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Overview of Biomass Conversion to Electricity and Hydrogen and Recent Developments in Low-Temperature Electrochemical Approaches

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A B S T R A C T

Biomass is plant or animal material that stores both chemical and solar energies, and that is widely used for heat production and various industrial processes. Biomass contains a large amount of the element hydrogen, so it is an excellent source for hydrogen production. Therefore, biomass is a sustainable source for electricity or hydrogen production. Although biomass power plants and reforming plants have been commercialized, it remains a difficult challenge to develop more effective and economic technologies to further improve the conversion efficiency and reduce the environmental impacts in the conversion process. The use of biomass-based flow fuel cell technology to directly convert biomass to electricity and the use of electrolysis technology to convert biomass into hydrogen at a low temperature are two new research areas that have recently attracted interest. This paper first briefly introduces traditional technologies related to the conversion of biomass to electricity and hydrogen, and then reviews the new developments in flow biomass fuel cells (FBFCs) and biomass electrolysis for hydrogen production (BEHP) in detail. Further challenges in these areas are discussed.

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1. Common technologies of biomass to electricity

1.1. Steam turbine generator

Electricity is a vital form of energy. Turbine-based generators from combustion of fossil oil and coal are still the main source of energy for the production of electricity. These generators account for about 63.5% of the electricity used in the United States today, of which 27.4% is produced from coal and 35.1% is produced from natural gas (according to data from 2018) [1]. However, the use of fossil fuels in conventional power plants has been continuously decreasing in recent years due to increased challenges in pollutant and greenhouse gas emission norms. On the global scale, viable and eco-friendly pathways for the alternate production of electricity from renewable resources have been growing. Fast-growing areas of electricity generation using sustainable resources include nuclear, wind, hydro, and solar energy. Biomass such as wood, grass, agricultural residues, animal and human waste, algae, and

so forth—is a naturally occurring renewable resource that is sustainably produced in bulk quantities in many areas of the world. It has been reported that the United States produces about 1.3 billion dry tonnes of forest and agricultural waste or unused materials every year, which is comparable to an electricity production of 2×10^{12} kW·h (considering a thermal energy conversion efficiency to electricity of approximately 30%), or around 50% of the electricity generation for the entire United States in 2014. Although the generation of electricity from biomass gasification or combustion combined with steam or gas turbines has been practiced commercially, the total electric power generated from biomass was actually only 1.4% of the total electricity supply of the United States in 2018 [1]. The use of biomass in electric power generation can be accomplished by different methods. Direct combustion of biomass material is the most common method. Gasification, pyrolysis, and anaerobic digestion are also adopted to produce biomass-based fuels that can be used as an energy source for turbines. In gasification, the biomass is heated with less oxygen than required for thorough combustion in order to produce a synthesis gas. In pyrolysis, rapid heating of biomass without oxygen produces bio oil. Anaerobic digestion of biomass produces a renewable natural gas upon the decomposition of organic matter by bacteria in the absence

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of oxygen. One of the key challenges of using biomass as a source for electricity production is due to the low energy density of biomass, which results in difficulties in collection and transportation. Most biomass power plants are actually operated at a loss. It is well known that common biomass power plants are based on gasification or pyrolysis followed by combustion, which provides energy to turbines and generators. Because so many operation units are installed in a single power plant, biomass power plants are huge. As a result, considerable amounts of biomass are required to sustain the day-to-day operation of biomass power plants. Clearly, this is not economically profitable. One possible solution is to reduce the size and capital costs of power plants to make biomass transportation feasible and profitable. The other disadvantages of current biomass-to-electricity production include fuel procurement, delivery, storage, and cost. Standard biomass-electricity-only systems have an efficiency of approximately only 20%. In the United States, the usual method of producing heat from biomass involves the combustion of biomass. Small-scale electric plants using biomass can be installed for a cost of 3000–4000 USD per kilowatt, and the charge for energy is maintained at 0.80–0.15 USD per kilowatt hour [2].

1.2. The high-temperature biomass fuel cell

Biomass fuel cells present an interesting alternative to the use of combustion heat and turbine generator technologies. Compared with heat engines that use fossil fuels, which convert thermal energy into mechanical work and then to electricity, the fuel cell is more attractive due to its advantageous properties and its ability to align with the emerging environmental norms. A fuel cell is a device that converts the chemical energy of a fuel into electrical energy, and produces heat, water, and carbon dioxide (CO_2) as byproducts [3]. The indirect biomass fuel cell (IDBFC) and the direct biomass fuel cell (DBFC) are two types of fuel cells that are driven by lignocellulosic biomass. In recent year's development, the IDBFC is able to convert biomass into utilizable sugars (e.g., xylose and glucose), syngas, biogas, and biochar, which can be used as fuels for the further generation of electricity in fuel cells [4]. The IDBFC includes high-temperature fuel cells operated at greater than 600 °C, such as the solid-oxide fuel cell (SOFC) and the direct carbon fuel cell (DCFC); it also includes microbial fuel cells (MFCs) operated at low temperatures, which are more efficient [5–7].

