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Electrocogeneration of hydrogen peroxide: Confocal and potentiostatic investigations of hydrogen peroxide formation in a direct methanol fuel cell

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HIGHLIGHTS

- Production, accumulation and removal of H_2O_2 were visualised at microscopic level.
- 3D distribution and concentration of H_2O_2 was quantified by fluorescence mapping.
- Effect of cell potential on cogeneration was studied by real-time investigations.
- Higher amount of H_2O_2 accumulation resulted in a decrease in cell potential.
- Electrocogeneration processes greatly improved with decreasing cell potentials.

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ABSTRACT

This work aims to fulfil some of the critical challenges associated with the electrochemical processes in commercialisation of an electrocogeneration direct methanol fuel cell: the understanding of the formation, decomposition and removal of hydrogen peroxide at the cathodic chamber. The better understanding of operating conditions on improving the electrocogeneration performance is also valuable for developing an optimal operating condition that enhances electrocogeneration activity. The production and removal of hydrogen peroxide are investigated by sensing the fluorescence signal in the cathodic chamber using confocal microscopy. It is found that the higher production of hydrogen peroxide promotes the intensity but reduces the cell potential due to the depletion of fresh reactant and the accumulation of hydrogen peroxide. Consequently, hydrogen peroxide should be removed efficiently in order to maintain the cell performance. The three-dimensional distribution and concentration of hydrogen peroxide are quantified at various operating potentials using fluorescence mapping, which is a correlation between the fluorescence signal and the concentration of hydrogen peroxide. The simultaneous fluorescence and potentiostatic investigations indicate that the electrocogeneration process is improved significantly by decreasing the cell potentials; the current efficiencies of 85.00, 64.78 and 51.13% are obtained at the operating potentials of 300, 400 and 550 mV respectively.

1. Introduction

An electrocogeneration fuel cell is a power generator and a chemical reactor that directly converts chemical energy into electricity plus useful chemicals. This novel type of fuel cells has become a promising alternative to a conventional chemical reactor and a traditional fuel cell that produces water as a by-product [1]. In general, an electrocogeneration process involves electrochemical reactions occurring in a conventional fuel cell; when the fuel and oxidant are supplied individually to the cell, electrons are harnessed through an external load while useful products are collected by a chemical recovery system.

Several electrocogeneration fuel cells were primarily developed in the middle of the 20th century in order to shorten a complicated chemical process to a single-step production [2]. The key benefits of electrocogeneration fuel cells over the conventional catalytic processes include:

(i) The reactants are supplied separately to the system; consequently they do not compete at the same reaction sites and the explosion risk is reduced.

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(ii) The reactor can be reduced in size with minimal corrosion. The required operating temperature is much lower.
(iii) The chemical production and selectivity of the process can be altered by varying either the external load or the electrode potential. The electrode catalyst also plays an important role in altering the selectivity.
(iv) The use of reactants is economical since they can be recirculated.

Most of the chemicals produced from the electrocogeneration processes have been commercially attractive such as cyclohexylamine [3], 1-propanol [4] and hydrogen peroxide [5–7]. Among these chemicals, hydrogen peroxide has received an increasing interest in a wide range of industrial processes such as the bleaching of mechanical pulp and the brightening of chemical pulp in the paper industry. Apart from the bleaching operational processes, the electrocogeneration fuel cells are particularly useful for remote applications, local waste water treatment and oxidation of organic compounds. Hydrogen peroxide has been used to replace other chemical oxidants due to low environmental impact. For example, chlorine is also used as a bleaching agent for wood-pulp industries but generates toxic chlorinated products. On the other hand, hydrogen peroxide undergoes oxidation of organics and then transforms into non-contaminant products including water and oxygen. Since 1957, the majority of hydrogen peroxide has been manufactured by the anthraquinone process [8] which is a catalysis process comprised of a multi-step operation that consumes high energy; hence, the production of hydrogen peroxide through this process is costly. In addition to the production cost, decomposition of hydrogen peroxide is thermodynamically favourable ($\Delta G^\circ = -119.2$ kJ mol^{-1}) and the rate of decomposition depends on the temperature, the concentration of hydrogen peroxide and the presence of impurities and stabilisers. Consequently, a simple reactor should be installed on site to produce hydrogen peroxide in the end-use industries which then reduces the production cost and improves the utilisation of hydrogen peroxide.

