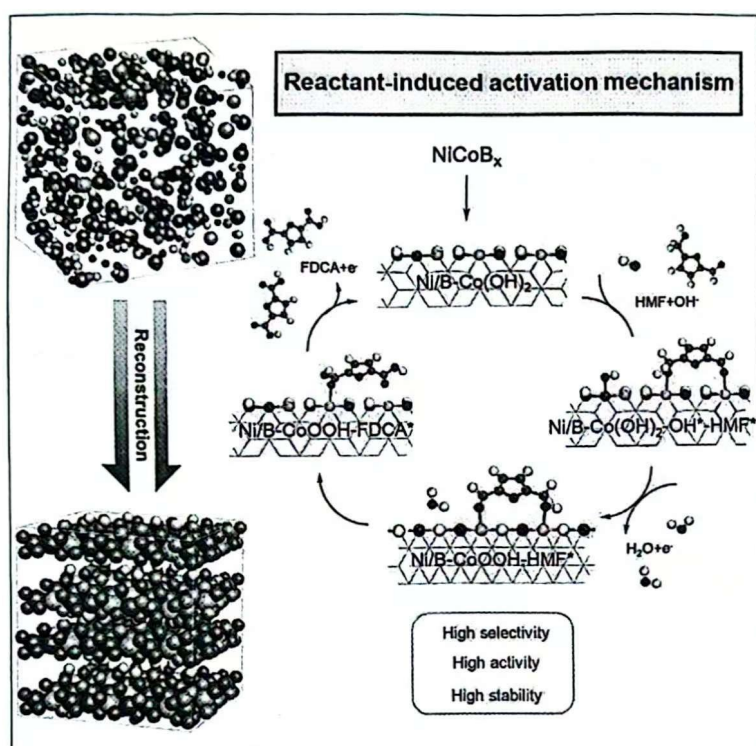


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Article

Reactant-induced activation over amorphous metal-metalloid electrocatalysts for HMF electrooxidation



We design the amorphous metal-metalloid NiCoB_x electrocatalysts for HMFOR, which exhibit extremely high catalytic performance. Moreover, in the coupled hydrogen production system with NiCoB_x as the anode, the energy consumption for hydrogen production can be successfully reduced (saving electricity input of ~1.03 kWh/m³ of H₂). We propose that HMF participates in the catalyst activation process, following the "reactant-induced activation mechanism," which accelerates the dehydrogenation process to generate abundant active sites (Ni/B-doped CoOOH), resulting in efficient HMFOR performance.

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Highlights

Reactant-induced activation mechanism directed to induce catalyst reconstruction

HMFOR//HER systems with low-energy hydrogen production

Interaction of electrocatalysts and reaction substrates



Chem

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Article

Reactant-induced activation over amorphous metal-metalloid electrocatalysts for HMF electrooxidation

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SUMMARY

The alternative anodic-oxidation-coupled cathodic hydrogen evolution offers substantial potential for reducing energy consumption in hydrogen production. However, the fabrication of catalysts that maintain high activity and stability in integrated systems remains a significant challenge. Herein, we have developed an amorphous metal-metalloid alloy catalyst (NiCoB_x) as anode for alkaline 5-hydroxymethylfurfural oxidation reaction (HMFOR) in integrated biomass electrooxidation-coupled hydrogen production system, which achieves a high current density of 400 mA cm⁻² with a low cell voltage of 1.62 V. It saves ~1.03 kWh/m³ of H₂ produced and maintains excellent stability (>100 h). *Operando/in situ* spectroscopic characterization and theoretical analysis unveiled a "reactant-induced activation strategy" for NiCoB_x: organic substrates with aldehyde groups preferentially adsorb on Co sites, reducing dehydrogenation adsorption energy and promoting the generation of Co³⁺ active sites. These insightful results present an inspiring outlook for the industrial application of biomass-coupled hydrogen production strategies.

INTRODUCTION

Water electrolysis driven with low power consumption per cubic meter of hydrogen holds a great potential for green hydrogen production in the future.^{1–6} However, the sluggish oxygen evolution reaction (OER) on the anode side occupies about 80% of the overall energy demand while producing low-economic-value oxygen.^{7,8} Moreover, the potentially dangerous explosion hazard of H₂/O₂ crossover through the membrane during large-scale production also limits the further deployment.^{9,10} Currently, to mitigate the numerous limitations of conventional anodic OER, a variety of anodic alternative electrooxidation reactions such as organic molecule electrooxidation^{11–14} and biomass electrooxidation^{15–18} have been developed, which can not only minimize the intrinsic thermodynamic energy consumption on the anode, but also yield high-economic-value oxidation products.^{8,19} In particular, 5-hydroxymethylfurfural (HMF) is a biomass-derived compound originating from C6 carbohydrates, which is considered to be a promising alternative anode reaction.²⁰ Its ultimate oxidation product, 2,5-furandicarboxylic acid (FDCA), is considered one of the top twelve prioritized green chemicals,²¹ can be used as a substitute for some petroleum derivatives such as terephthalic acid (TPA) to manufacture fine chemicals.²¹ Meanwhile, the theoretical oxidation potential of HMF (0.113 V versus reversible hydrogen electrode [vs. RHE], all potentials were vs. RHE if not mentioned) is much lower than the standard potential of OER (1.23 V), which can

THE BIGGER PICTURE

Utilizing alternative anodic half-reactions with thermodynamic advantages, such as 5-hydroxymethylfurfural oxidation reaction (HMFOR), instead of oxygen evolution reaction, can effectively reduce the electricity consumption in alkaline water electrolysis for hydrogen production. However, previous studies on electrochemical HMFOR have not fully assessed the practical industrial application potential of integrated systems. Herein, we design the amorphous metal-metalloid NiCoB_x electrocatalysts for HMFOR, which exhibits extremely high catalytic performance. We propose that NiCoB_x follows the "reactant-induced activation mechanism" with accelerated dehydrogenation process to generate abundant active sites (Ni/B-doped CoOOH), resulting in efficient HMFOR performance.

We believe that the proposed new mechanism of reactant-induced activation will provide a general guidance for future electrocatalytic studies of small-molecule organics.