



Review Article

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

Jae Hyung Kim¹, Yong-Tae Kim² and Sang Hoon Joo¹**Abstract**

Selective two-electron ($2 e^-$) 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 $2 e^-$ 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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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 ($4 e^-$) pathway, where oxygen is converted to H_2O by complete reduction and the two-electron ($2 e^-$) pathway involving partial reduction of O_2 to generate hydrogen peroxide (H_2O_2)

[3]. The $2 e^-$ pathway ORR has been regarded as an adverse side reaction that impedes the efficient $4 e^-$ 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 $2 e^-$ 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 $2 e^-$ pathway ORR while suppressing the competing $4 e^-$ 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 $*OOH$, which can produce both H_2O_2 and H_2O [3,17–19]. To promote the $2 e^-$ 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