The SOFC is a capable technology for the generation of electricity with favorable thermodynamic efficiency, as compared with conventional technologies. The SOFC is preferred over other fuel cells because it operates at a high temperature to better utilize heat and has a high tolerance to fuel gas constituents and contamination [8]. Different types of fuels (i.e., hydrocarbons) can be utilized in these fuel cells due to their diverse nature. Potential fuels for SOFC are natural gas, biogas, syngas derived from biomass/coal gasification, and hydrogen (H_2). Conventionally, methanol has been the favorable fuel for most previous SOFC integrated systems. Recently, lignin was used as a fuel in SOFCs and MFCs to produce electrical power. In SOFCs, lignin is initially converted to syngas by gasification and then further converted into electricity [9,10].

In an SOFC, fuel oxidation takes place in the anode chamber. Oxygen ionizes at the cathode and moves through the electrolyte to the anode. In the anode compartment, the fuel gas disperses in anode over the interface of the electrolyte and catalyzes the electrochemical reaction. The electrons present in the fuel molecules move through an external circuit, thereby producing electricity. The cathode accepts electrons through the external circuit to reduce oxygen molecules to form oxide ions at its interface with the solid electrolyte. The oxide ions pass through the solid electrolyte to the anode and form H_2O or CO_2 based on the type of fuel [11]. The nature of the electrolyte in a fuel cell determines the operating temperature. In an SOFC, the operating temperature is very high and is similar to the temperature of the gasification process. The SOFC's high operating temperature makes it possible to combine the technology of biomass gasification with the SOFC, resulting in greater efficiency in electricity generation. For several years, focus has been placed on optimizing the conditions of biomass gasification and removing the difficulties that arise in this process, which include the formation of impurities such as ash, tar, and other alkaline complexes [12]. Steam gasification of biomass coupled with the SOFC yields maximum electrical efficiency as compared with oxygen and air gasification [13]. The overall energy conversion process has several performance criteria, including thermodynamic conversion efficiency, capital and operating costs, and environment impact. Further developments are required to overcome the challenges of material selection based on material properties that can be clearly identified to maximize electricity generation [14–17].

DBFC technology has recently been reported in the literature. This technology produces electricity directly from biomass without pre-converting or processing biomass to obtain liquid or gaseous fuels. In DBFCs, different forms of lignocellulosic biomass such as wood, grass, agricultural residue, algae, and so forth can be converted into electricity. However, the presently available DBFC only utilizes refined biomass, such as starch or cellulose. In order to develop advanced power-generation technology for the direct conversion of biomass into electricity using fuel cells, many lacunas and challenges remain to be addressed [18–20].

1.3. The microbial fuel cell

To overcome the difficulties arising in conventional technologies, the MFC has been garnering the attention of the scientific community in the last decade. This type of fuel cell produces electricity from organic biomass. MFCs are heterogeneous reactors that convert organic compounds to electricity using microorganisms at a low temperature. In lignocellulosic biomass-based MFC, the biomass is first transformed into fuels in the form of glucose, xylose, acetate, and so forth for further redox reactions by microorganisms [18]. An MFC comprises two electrolytic compartments with two electrodes separated by a semipermeable membrane (proton-exchange membrane (PEM) or anion-exchange membrane (AEM)) and an external electrical circuit. Microorganisms oxidize the fuel in the anodic chamber and typically produce CO_2, protons, and electrons. The electrons are captured by the anode and passed to the cathode through the external electrical circuit, while the protons at the anode move through the membrane to the cathode, forming water with oxygen and electrons. The difference between the potential of the cathode and the anode generates electrical power [18]. The microorganisms function as a "bridge" that links the fuels' chemical energy with electric energy. In the process of oxidizing the fuels into metabolic products, the microorganisms in an MFC gain energy by transferring the electrons produced during the process [21]. However, further findings are needed in order to understand the complete anodic electron-transfer mechanism [22].

In a MFC, the substrate/fuel types play a major role in the overall efficiency of the process. Substrates directly used in an MFC include pure cellulose and cellulosic sources, such as corn stover and marine algae after pretreatment [23]. However, the complex structure of lignocelluloses makes the process less efficient, resulting in low power output. For better MFC efficiency, pre-hydrolysis of the biomass is necessary, in which the biomass is converted to soluble sugars, degraded phenolic compounds, acetic acid, furfural, and 5-hydroymethylfurfural (HMF). Pre-hydrolysis yields different kinds of fermentable substrates from biomass. Glucose is one of the important fuels derived from biomass, and is obtained from

cellulose hydrolysis. Similarly, hydrolysis of hemicelluloses results in different pentose and hexose sugars, uranic acids, and acetic acid. These organic compounds show excellent efficiencies as carbon sources in MFCs to generate electricity. In contrast to sugars from cellulose and hemicelluloses, phenolics from lignin depolymerization inhibit the microorganisms [18].

Although the concept of the MFC was developed a long time ago, industrial application of the MFC has been unachievable. Limiting factors include the high costs of the electrode materials and PEMs, low energy yields, and limited durability [24,25]. Overall MFC performance relies on several factors, including: biofouling (i.e., reduction of surface area due to blockage of the electrode surface), deactivation of the catalyst (if present), and excess biofilm growth. Excess biofilm growth results from the formation of non-conductive polymeric debris or dead cells, which leads to a reduction in current generation [26,27]. Other factors responsible for low MFC efficiency include electro-catalyst deactivation, and the permeation of fuels from the anode compartment to the cathode compartment and vice versa, which leads to biofilm inactivation and mixed potentials (i.e., the system short circuits) [28,29].

