

The dual role of hydrogen peroxide in fuel cells

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Received: 23 November 2014 / Accepted: 25 November 2014
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Abstract Clean and highly efficient energy production has long been sought after, as a way to solve global energy and environmental problems. Fuel cells, which convert the chemical energy stored in fuel directly into electricity, are expected to be a key enabling technology for the pressing energy issues that plague our planet. Fuel cells require oxygen as an oxidant and require oxygen tank containers when used in air-free environments such as outer space and underwater. Hydrogen peroxide has been extensively utilized as an alternative liquid oxidant in place of gaseous oxygen. In addition to being an oxidant, hydrogen peroxide can donate electrons in the oxidation reaction to act as a fuel. This article provides an overview of the dual role of hydrogen peroxide in fuel-cell applications, including working principle, system design, and cell performance. Recent innovations and future perspectives of fuel cells that use hydrogen peroxide are particularly emphasized.

Keywords Fuel cell · Hydrogen peroxide · Mixed potential · Hydrogen peroxide reduction reaction · Hydrogen peroxide oxidation reaction · Performance

1 Introduction

Both energy-efficient and environmentally benign fuel cells are emerging as alternative energy conversion devices for portable, mobile, and stationary power applications [1–4]. Fuel cells generally require oxygen as the electron

acceptor (oxidizer), typically from ambient air [5, 6]. Their application, however, in air-free environments, such as outer space and underwater, leads to the requirement of an additional oxygen tank in the system, which significantly lowers the energy density of fuel cells. As an alternative oxidizer, hydrogen peroxide (H_2O_2) has recently received increasing attention [7, 8], primarily due to several advantageous characteristics in comparison with gaseous oxygen [9–12]: (1) fuel cells that use hydrogen peroxide can operate within an oxygen-free environment (outer space and underwater) [9]; (2) the use of hydrogen peroxide as an oxidant can substantially increase the fuel cell's theoretical voltage and subsequently improve performance [10]; (3) hydrogen peroxide offers low activation loss of the reduction reaction due to two-electron transfer [11]; and (4) fuel cells that use hydrogen peroxide avoid the problem of water flooding due to its intrinsically liquid phase [12]. For these reasons, much effort has been devoted to developing fuel cells that can use hydrogen peroxide as an oxidant and significant progress has been made [7]. In addition to being an oxidant, hydrogen peroxide has also been evaluated as a fuel, particularly in one-compartment and membraneless fuel cells [13]. The objective of this review was to introduce the dual role of hydrogen peroxide in fuel-cell applications, summarize recent developments on the improvement of performance of fuel cells that employ hydrogen peroxide, and provide an outlook for future research directions.

2 General description

Hydrogen peroxide has intrinsic characteristics of possessing poor thermal and chemical stability, regardless of whether its role is a fuel or oxidant. Poor stability is

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problematic because it leads to hydrogen peroxide decomposition, both chemically (homogeneous) and electrochemically (heterogeneous) [14]. The following subsections will introduce the mechanisms of chemical and electrochemical decompositions, mixed-potential phenomenon, as well as heat generation, sequentially.

2.1 Chemical (homogeneous) decomposition

Hydrogen peroxide is generally unstable in an aqueous solution, with decomposition products of oxygen and water. Chemical decomposition in fuel cells will lower the utilization efficiency of hydrogen peroxide and cause a two-phase counterflow, which increases mass transport resistance of liquid reactants. The decomposition reaction is as follows:



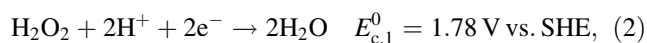
The chemical decomposition rate of hydrogen peroxide is highly dependent on three factors: pH value, hydrogen peroxide concentration, and temperature [10]. For example, an acidic media is beneficial for stabilizing hydrogen peroxide and alleviating decomposition due to a lowered ionization rate. Additionally, the rate of hydrogen peroxide decomposition is lower with low hydrogen peroxide concentrations and at low temperatures. Chemical decomposition of hydrogen peroxide must be alleviated by optimizing the operating parameters, without sacrificing the overall power density output.

2.2 Electrochemical (heterogeneous) decomposition

Unlike chemical decomposition, the electrochemical decomposition of hydrogen peroxide takes place alongside electron transfer at the electrode. Due to the fact that the electrode generally plays a role in speeding up electrochemical decomposition, its rate is much higher than that of chemical decomposition under identical conditions [10]. The following subsections will introduce the mechanisms of hydrogen peroxide electrochemical decompositions in both acid and alkaline media.

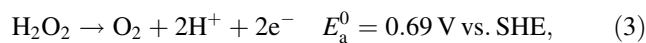
2.2.1 In acid media

When hydrogen peroxide is adsorbed at the electrode, hydrogen peroxide reduction reaction (HPRR) will take place by combining protons and electrons to form water according to the following equation:

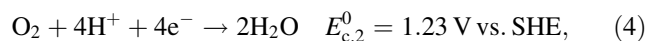


where $E_{\text{c},1}^0$ represents the standard electrode potential of the HPRR and SHE means standard hydrogen electrode.

However, hydrogen peroxide oxidation reaction (HPOR) can easily take place at such a high potential to release oxygen, protons, and electrons according to



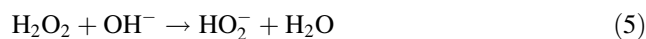
where E_{a}^0 stands for the standard electrode potential of the HPOR. In addition, since oxygen is produced based on Eq. (3), the oxygen reduction reaction (ORR) is able to take place according to



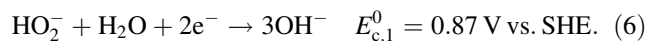
where $E_{\text{c},2}^0$ represents the standard electrode potential of the ORR. Under an open-circuit condition, the net current is zero. The overall reaction on the electrode can be expressed as Eq. (1). It should be noted that the overall reactions for the chemical and electrochemical decompositions are the same, but the mechanisms are different.

2.2.2 In alkaline media

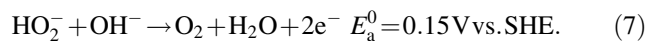
Unlike in acid media, hydrogen peroxide exists in the form of HO_2^- in alkaline media according to



Hydrogen peroxide reacts with water and electrons to form hydroxyl ions as follows:



Similarly, the HPOR can also take place in alkaline media to form oxygen, water, and electrons according to



In addition, the ORR takes place in alkaline media according to



The overall reaction for the electrochemical decomposition of hydrogen peroxide in alkaline media can also be described by Eq. (1), but it should be noted that the mechanism is different from that in acid media.

In addition to the operating parameters (temperature, hydrogen peroxide concentration, and pH value), the electrochemical decomposition rate is strongly dependent on the electrochemical properties of the employed electrode [10]. For instance, electrochemical decomposition occurs rapidly on a Pt electrode, whereas its rate can be lowered on Pd or Au electrodes. Thus, Pd and Au have been widely used as electrocatalysts toward hydrogen peroxide electroreduction and electrooxidation [15]. Similar in nature to chemical

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