Application of Nanomaterials in Microbial Electrolysis Cells

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Microbial Electrolysis Cells (MECs) are one of the bioreactors that have been used to produce bio-hydrogen by biological methods. Nanomaterials, especially when used to produce bio-hydrogen using MEC, are distinguished by their high electrical conductivity, high interaction surface area, high durability of materials, high catalytic ability to produce bio-hydrogen in MEC, biocompatibility with microorganisms and non-toxicity.

Microbial Electrolysis Cells (MECs) | bio-hydrogen production rates (Bio-HPR) | nanomaterials

1. Introduction

Hydrogen is considered one of the most promising and clean energy sources in the twenty-first century (future fuel) due to the fact that it contains many distinctive and effective properties, such as high energy conversion, large storage capacity, broad specific energy, renewable production and is environment friendly with zero emissions. It is widely used in industrial processes such as ammonia synthesis and petroleum refining, and thus hydrogen production is finding significant global interest [1][2].

Hydrogen is produced from fossil fuel sources with 96% of global hydrogen as follows: 48% from natural gas reforming, steam reforming or partial oxidation, 30% from naphtha reforming, and 18% from coal gasification [3]. However, hydrogen production in this way causes high-energy consumption and serious environmental pollution. Therefore, alternative ways to produce hydrogen from renewable environmental sources called biomass were searched for using biological methods [4].

Hydrogen production using biomass is considered better because of its high annual production and the reserves of its presence in the environment in large quantities, in addition to the ease of oxidation compared to hydrogen production using fossil fuel sources. The sources of biomass used in hydrogen production include agricultural waste, forest waste, domestic wastewater, industrial wastewater, carboxylic acids, polyols, sugars, wood waste, cellulose, lignin and microorganisms such as algae and bacteria [5][6].

There are several methods used to produce hydrogen fuel, called biological methods, including the photolysis method, photo fermentation method (PF), dark fermentation method (DF), double light fermentation method and microbial electrolysis method (MEC). Hydrogen produced from the use of biological methods is called bio-hydrogen [7].

Microbial electrolysis cell (MEC) is a biological method used to produce bio-hydrogen. Bio-hydrogen is produced in the MEC using multiple substrates, such as acetate, glycerol, glucose and various environmental wastes such as domestic wastewater and industrial wastewater. Bacteria and an applied voltage are used in MEC to decompose organic matter and produce electrons, protons and carbon dioxide. Bio-hydrogen in the MEC is produced by combining electrons with protons in a cathode chamber [8].

MEC was discovered and named for the first time as "electrochemical assisted hydrogen generation", then "bio-catalyzed electrolysis", "photoelectric generation", and finally researchers agreed in their studies on the name "Microbial Electrolysis Cells'' (MEC) [9]. MECs have many advantages that make them the best biological methods used for bio-hydrogen production. Firstly, environmental waste and renewable resources can be used as substrates for hydrogen production instead of fossil fuels. Secondly, bacteria can be used to transform various organic materials such as acetate, glucose, glycerol, cellulose, acetic acid, domestic wastewater and industrial wastewater to bio-hydrogen in the MEC. Thirdly, the productive efficiency of bio-hydrogen production using MEC is from 80–100%, compared to that of the electrolysis of water, which is about 65%, and that of dark fermentation, which is about 33%. In addition, MECs need an electric power supply of about 0.2–0.8 V, which is smaller than the voltage required for the electrolysis of conventional water (1.8–2 V) [10].

Nanomaterials have been used in many different engineering fields with the aim of finding a solution to technical problems and finding inexpensive solutions to improve and raise production and technical efficiency, due to the distinctive and different properties of nanomaterials that are not found in their bulk counterparts. The main objective of using nanomaterials in MEC is to improve the properties and performance of the basic components of MEC, which are the electrodes (anode and cathode), proton exchange membranes (PEM) and hydrogen production catalysts, or to replace the high-cost components with inexpensive components commensurate with the economics of hydrogen production in this way. Nanomaterials, especially when used to produce bio-hydrogen using MEC, are distinguished by their high electrical conductivity, high interaction surface area, high durability of materials, high catalytic ability to produce bio-hydrogen in MEC, biocompatibility with microorganisms and non-toxicity [11][12].

2. Microbial Electrolysis Cells (MECs)

MECs are one of the bioreactors used to produce bio-hydrogen. Hydrogen fuel is a renewable energy source. Hydrogen is produced in the MEC using organic waste. Bacteria decompose and oxidize the organic matter in the substrates and produce electrons, protons and carbon dioxide. Electrons are released by bacteria in the anode chamber and then collect at the anode electrode. The electrons are then transferred from the anode electrode to the cathode electrode via external electrical circuits [13]. Protons are transferred from the anode chamber to the cathode chamber through the PEM in a double-chamber MEC and directly through solution in a single-chamber MEC. The protons combine with the electrons in the cathode chamber to produce hydrogen gas. However, the production of bio-hydrogen at the cathode is an endothermic reaction and therefore requires an applied voltage (0.2–0.8 V) [14]. The applied voltage (power supply) for bio-hydrogen production at the MEC (0.2–0.9 V) is much lower than for water electrolysis (1.23–1.8 V). The role of microbes is at play in producing electrons during the oxidation and decomposition of organic matter in substrates [15]. The basic reactions of bio-hydrogen production in MEC can be illustrated using acetate as a substrate for hydrogen production.