1.4. The concept of the low-temperature biomass flow fuel cell

Fuel cells produce electricity from chemical energy with a much higher conversion efficiency than traditional thermal conversion based on a turbine-driven generator. However, the use of biomass as a fuel in fuel cells is not yet possible due to the lack of an effective catalyst. Low-temperature fuel cells for the conversion of biomass to electricity that operate at temperatures below 100 °C have been developed recently, with the MFC as the main example. At low temperatures, the practical applications of the MFC are limited due to its low efficiency and power density. Here, we focus on recent advancements in electricity production using fuel cells at low temperatures. The principles, advantages, and disadvantages of flow biomass fuel cells (FBFCs) will also be discussed.

Great progress has been achieved in fuel cell research using small-molecule organic matter, such as methanol, formic acid, and so forth. However, the development of low-temperature fuel cells using polymeric organic matter met a bottleneck until the novel concept of the liquid flow fuel cell (LFFC) was first reported by Liu et al. at the Georgia Institute of Technology [30,31]. The solar-induced hybrid fuel cell reported by Liu et al. [30] for the first time utilizes $H_3PMo_{12}O_{40}$ as the photocatalyst to oxidize different types of biomass at the anode, as shown in Fig. 1. At the cathode, oxygen (O_2) accepts the final electron under the Pt/C catalyst sys-

tem. The solar-induced hybrid biomass fuel cell has a power density of 0.72 mW·cm^{-2} when using cellulose as the fuel, which is 100 times greater than that of an MFC using a cellulosic fuel. Liu et al. [31] also built a noble-metal-free fuel cell using a polyoxometalate (POM) catalyst based on their previous research in order to increase the efficiency of biomass flow fuel cells. In this upgraded LFFC, POMs—instead of a noble metal catalyst—are introduced to the cathode to transfer electrons to oxygen, as shown in Fig. 2. Based on this new design, the oxidation of biomass and the reduction of oxygen were accomplished using by two different POM catalysts: $H_3PW_{11}MoO_{40}$ solution in the anode and $H_{12}P_3Mo_{18}V_7O_{85}$ solution in the cathode. This resulted in a high power density output even when using untreated raw biomass as a fuel. When the cell was directly fueled by starch at 80 °C and was run constantly for more than 10 h, a stabilized power density of 30 mW·cm^{-2} was achieved, with a discharge current density of 160 mA·cm^{-2}. In a direct biomass LFFC, various types of biomass including cellulose, starch, wood powders, and polyols can be used as fuels. Due to the use of liquid catalysts to replace noble metal catalysts, the fuel cell has very strong tolerance of organic and inorganic impurities, as well as a lower cost.

The mechanism of the biomass-based LFFC can be summarized as follows: The two liquid electrolyte solutions have different redox potentials. The anode tank is filled with POM-I electrolyte solution ($H_3PW_{11}MoO_{40}$ solution) with the biomass. Here in the anode electrolyte solution, solar or thermal biomass oxidation takes place. The reduced anode electrolyte solution with a lower potential cyclically flows through the anode by a pump. At the cathode, a reaction takes place between the POM-II electrolyte solution ($H_{12}P_3Mo_{18}V_7O_{85}$ solution), which has a higher potential with the oxygen. In the anode tank, the biomass is partially oxidized to small molecules or is completely decomposed into CO_2 at elevated temperatures or under photo irradiation by sunlight. In an oxidized state, the selected electrolyte usually contains a multivalent metal in its highest valence state. First, the higher valence state cation (M^{i+}) is reduced to its lower valence state (M^{j+}) by capturing electrons from the organics. The biomass with its long polymeric chains acts as an electron and proton donor, and is converted into small degraded chemicals and CO_2. This process is described in Eq. (1):

