

Review Article

Electrocatalyst design for promoting two-electron oxygen reduction reaction: Isolation of active site atoms

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Abstract

Selective two-electron (2e^-) pathway oxygen reduction reaction (ORR) has gained prominence for enabling small-scale, on-site electrochemical H_2O_2 production and has emerged as a promising alternative to the conventional anthraquinone process. The rational design of catalysts that can suppress the competing four-electron pathway ORR is critical. This review highlights catalyst design strategies for promoting the selective 2e^- pathway ORR, including alloying with inert metals, partial surface poisoning, and generating atomically dispersed sites. The major results and advances, as well as unresolved challenges are summarized.

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Current Opinion in Electrochemistry 2020, 21:109–116

This review comes from a themed issue on **Energy Transformation**

Edited by **Hirofumi Uchida**

For a complete overview see the [Issue](#) and the [Editorial](#)

Available online 1 February 2020

<https://doi.org/10.1016/j.coelec.2020.01.007>

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Keywords

Electrocatalysis, Oxygen reduction reaction, H_2O_2 production, Catalyst design, Metal isolation.

Introduction

The oxygen reduction reaction (ORR) is arguably one of the most important electrochemical reactions affecting the efficiency of energy conversion devices such as fuel cells [1] and metal-air batteries [2]. Two ORR pathways are possible: the four-electron (4e^-) pathway, where oxygen is converted to H_2O by complete reduction and the two-electron (2e^-) pathway involving partial reduction of O_2 to generate hydrogen peroxide (H_2O_2)

[3]. The 2e^- pathway ORR has been regarded as an adverse side reaction that impedes the efficient 4e^- pathway in polymer electrolyte membrane fuel cells (PEMFCs), as it degrades the performance of PEMFC by destroying the Nafion membrane [4,5]. However, the selective 2e^- pathway has recently garnered a surge of interest as a means of the electrochemical production of H_2O_2 [6–16].

H_2O_2 is strongly oxidizing yet environmentally benign and is thus widely exploited in polymer and pharmaceutical syntheses, pulp and textile bleaching, as well as wastewater and ballast water treatment [6–9]. The annual global production of H_2O_2 is estimated to reach a value of ~ 6 billion US dollars by 2023 [8]. Ninety-five percent of the current H_2O_2 production uses the anthraquinone process [6], which undesirably requires high pressure H_2 and expensive Pd-based catalysts, large infrastructures, and energy-intensive distillation steps. This process typically produces H_2O_2 in high concentration in a large volume, with attendant safety risks related to the storage and transportation of H_2O_2 . Recently, electrochemical H_2O_2 production has emerged as a promising alternative to the anthraquinone process [6–9]. Electrochemical H_2O_2 production allows continuous, on-site H_2O_2 production with dilute H_2O_2 , mitigating the drawbacks of the anthraquinone process.

Pivotal to efficient H_2O_2 electrosynthesis is the design of electrode catalysts that can promote the selective 2e^- pathway ORR while suppressing the competing 4e^- pathway ORR [9]. In the ORR, oxygen can be adsorbed on the surface of metal catalysts in two different configurations: (i) dissociative side-on adsorption which leads to the increased bond length and weakening of the oxygen double bond, yielding H_2O as the product; (ii) associative end-on adsorption where oxygen is adsorbed in the form of $^*\text{OOH}$, which can produce both H_2O_2 and H_2O [3,17–19]. To promote the 2e^- pathway ORR, ensemble or hollow sites that facilitate the side-on adsorption of O_2 should be eliminated by isolating the surface metal atoms.

In this short review, we present catalyst preparation strategies for isolating the active metal atoms to promote electrochemical H_2O_2 production. Three major