The following equations show the substrate decomposition reactions in the anode chamber and the hydrogen production reactions in the cathode chamber:

$$\text{Anode: } C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$$

$$\text{Cathode: } 8H^+ + 8e^- \rightarrow 4H_2$$

The rate of bio-hydrogen production in the MEC is influenced by several main factors that affect the efficiency of the performance of the MEC, which are the shape and type of the MEC (double-chamber or single-chamber), the type of materials from which the electrodes are made (anode and cathode) and the raw materials or substrate used to produce bio hydrogen [16][17].

2.1. MEC Types and Shapes

Bio-hydrogen production rates are directly affected by MEC formation. MEC is divided into two main configurations: (1) double chamber MEC and (2) single chamber MEC. They have almost the same work principle. There is one difference between them, which is that there is only a PEM in the formation of the double-chambered MEC. There are many shapes of MEC, such as H-shaped, cubic, tubular or cassette-like [18].

2.1.1. Double-Chamber MEC

Double-chamber MEC is characterized by the presence of a PEM that separates the anode and cathode chambers. Double-chamber MEC takes an H-shape. The PEM is located in a channel connecting the anode and the cathode chambers. PEM is an important component of MEC because it prevents hydrogen diffusion from the cathode chamber to the anode chamber. Examples of membranes that have been used in MEC double chambers are proton exchange membranes (PEM), cation exchange membranes (CEM), and charge mosaic membranes (CMM). Bio-hydrogen is formed in the cathode chamber as a result of electron transfer from the anode to the cathode through the external circuit connecting the anode to the cathode, while H^+ ions move across the membrane towards the cathode chamber [17][19].

Bio-hydrogen is produced in MEC under anaerobic conditions for both the anode and the cathode chambers. The anode chamber contains bacteria that decompose the organic matter of the materials used to produce bio-hydrogen, and electrons are released. In the cathode chamber, the electrons combine with H^+ ions forming hydrogen gas, which is collected in a tube above the cathode chamber [20].

The double-chamber MEC is characterized by its high efficiency in hydrogen production because it works on the migration of hydrogen ions from the anode chamber to the cathode chamber through the PEM and prevents the diffusion of oxygen hydrogen. A disadvantage of the double-chamber MEC is the higher manufacturing cost of expensive PEMs and the increased internal resistance [21].

2.1.2. Single-Chamber MEC

The single-chamber MEC system was proposed and designed in 2008. Single-chamber MEC does not require an ion exchange membrane and both anode and cathode electrodes are located in one anaerobic chamber. Single-chamber MEC is not very different from double-chamber MEC in bio-hydrogen production reactions. In a single-chamber MEC, the organic matter in the substrate used to produce hydrogen is degraded by bacteria, releasing electrons, hydrogen ions and carbon dioxide. Electrons transfer from the anode to the cathode through the external circuit. The protons move directly to the cathode and combine with the electrons to produce bio-hydrogen [22].

The single-chamber MEC has the advantage of suitable design for practical applications due to its low manufacturing cost. The disadvantage of a single-chamber MEC is the easy diffusion of hydrogen to the anode, which leads to methane production and significant energy loss due to the discontinuation of anode reactions and methanogenic bacteria consuming the resulting hydrogen [23].

3. Application of Nanomaterials in MECs

The use of nanomaterials for bio-hydrogen production in MEC has been applied in many different ways, including thermal annealing, electrochemical anodizing, and electrodeposition. For example, in the thermal annealing method, the metal is exposed to a higher temperature than the normal temperature and then recrystallized. Fan et al. (2011) collected Au and Pd elements and exposed them to different temperatures ranging from 600 to 800 °C in order to convert them into nanomaterials [24]. In another study by Kim et al. (2018), the electrochemical oxidation method of Ti flakes with ethylene glycol electrolyte was used to obtain an external photo-anode of TiO_2 array of nanotubes. The aim of the study was to modify the surface of the electrode to improve the reaction efficiency [25]. Several studies have shown that the electrodeposition method increases the Bio-HPR in the MEC [26].

Jayabalan et al. (2020, 2021) used a chemical deposition method to manufacture cathode catalysts from nickel molybdate ($NiMoO_4$), nickel oxide (NiO) and cobalt oxide (Co_3O_4) nanoparticles [27][28]. Raney et al. (2021) also synthesized cathode catalysts from magnetite (Fe_3O_4) nanoparticles using a chemical deposition method [29].

The use of nanomaterials in MEC has been applied in different ways, including: (1) the addition of nanomaterials to the anode electrodes to improve the oxidation reactions of organic matter and electron transfer reactions; (2) using nanomaterials as cathode catalysts for the cathode electrode to improve bio-hydrogen production rates; and (3) the addition of nanomaterials to PEM to improve the membrane efficiency in bio-hydrogen production rates through the speed of proton exchange and resistance to biofouling of the membranes [30].

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