$$Biomass + nM^{i+} \xrightarrow{Heating/sunlight} Degraded\ chemicals + nM^{j+} \\ + nH^+ + xCO_2 \tag{1}$$
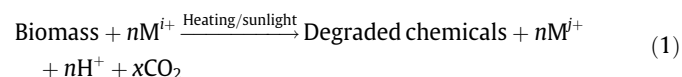
Next, the reduced M^{j+} releases electrons to the anode and gain its initial valence state according to Eq. (2):
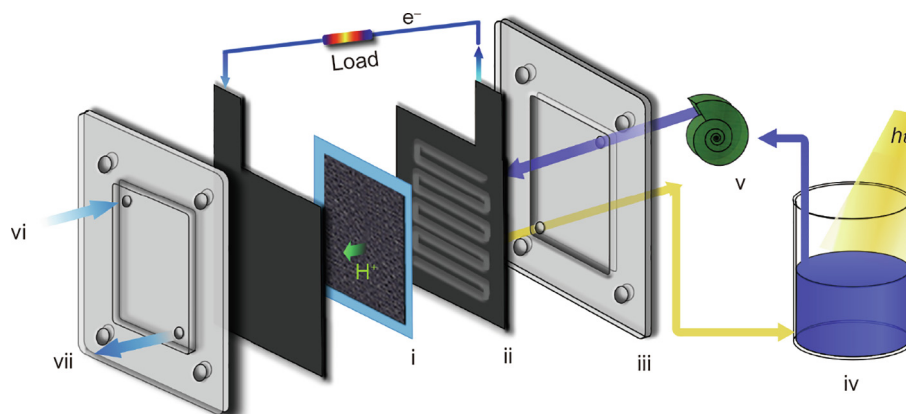
Fig. 1. Structure of the solar-induced hybrid fuel cell. (i) Membrane-electrode assembly (MEA; Nafion 117 polymer-exchange membrane, anode made of carbon cloth, and cathode loaded with Pt/C catalyst); (ii) graphite bipolar plate; (iii) acrylic plastic end plate; (iv) transparent glass vessel with starch-$H_3PMo_{12}O_{40}$ (PMo$_{12}$) solution; (v) pump; (vi) oxygen inlet; (vii) water and oxygen outlet. $h\upsilon$ represents photo irradiation by sunlight.
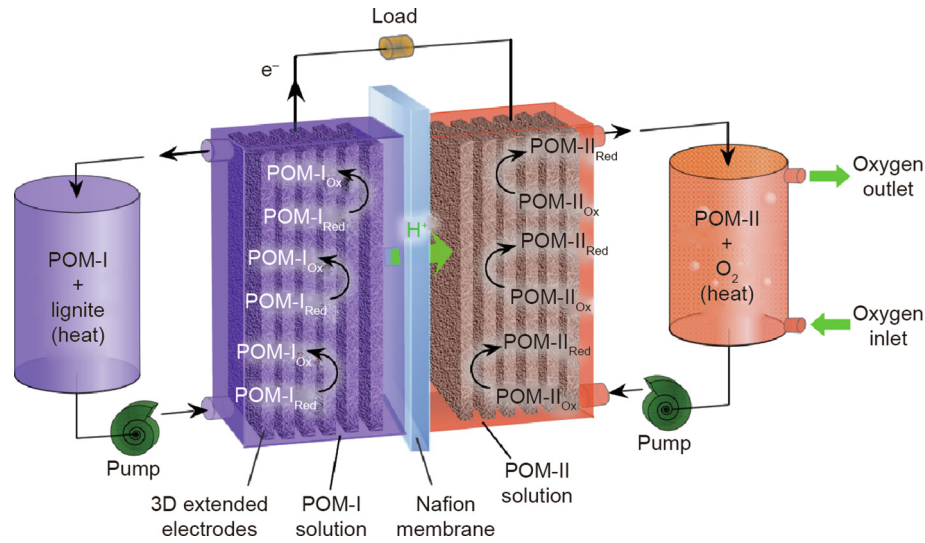
Fig. 2. Structure of the liquid catalyst fuel cell. Subscript Ox and Red refers to oxidized form and reduced form, respectively. Reproduced from Ref. [31] with permission of John Wiley & Sons, Inc., ©2014.

$$M^{j+} \rightarrow M^{i+} + e^- \quad (2)$$

In the second redox tank, a different active electrolyte (which may be the same as or different from the catalyst used in the first tank) is reduced by accepting the electrons on the cathode of the flow fuel cell, which is installed between two tanks. The reduced electrolyte in the second tank will then be regenerated by the oxidation of oxygen, as described by Eq. (3):

$$(1/2)O_2 + 2e^- + 2H^+ \rightarrow H_2O \quad (3)$$

The overall reaction can be described by the following equation:

$$\text{Biomass} + nO_2 \rightarrow \text{Degraded chemicals} + CO_2 + nH_2O \quad (4)$$
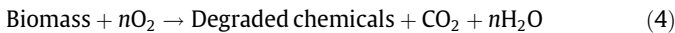
The core of this system is the catalytically and redox active electrolyte, which transforms the biomass chemical energy into the difference in the electrochemical potentials of the solution. In contrast to direct fuel cells, the catalysts in an LFFC are not immobilized on electrodes; instead, they are in the solutions. No activation overpotential area or concentration over the potential area was observed in a typical current–voltage characteristic (I–V) curve of the LFFC, as shown in Fig. 3.
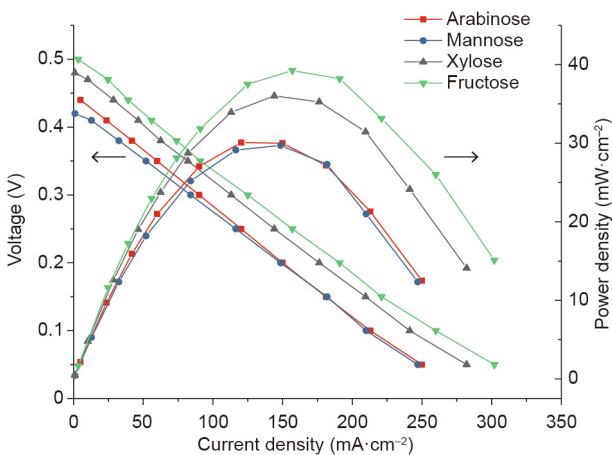

Fig. 3. Voltage and power densities of different types of biomass used as fuel for the POM-mediated novel LFFC at 80 °C. Reproduced from Ref. [32] with permission of John Wiley & Sons, Inc., ©2014.

