氟化高熵层状双氢氧化物激活晶格氧机理研究

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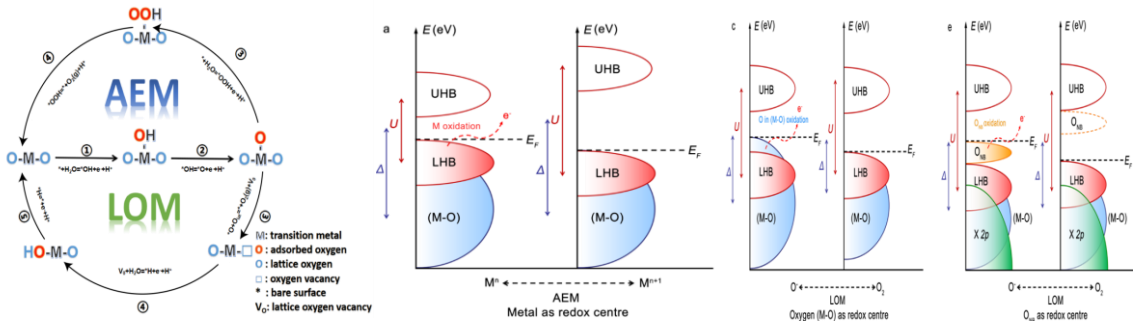
层状双氢氧化物（LDH）作为电催化领域重要材料，比起传统 AEM 机理，其氧相关催化反应活性提高最有利的为晶格氧行为。高熵构型可通过多金属协同调控电子结构与晶格环境，为优化晶格氧活性提供新思路，而氟化改性能够进一步调控材料表面缺陷、键合环境与离子传输特性。本文围绕氟化高熵层状双氢氧化物体系，系统探究氟掺杂以激活高熵效应对晶格氧的调控机制，重点分析氟引入对金属－氧键强度、氧空位形成能、晶格氧迁移能力及反应路径的影响，揭示高熵构型与氟化改性协同激活晶格氧的内在机理，阐明电子转移、晶格畸变与界面效应对催化反应本征活性的作用规律。研究可为高活性羟基化合物基电催化材料的设计与机理研究提供理论依据，对深化晶格氧氧化机制理解具有重要意义。具体而言，高熵构型凭借多金属元素的均匀固溶特性，构建了无序且可调的晶格环境，有效抑制活性金属离子的溶出与偏析，为晶格氧的稳定激活奠定结构基础，同时通过多金属位点的协同作用调控电子云分布，优化晶格氧的电子态密度，打破传统单一金属 LDH 晶格氧活性不足的局限，这与低价元素掺杂高熵 LDH 可形成氧非键态以提升催化稳定性的研究规律相一致。氟化改性作为关键调控手段，其高电负性特征可显著重构金属－氧键合网络，通过电子抽离效应削弱金属－氧键强度，降低氧空位形成能，促进晶格氧从晶格内部向表面迁移，同时诱导材料表面形成丰富的氧空位缺陷，进一步提升晶格氧的暴露程度与反应活性，这一过程与氟掺杂诱导自旋态重构、加速电子转移的作用机制相呼应，可推动催化反应从传统 AEM 机理向 LOM 机理转变，有效突破 AEM 机理的热力学限制，提升反应动力学性能。

并且将结合密度泛函理论（DFT）计算与原位表征技术，如原位 X 射线吸收精细结构（XAFS），同位素标记-质谱、原位拉曼光谱等，精准捕捉氟掺杂与高熵构型协同作用下晶格氧的动态演化过程，量化分析金属－氧键共价性、氧空位浓度、晶格氧迁移速率等关键参数的变化规律，明确电子转移路径与晶格畸变程度的关联的关系，揭示氟掺杂如何通过调控高熵 LDH 的电子结构与晶体结构，协同增强晶格氧活性的核心机制，弥补当前氟化高熵 LDH 体系中晶格氧调控机制研究的不足，解决 LOM 机理下催化剂稳定性不佳的关键难题。

关键词：高熵层状双氢氧化物；氟离子掺杂；晶格氧激活；氧空位



Study on the Mechanism of Lattice Oxygen Activation in Fluorinated High-Entropy Layered Double Hydroxides

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Abstract: Layered double hydroxides (LDHs), as pivotal materials in electrocatalysis, demonstrate most favorable oxygen-related catalytic activity enhancement through lattice gas behavior compared to conventional AEM mechanisms. High-entropy configurations can optimize lattice oxygen activity via multi-metal coordination in regulating electronic structures and lattice environments, while fluorination modifications further control surface defects, bonding environments, and ion transport characteristics. This study systematically investigates fluorine doping mechanisms for activating high-entropy effects in fluorinated high-entropy LDH systems, focusing on fluorine's impacts on metal-oxygen bond strength, oxygen vacancy formation energy, lattice oxygen migration capacity, and reaction pathways. The research elucidates the intrinsic mechanisms of high-entropy configurations and fluorination modifications synergistically activating lattice oxygen, clarifying how electron transfer, lattice distortion, and interfacial effects govern catalytic activity. These findings provide theoretical foundations for designing high-performance hydroxyl compound-based electrocatalytic materials and deepen understanding of lattice oxygen oxidation mechanisms. Specifically, high-entropy configurations leverage uniform solvation properties of multi-metal elements to create disordered yet tunable lattice environments that effectively suppress active metal ion dissolution and segregation, establishing structural foundations for stable lattice oxygen activation. Through coordinated multi-metal site interactions, the study optimizes electronic state density distribution of lattice oxygen, overcoming the inherent limitations of single-metal LDHs with insufficient lattice oxygen activity. This aligns with established principles that low-valent element doping in high-entropy LDHs forms non-covalent oxygen states to enhance catalytic stability. Fluorine modification serves as a pivotal regulatory approach. Its high electronegativity significantly restructures metal-oxygen bonding networks by weakening metal-oxygen bond strength through electron-withdrawing effects, reducing oxygen vacancy formation energy, and facilitating lattice oxygen migration from internal lattice structures to surface regions. This process simultaneously induces abundant oxygen vacancy defects on material surfaces, thereby enhancing lattice oxygen exposure and reaction activity. These mechanisms align with fluorine doping-induced spin state reconstruction and accelerated electron transfer, enabling catalytic reactions to transition from conventional AEM mechanisms to LOM mechanisms. This transformation effectively overcomes thermodynamic limitations inherent in AEM mechanisms while improving reaction kinetics performance.

The study will integrate density functional theory (DFT) calculations with in-situ characterization techniques such as in-situ X-ray absorption fine structure (XAFS), isotope labeling-mass spectrometry, and in-situ Raman spectroscopy to precisely capture the dynamic evolution of lattice oxygen under the synergistic effects of fluorine doping and high-entropy configurations. Key parameters including metal-oxygen bond covalency, oxygen vacancy concentration, and lattice oxygen migration rates will be quantitatively analyzed to elucidate the correlation between electron transfer pathways and lattice distortion extent. This approach aims to reveal the core mechanism by which fluorine doping modulates the electronic structure and crystal structure of high-entropy LDHs to synergistically enhance lattice oxygen activity. The research addresses existing gaps in lattice oxygen regulation mechanisms within fluorinated high-entropy LDH systems and resolves critical challenges related to catalyst stability under the LOM (Lattice Oxygen Mechanism) framework.

Keywords: High-entropy layered double hydroxides; fluorination modification; lattice oxygen activation; oxygen vacancy; electrocatalytic mechanism