable-electricity-driven nitrate valorization. Similarly, Hao et al. employed a bifunctional high-entropy perovskite catalyst to couple NO₃RR with SOR, achieving significantly lower operating voltages than conventional NO₃RR||OER and HER||SOR configurations while simultaneously producing NH₃ at the cathode and elemental sulfur at the anode (**Figures 8d and 8e**).^[55] These studies demonstrate that anodic reaction engineering can complement catalyst design by lowering the electrical demand of nitrate electrolysis while enabling the co-valorization of two waste streams. Nevertheless, broader implementation will depend on the availability of suitable anodic feedstocks and the compatibility of coupled oxidation and reduction processes under practical operating conditions.

A complementary systems-level approach integrates nitrate reduction directly with electrochemical energy-storage devices. Unlike paired electrolysis, which reduces energy demand through anodic reaction engineering, battery-based systems couple NO₃RR with electricity generation, allowing chemical production and energy recovery to occur simultaneously. Wang et al. demonstrated this concept by developing a Zn-NO₃ battery employing a multimetallic perovskite cathode, in which

nitrate reduction proceeded concurrently with battery discharge (**Figure 8f**).^[64] The device delivered a peak power density of 10.19 mW cm⁻², as determined from the discharge polarization and power-density curves (**Figure 8g**), while charge-discharge cycling demonstrated stable operation (**Figure 8h**). These results illustrate the feasibility of integrating NH₃ synthesis with electrochemical energy storage and further broaden the potential role of perovskite oxides in multifunctional electrochemical devices.

Taken together, these emerging technologies indicate that practical perovskite-based NO_x valorization requires consideration of both catalytic performance and electrochemical system architecture. Paired electrolysis reduces the energy demand of nitrate conversion through anodic reaction engineering, whereas battery-based devices directly couple nitrate reduction with electrical energy generation. Future progress will therefore require coordinated development of perovskite catalysts, reactor architectures, renewable-energy integration, and multifunctional electrochemical devices, with the aim of advancing nitrate remediation toward energy-efficient resource recovery and sustainable NH₃ production.

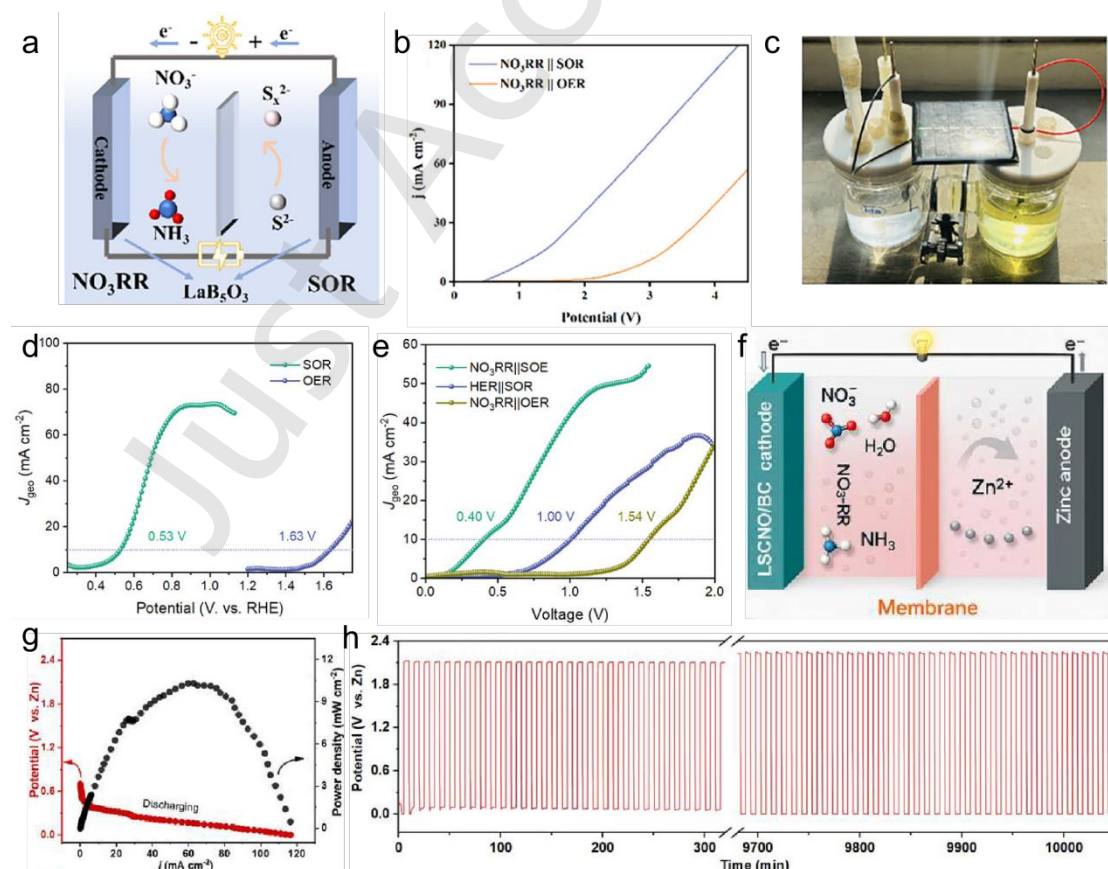


Figure 8. Self-powered and integrated electrochemical systems for practical NO₃RR. (a) Schematic of the NO₃RR||SOR electrolyzer. (b) Cell-voltage comparison of

NO₃RR||SOR and NO₃RR||OER configurations. (c) Photovoltaic-powered NO₃RR||SOR system. Reproduced with permission.^[50] Copyright 2026, Wiley-VCH. (d) Polarization curves of different paired electrolysis configurations. (e) Comparison of operating cell voltages for paired electrolysis systems. Reproduced with permission.^[55] Copyright 2026, Wiley-VCH. (f) Schematic of the Zn-NO₃ battery. (g) Discharge polarization and power density curves. (h) Charge-discharge cycling performance. Reproduced with permission.^[64] Copyright 2026, American Chemical Society.