2. Common technologies for biomass-to-hydrogen conversion

2.1. Gasification and reforming

Biomass is considered to be one of the most abundant and renewable resources for hydrogen production. Biomass gasification is a favorable process for hydrogen generation in which dried feedstock undergoes pyrolysis followed by the combustion of intermediates and, finally, gasification of the subsequent compounds. This process operates in a reactor known as a gasifier at higher temperatures (700–1400 °C) in the presence of a medium such as air, O_2, steam (H_2O), or CO_2 [33,34]. Unlike combustion, ideal pyrolysis and gasification processes convert the chemical energy of organic materials into a mixture of gases, organic liquid molecules, and solid chars [35]. These methods are considered to be favorable future methods for the production of hydrogen gas or syngas from biomass in order to meet environmental requirements and achieve cost effectiveness. The gasification of biomass in steam, air, or oxygen medium results in a mixture of gases with different concentrations of hydrogen. Among these methods, steam gasification yields a higher hydrogen concentration with a better heating value of the product gas than air or oxygen gasification [36]. Under such thermal environments, biomass undergoes partial oxidation, steam-reforming reactions, or both, producing syngas and solid char. The char formed is further fractionated by reduction to produce hydrogen gas, oxides of carbon, and methane. The conversion process can be expressed as follows:

$$C_xH_yO_z + H_2O + O_2 \rightarrow H_2 + CO_x + CH_4 + HCs + Char \quad (5)$$
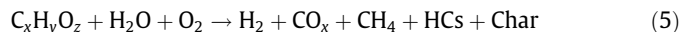
In the first step of gasification, thermal degradation of biomass volatilizes the lighter components and produces raw syngas. The downward reactions and the performance of the process depend on the gasification medium and the process parameters. Biomass gasification products primarily contain gases; therefore, this method is more suitable than pyrolysis for the production of hydrogen gas. Effective biomass gasification relies on the exploration of low-cost feedstocks, intensification in method efficiencies, lower installation and operative overheads, and lower environmental impacts.

The formation of tar during biomass gasification is a major concern, as it causes operational issues and degrades the quality of the gas produced. Tar is a thick and viscous liquid that is a mixture of

higher-end aromatic hydrocarbons and heavy metals. Thermal cracking, steam reforming, and partial oxidation methods are generally adopted to reduce tar and maintain the quality of the final product. Several experimental processes have recently been described for the production of hydrogen using different types of biomass, diverse experimental setups, and different catalytic paths in order to develop better technologies [37,38]. The use of catalysts in hydrogen production is important in order to intensify productivity and increase the yield by promoting the cracking of C–O and C–C bonds. Different catalysts, including alkaline metals (mostly Na and K), zeolites, dolomite (CaMg(CO$_3$)$_2$), and limestone, in addition to nickel (Ni)-, zinc (Zn)-, platinum (Pt)-, and ruthenium (Ru)-based catalysts, have been successfully used to produce hydrogen through the electrolysis of water and the gasification and pyrolysis of biomass. Alkali metal catalysts such as potassium (K), sodium (Na), and calcium (Ca) increase the yield of hydrogen in the biomass gasification process. Moreover, alkali metal catalysts and Ni-based catalysts increase the conversion of carbon and prevent tar formation by promoting reformation reactions during the gasification of biomass [39–41]. Alkaline metal oxides, dolomite, and Ni-based catalysts have a favorable effect on gasification due to their ability to promote reformation reactions [42]. The addition of dolomite to biomass gasification reduces tars, while zeolites are effective in enhancing char gasification. Ni-based catalysts have been found to be best for reforming reactions in industrial applications of biomass gasification [43]. Future developments are required to design more effective green catalysts to increase hydrogen production while minimizing char and tar residues [44].

2.2. Microbial approaches

Thermochemical methods of H$_2$ production from biomass generally have a costly design setup and require higher temperature and pressure. Microbial approaches for H$_2$ production have several key advantages over thermochemical methods in terms of these issues. The main advantages of microbial approaches are that they produce no greenhouse gas emissions and may be able to reuse biomass waste as feedstocks. Therefore, it is worth developing bio-hydrogen fuel technology as a future outlook [45].

The biological conversion of biomass to H$_2$ can be accomplished by photosynthesis and fermentation. Fermentation can be subdivided into dark- and photo-fermentation, while photosynthesis includes direct and indirect photolysis [46]. In fermentative hydrogen production, the organic substrate is converted into bio-hydrogen by fermentation using multi-enzyme systems of varied groups of bacteria. Under anaerobic conditions, the degradation of organic matter by hydrogenase enzymes and protons produces hydrogen, which acts as an electron sink to eliminate excess electrons. This process is known as dark fermentation for the production of hydrogen; in contrast, the photo-fermentative process requires light, and is thus similar to hydrogen production by photosynthesis. Dark fermentation produces H$_2$ at 30–80 °C from biomass that is rich in carbohydrates. Similarly, the photo-fermentative method can produce hydrogen at standard temperature and pressure in aqueous environments [47].

