Energy Materials

Supplementary Materials

Site engineering of spinel electrocatalysts for water oxidation: from bulk modulation to confined interfaces

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1. Comparison table

Supplementary Table 1. Comparison of Core Research Dimensions of Spinel-Based Electrocatalysis Review Papers

scope	organizing principle	mechanism focus	scope of materials	Scope not covered / Not a primary focus	References
Defect engineering in spinels for water and organic oxidation	Defect types, electronic effects, and dynamic evolution	Defect regulated active sites and operando evolution	Spinels for oxygen evolution reaction (OER) and organic electrooxidation	Confined interfaces and device level water electrolysis	[1]
Covering 3d transition metal (oxy)hydroxides and spinels	Reaction stage based	Surface transformation and performance	3d oxyhydroxides and spinels	Bulk regulation, confined interfaces, and device assessment	[2]
Ligand Field Theory (LFT)-guided design of spinel electrocatalysts	From LFT concepts to optimization strategies (progressive)	e_g filling, spin state, covalency, and reconstruction	Doped, defective, and high entropy spinels	Interfacial microenvironment and device assessment	[3]
Acidic OER stability of Co_3O_4 based spinels	Stability oriented strategies	Adsorbate Evolution Mechanism (AEM), Lattice Oxygen Mechanism (LOM), and Oxide	Co_3O_4 based spinels in acidic media	Alkaline and neutral systems, high entropy oxides, and confinement	[4]

		Path Mechanism (OPM), dissolution, and covalency			
Spinel type oxides for acidic OER	Mechanisms and modulation strategies	Acidic AEM and LOM, activity, and stability	Mainly Co_3O_4 based spinels for acidic OER	Alkaline and neutral OER, high entropy spinels, and cross scale design	[5]
Multi-scale site engineering for OER	Bulk, surface, interfaces, and microenvironment	Mechanism evidence, reconstruction, and interfacial water	Binary and multi-cation spinels, heterojunctions, and single atom systems	Quantitative meta-analysis and condition matched cross study ranking	This paper

2. Literature-search and selection approach

This Review used a structured narrative literature-survey approach rather than a systematic review or meta-analysis. Relevant literature was identified through searches of Web of Science, Scopus, and Google Scholar, with most selected studies published between 2023 and 2026. The literature search was last updated on September 16, 2026, and publications available up to that date were considered. The core Boolean search string was: ("spinel oxide" OR "spinel-type oxide" OR AB_2O_4) AND ("oxygen evolution reaction" OR OER OR "water oxidation") AND ("site engineering" OR defect OR dop OR substitution OR reconstruction OR "high entropy" OR interface OR confinement). Additional searches combined these terms with "lattice oxygen mechanism", LOM, "oxide path mechanism", OPM, "surface reconstruction", "built-in electric field", BIEF, and "interfacial water". Records were screened by title and abstract, duplicates were removed, and potentially relevant full texts were assessed for material scope, OER relevance, site-engineering strategy, and structural or mechanistic evidence. "Significant impact" was used to denote studies that introduced a distinct design strategy, provided meaningful structural or performance evidence, or substantially advanced mechanistic understanding. "Redundant results" referred to reports that addressed essentially the same material–strategy combination without adding distinct evidence or interpretation. "Deep mechanistic insight" referred to evidence linking a defined structural feature to a reaction pathway or catalytic behavior through complementary theoretical, spectroscopic, isotope-labeling, or operando characterization. Earlier studies were retained selectively when they provided foundational concepts or landmark evidence. Battery, HER, ORR, non-oxide, and pseudo-spinel studies were not treated as direct OER evidence and were included only as explicitly labeled contextual or transferable concepts. Because the search was not preregistered and no quantitative meta-analysis was performed, this work is presented as a structured narrative literature survey.

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