Electrocogeneration fuel cells meet all the requirements with an additional benefit of power generation. In the early stages of the development, Oloman and Watkinson [9] developed a trickle bed electrochemical reactor to produce alkaline peroxide solutions by the reduction of oxygen. The reactor was composed of a packed bed cathode made of graphite particles which was separated from a metal anode plate by a porous diaphragm. Oxygen and sodium hydroxide were fed concurrently through the cell while a current density of 100 mA cm^{-2} was supplied across the anode and cathode at 60 °C, leading to a production of 2 wt.% hydroperoxide ion in 6 wt.% sodium hydroxide with the current efficiency of 75%. Later on, economical reactors that do not require the passage of current to drive the electrochemical reactions have been proposed. Otsuka and Yamanaka [10] have proposed a hydrogen/Nafion® 117/oxygen fuel cell to cogenerate hydrogen peroxide and electricity using different catalyst materials on the cathode such as platinum, palladium, gold and graphite. By using platinum catalyst, the current efficiency for the formation of hydrogen peroxide was initially 100% with the maximum concentration of 0.2 wt.% (i.e. ~59 mM) and the current density of 30 mA cm^{-2}. After a period of time, the efficiency decreased dramatically since hydrogen peroxide was further electrochemically reduced at the active platinum and/or thermally decomposed by the waste heat released from the fuel cell reaction. Less active catalysts such as graphite or gold mesh was found to have better long-term current efficiency. A similar work was carried out in a new reactor design using a porous cathode made of hot-pressed carbon and PTFE powder [7]. The porous graphite structure allowed effective access of oxygen to the active sites; hence, the production of hydrogen peroxide was improved. Sodium hydroxide solution was continuously supplied to the cathodic chamber as an additional catholyte to provide an alkaline environment and to remove hydrogen peroxide from the cell. The discharged solutions contained hydrogen peroxide up to 7 wt.% (2.06 M) with the maximum current density of 100 mA cm^{-2}. Instead of Nafion® 117, potassium hydroxide was used as an alternative in an undivided fuel cell. With the simpler design, however, a smaller amount of hydrogen peroxide (<22.5 mM) was obtained [6].

Agladze and co-workers [11] developed a direct methanol fuel cell (DMFC) that is composed of the Nafion 115 membrane sandwiched by the "Black Pearls 2000" cathode and the carbonaceous anode (Pt). A mixture of 1 M methanol and 7 M potassium hydroxide was supplied to the anode while air was fed to the cathode with the additional feed of sodium chloride brine or seawater catholyte. The current efficiency of 87–95% and the current density of 15 mA cm^{-2} were generated at the production rate of 5.286–9.44 mg h^{-1} cm^{-2}.

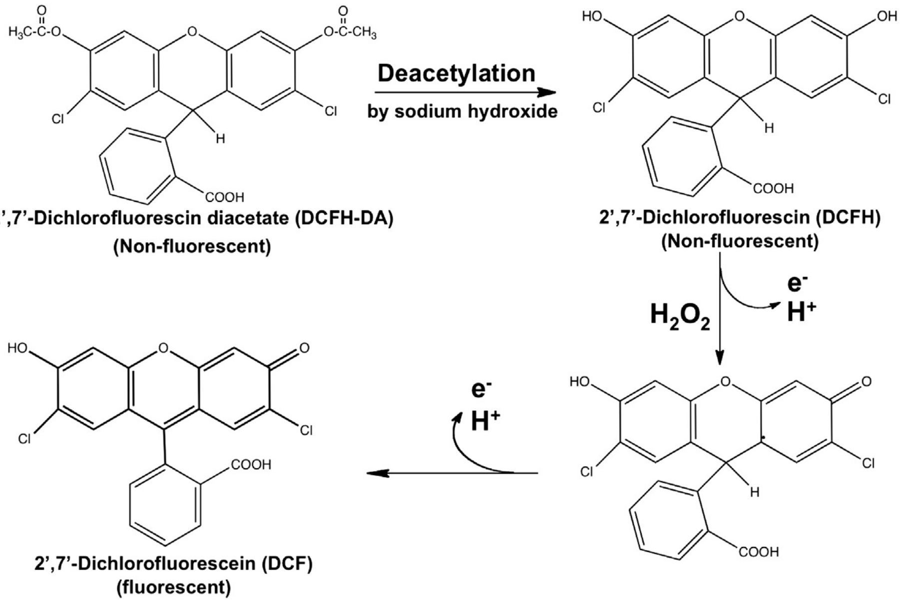

Fig. 1. Reaction mechanism of dichlorofluorescin synthesis and oxidation. The non-fluorescent DCFH is rapidly oxidised to highly fluorescent DCF with the presence of hydrogen peroxide.