Biological H$_2$ production processes are basically dependent on hydrogen-producing enzymes. The three types of enzymes that catalyze H$_2$-producing reactions are nitrogenase, iron (Fe)-hydrogenase, and NiFe hydrogenase. The hydrogenase enzymes consist of metal clusters as active centers, which synthesize hydrogen by a complex processes of biosynthetic pathways [48]. Anaerobic bacteria that have been used in dark fermentation for the production of hydrogen include the Clostridia species, such as *Clostridium* (*C.*) *lentocellum*, *C. butyricum*, *C. thermosuccinogenes*, *C. pastuerianum*, *C. paraputrificum*, *C. saccharoperbutylacetonicum*, and *C. thermolacticum* [49]. Various strains of photosynthetic bacteria have been used for photo-fermentative hydrogen production, such as *Rhodopseudomonas palustris*, *Rhodobacter sulfidophilus*, *Rhodobacter capsulitis*, and *Rhodobacter sphaeroides* RV [50]. Strict control of the anaerobic environment, pH, and temperature is necessary for the effective production of bio-hydrogen. Integrated fermentative bio-hydrogen production has been practiced using various stages of the photo- and dark-fermentative processes. The integration of dark-fermented effluent with photo-fermentative hydrogen production produces hydrogen with an improved H$_2$ yield. The production of H$_2$ using an integrated process is catalyzed by nitrogenases and hydrogenase enzymes [51,52].

To date, extensive developments in fermentative H$_2$ production have been achieved in several directions, such as the use of various types of biomass as a substrate, the immobilization of enzymes on different supports, bioreactor designs, the search for novel microbial strains, and the control of inhibitor production during fermentation. However, versatile and stable bio-hydrogen production techniques for practical applications have not yet been satisfactorily accomplished [53,54].
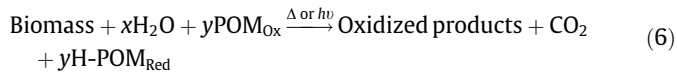
2.3. The low-temperature electrochemical approach to biomass-to-hydrogen production

Producing hydrogen from water electrolysis is a well-known industrial method. The advantage of the electrolytic method is that it can produce high-purity hydrogen without carbon monoxide (CO) or CO$_2$ contaminants. However, in most cases, water electrolysis requires around 4.5–5 kW·h per cubic meter H$_2$ consumption to split water [55,56]. The high cost of generating hydrogen from water electrolysis limits the application of this method on a large scale. Using biomass as a sacrifice to substitute for part of the water in order to function as a hydrogen and electron donor in electrolysis can significantly decrease the electric energy consumption and thus the processing cost. Due to the polymeric state and complexity of biomass, high-temperature (~500 °C) biomass gasification combined with electrolysis and the intermediate-temperature (~150 °C) electrolysis of biomass in H$_3$PO$_4$ medium for hydrogen production have been developed [57–59]. However, high-temperature electrolysis presents the issue of obvious heat loss and catalyst deactivation because of biomass coking. Therefore, the low-temperature (< 100 °C) electrochemical approach of converting biomass into hydrogen is promising in terms of energy efficiency for sustainable hydrogen production. Nevertheless, great challenges still remain to be addressed.
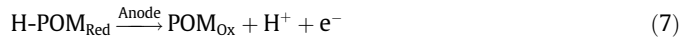
The proton-exchange membrane electrolysis cell (PEMEC) and the microbial electrolysis cell (MEC) are usually used to produce H$_2$ from biomass at a low temperature [60]. Although some improvements have been carried out recently [61–63], several issues still hinder the performance of these technologies [62]. First, neither of these two approaches can treat raw biomass directly; instead, lignocellulosic molecules must first be converted into chemicals with small molecular weights, such as methanol, ethanol, and ethylene glycol. This is due to the poor performance of noble metal catalysts in the conversion reactions of lignocellulosic molecules at a low temperature. In addition, noble metal catalysts are highly sensitive to contaminants, including the sulfur components, carbon monoxide, and so forth that are generated in the electrolysis process, resulting in catalyst deterioration [64,65]. Moreover, NaOH is consumed in the PEMEC process since it reacts with the organic acids formed by the oxidation reaction in electrolysis, which increases the cost. Finally, the H$_2$ generation rate is very low, which further limits the industrial application of this method.

Recently, Liu et al. [66] reported a novel approach to generate hydrogen from native lignocellulosic biomass through a chemical-electrolysis conversion (CEC) process with POMs as both catalyst and proton carrier. With this technology, native biomass

such as cellulose, lignin, and even wood and grass powders can be reacted and decomposed directly and effectively at relatively low temperature by POM solutions. Hydrogen gas is then formed by electrolysis with low electric energy consumption. This process is shown in Fig. 4 [66]. A PEM is sandwiched between a non-pretreated graphite-felt anode and a carbon cathode coated with Pt black. Biomass and phosphomolybdic acid ($H_3PMo_{12}O_{40}$) solution are mixed and stored in the anode tank of the electrolysis cell. Under heating (Δ) or sunlight irradiation ($h\upsilon$), $H_3PMo_{12}O_{40}$ can oxidize biomass and be converted into its reduced form ($H\text{-}POM_{Red}$) by receiving electrons, resulting in a color change from yellow to dark blue, as shown in Figs. 4(b) and (c):

$$\text{Biomass} + x\text{H}_2\text{O} + y\text{POM}_{Ox} \xrightarrow{\Delta \text{ or } h\upsilon} \text{Oxidized products} + \text{CO}_2 \\ + y\text{H-POM}_{Red} \tag{6}$$

An external electric potential between the anode and cathode is applied to carry out the electrolysis, during which the reduced POM loses its electrons and is gradually re-oxidized to its initial state. The color of the solution turns back to yellow on the anode side and hydrogen bubbles are released from the cathode electrode:

$$\text{H-POM}_{Red} \xrightarrow{\text{Anode}} \text{POM}_{Ox} + \text{H}^+ + \text{e}^- \tag{7}$$

$$\text{H}^+ + \text{e}^- \xrightarrow{\text{Cathode}} 1/2\text{H}_2 \tag{8}$$

The full color conversion of the reduced POM solution from blue to yellow in the anode tank indicates a completed CEC cycle, as shown in Fig. 4(d). The energy consumed in this cycle can be as low as 0.69 kW·h per normal cubic meter (Nm^3) H_2 (where Nm^3 is normal cubic meter) when the current density is 0.2 A·cm^{-2}, which is only 16.7% of the energy consumption of water electrolysis. Furthermore, unlike the traditional electrolysis of alcohols, a noble metal catalyst is not required at the anode, which significantly decreases the processing cost.