5. Challenges and Outlook

Despite substantial progress in understanding and engineering perovskite oxides for electrochemical NO_x reduction, several fundamental scientific and technological challenges continue to limit their practical implementation. A central challenge arises from the dynamic nature of perovskite catalysts under operating conditions, where surface reconstruction, cation migration, oxygen-vacancy evolution, and in situ exsolution can continuously redefine the identity of catalytically active sites. Consequently, structure-activity relationships derived from ex situ characterization may not fully capture the catalytic environment under operating conditions. Future research should therefore move beyond static catalyst characterization toward identifying the dynamic active phases that govern catalytic performance under working conditions. Achieving this goal will require the integration of advanced operando characterization with multiscale theoretical modeling to establish predictive electronic descriptors that quantitatively correlate catalyst structure with nitrate activation, intermediate evolution, and hydrogen-transfer kinetics. An equally important challenge will be determining whether the mechanistic concepts discussed throughout this review, including symmetry polarization, electronic structure regulation, and hydrogen management, can be generalized across diverse perovskite compositions and reaction environments. Such descriptor-based frameworks will be essential for transforming catalyst development from empirical optimization into predictive materials design.

Beyond mechanistic understanding, future advances will increasingly depend on evaluating catalyst performance under conditions relevant to practical nitrate remediation rather than idealized laboratory environments. Many current studies employ relatively high nitrate concentrations, simplified electrolytes, and limited-duration electrolysis, whereas real wastewater contains fluctuating nitrate concentrations, competing ions, and organic contaminants that can substantially influence catalyst stability and reaction selectivity. Future research should therefore

prioritize long-term continuous operation, realistic wastewater evaluation, and more consistent testing protocols to enable meaningful comparison across catalyst systems. At the same time, catalyst optimization should be integrated with reactor engineering and flow-cell design to maximize catalyst utilization and overcome mass-transport limitations. Coupling NO₃RR with thermodynamically favorable anodic oxidation reactions, renewable electricity, or electrochemical energy-storage devices could further reduce the overall energy demand of nitrate valorization while expanding opportunities for simultaneous resource recovery.

The compositional flexibility of perovskite oxides presents both an opportunity and a challenge for catalyst discovery. Because the vast compositional and structural design space cannot be explored efficiently through conventional trial-and-error experimentation, future progress will increasingly rely on the convergence of high-throughput density functional theory, machine learning, autonomous experimentation, and AI-assisted inverse-design strategies. Rather than simply screening large numbers of compositions, these approaches offer the opportunity to identify electronic descriptors governing catalytic behavior and use them to predict new perovskite architectures with targeted catalytic functions. Integrating data-driven discovery with mechanistic insights obtained from operando studies could accelerate the rational development of NO_x electrocatalysts while shortening the catalyst discovery cycle.

Ultimately, the future of perovskite-based NO_x electrocatalysis will depend not on discovering isolated high-performance catalysts, but on establishing an integrated design framework that unifies mechanistic understanding, rational materials engineering, reactor and device optimization, and data-driven catalyst discovery. Bridging these disciplines will be important for translating perovskite oxides from laboratory electrocatalysts toward scalable technologies for wastewater remediation, sustainable NH₃ production, and circular nitrogen utilization.

6. Conclusions

Electrochemical NO_x reduction has evolved from the pursuit of increasingly active catalysts toward a mechanistic understanding of how catalyst electronic structure governs nitrate activation, intermediate evolution, hydrogen transfer, and ultimately NH₃ selectivity. Within this context, perovskite oxides have emerged as versatile materials platforms because their structural and compositional flexibility enables these elementary processes to be systematically regulated through rational lattice and interfacial engineering. As highlighted throughout this review, symmetry polarization,

electronic structure regulation, and hydrogen management provide a unified mechanistic framework that links catalyst structure with catalytic performance, moving perovskite catalyst development beyond empirical optimization toward mechanism-guided design. At the same time, advances in catalyst design alone are unlikely to ensure practical nitrate valorization. The successful translation of intrinsic catalytic activity into practical performance increasingly depends on integrating catalyst engineering with reactor design and electrochemical system optimization. Recent progress in flow reactors, paired electrolysis, and self-powered devices demonstrates that maximizing catalyst utilization, improving mass transport, and reducing overall energy demand are important considerations for developing scalable NO_x conversion technologies. Looking forward, a major opportunity lies in establishing predictive design frameworks that integrate mechanistic understanding with rational materials engineering, operando characterization, theoretical modeling, data-driven catalyst discovery, and practical device engineering. Such an interdisciplinary approach can provide a basis for advancing perovskite electrocatalysts and developing efficient and scalable electrochemical platforms for sustainable NO_x remediation, NH₃ synthesis, and circular nitrogen utilization.

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Conflicts of interest

The authors declare no competing financial interest.

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