Li et al. [67] recently reported a self-powered biomass-to-hydrogen process that combines the technologies of a fuel cell and an electrolysis cell. In this process, electrical energy generated from a biomass-based fuel cell is utilized in an integrated electrolysis cell for hydrogen evolution, thereby avoiding the application of external power that is required in traditional electrolysis. Here, the catalyst is POM, which rapidly oxidizes glucose to CO_2 and oxidized products, and finally self-regenerates in the course of
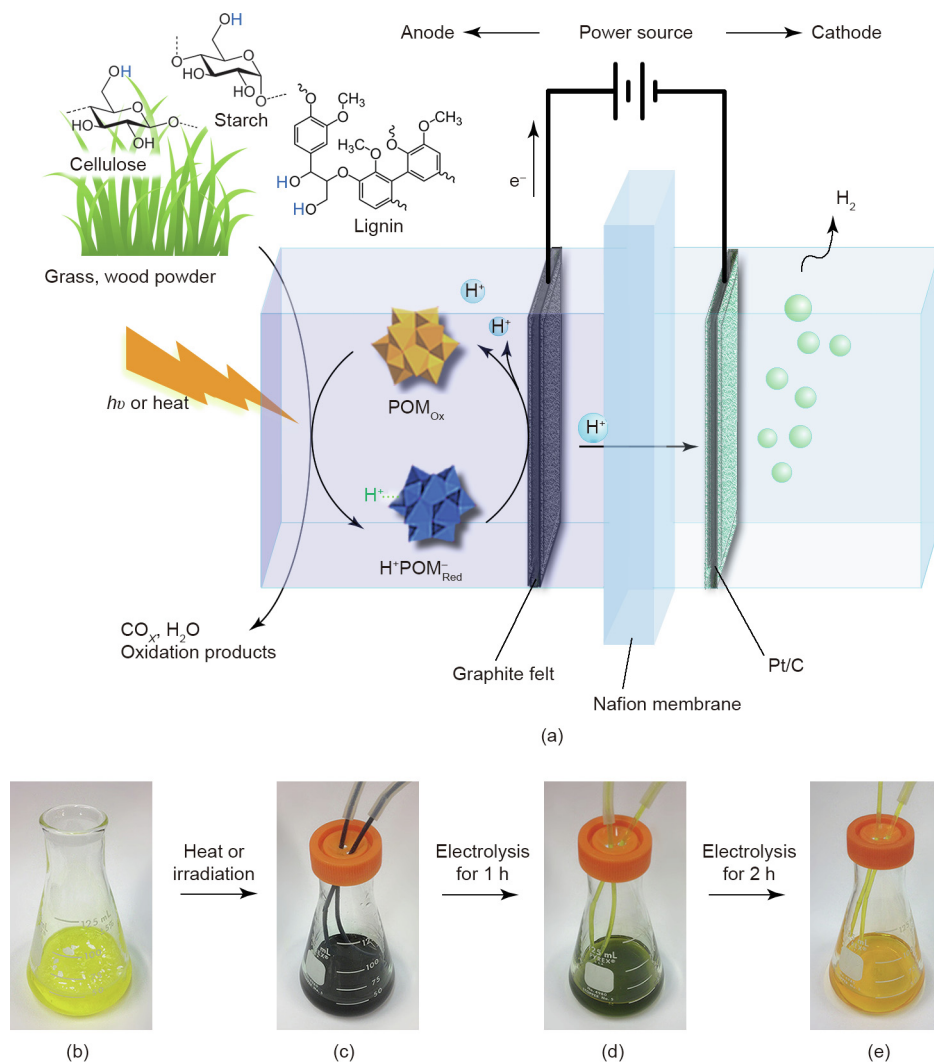
Fig. 4. (a) A schematic illustration of the CEC process. The anode side is a simple graphite-felt electrode with a biomass-POM solution; the cathode side is a gas-diffusion electrode loaded with Pt black catalyst, with H_3PO_4 as the electrolyte. (b) Solution of POM-biomass before heating or light irradiation. (c) Color change of the biomass-POM mixture after heating. (d) Biomass-POM solution after (d) 1 h and (e) 2 h electrolysis for hydrogen production.

the process. A unique "sharedcell" is designed in this process, in which the Fe^{3+}/Fe^{2+} redox couple reacts and then acts as the fuel cell cathode and electrolyzer anode, respectively, as shown in Fig. 5 [67]. As a result, this self-powered process effectively converts biomass to hydrogen at 85 °C with a production rate of 0.0432 mL H_2 per cubic meter per minute.

3. Biomass flow fuel cells

3.1. Based on polyoxometalate

The catalyst plays a critical role in the low-temperature biomass-to-electricity conversion process. The candidate catalyst should possess a strong oxidizing property that can oxidize various organic substrates and cleave C–C bonds at low temperatures. POMs, which have a polyatomic structure consisting of three or more transition metal oxyanions linked together by shared oxygen atoms, exhibit good physical and chemical properties due to their special structure. POMs are considered to be promising catalysts for LFFC due to their good catalytic performance in organic hydrolysis and oxidation processes [68,69].

Several research works have been done on this kind of POM-biomass flow fuel cell. Different types of POMs, including Keggin-type and non-Keggin-type, are employed for both biomass oxidation and oxygen reduction. Liu et al. [70] investigated the use of combustible agricultural waste (wheat straw and wine residues) as fuel with $H_3PMo_{12}O_{40}$; the corresponding power density reached 111 mW·cm^{-2}. Zhao and Zhu [10] used $H_3PW_{12}O_{40}$, $H_4PVW_{11}O_{40}$, $H_4PMo_{11}VO_{40}$, $K_5PV_2Mo_{10}O_{40}$, and $H_3PMo_{12}O_{40}$ to oxidize lignosulfonate at 95–100 °C, and reported high lignin conversion and electricity yield with a current density in the range of 0.3–45 mW·cm^{-2}, depending on the POMs.

The open-circuit voltage is a key factor in determining LFFC performance. Obviously, a greater potential difference between the POMs of the anode and cathode can improve the performance of the fuel cell. For the anode, POMs with strong oxidation ability are preferred, while the reduced electrode potential should be as low as possible. For the cathode, POMs should have a high electric potential in order to ensure a large circle voltage difference with the anode, but should also be easily oxidized by oxygen for the purpose of full regeneration.

Lewis acids such as Sn^{4+}, Fe^{3+}, VO^{2+}, and Cu^{2+} have been introduced as co-catalysts with POM. Liu et al. [30] added Fe^{3+} and Cu^{2+} as promoters to POM in a cellulose-fueled fuel cell, and found that the power density increased from 0.45 to 0.72 mW·cm^{-2}. It has been reported that metal ions function as Lewis acids are more effective than Brønsted acids in breaking the glycosidic bonds of cellulose [71,72]. Xu et al. [73] investigated the co-catalytic effect of $FeCl_3$ and POMs. The addition of Fe^{3+} ions improved the whole performance significantly, since Fe^{3+} accelerated the hydrolysis of the biomass and enhanced electron transfer.

3.2. Based on other redox ion pairs

Besides POMs, other ion redox couples have been developed to serve in DBFCs. Gong et al. [74] reported a biomass flow fuel cell mediated with a Fe^{3+}/Fe^{2+} redox couple at the anodic half-cell and a VO_2/VO^{2+} redox couple at the cathode. Biomass was oxidized by Fe^{3+} at the anode side. The reduced Fe^{2+} released electrons and was converted back to Fe^{3+} at the anode. Biomass oxidation with an Fe^{3+}/Fe^{2+} ion pair was studied [75]. $FeCl_3$ acts as both the oxidant and the catalyst to oxidize the biomass, and is reduced to Fe^{2+}. Using glucose as a model biomass compound, the reaction in the anolyte can be written as follows:

$$C_6H_{12}O_6 + Fe^{3+} \rightarrow Degraded\ chemicals + Fe^{2+} \tag{9}$$
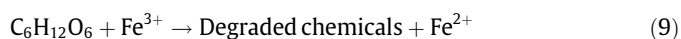
Fe^{2+} then releases the electrons to the anode, as shown in Eq. (10):

$$Fe^{2+} = Fe^{3+} + e^- \tag{10}$$

As a result, Fe^{3+} is regenerated.

The electrons pass through the external circuit and are captured by VO_2^+ at the cathode to form VO^{2+}. The maximum current density was found to reach 100 mA·cm^{-2}, and the energy conversion efficiency was as high as 76.5%.

Li and Song [76] demonstrated a straw-based fuel cell that included methyl violet as an electron carrier, nickel foam as an anode, and Pt/C as a cathode. They reported that when 65 wt% $ZnCl_2$ solvent was used, this fuel cell showed excellent performance. Furthermore, the addition of methyl viologen to the system greatly improved the performance, with a maximum power output of 0.3 mW·cm^{-2}. Hibino et al. [77] developed a direct cellulose-based fuel cell using a $Sn_{0.9}In_{0.1}P_2O_7$-polytetrafluoroethylene (PTFE) composite electrolyte with a Pt/C anode and cathode. The cellulosic material was set at the anode after pretreatment with 85% H_3PO_4. The maximum power density recorded at 250 °C was 32.7 mW·cm^{-2} for cellulose. In this electrochemical process, H_2O acted as a major reactant, and the discharge product was CO_2. Ding et al. [78] reported another process using $H_3[PMo_{12}O_{40}]$ and $FeCl_3$ as the electron mediators and proton carriers to realize an integration of wheat straw pretreatment for ethanol production and the conversion of biomass into electricity.

3.3. A fundamental study using model biomass compounds

The chemical structure of the biomass used is closely related to the performance of LFFCs. A wide variety of biomass feedstocks are used as fuel in LFFCs, as shown in Table 1 [10,30,31,70,73–80]. It
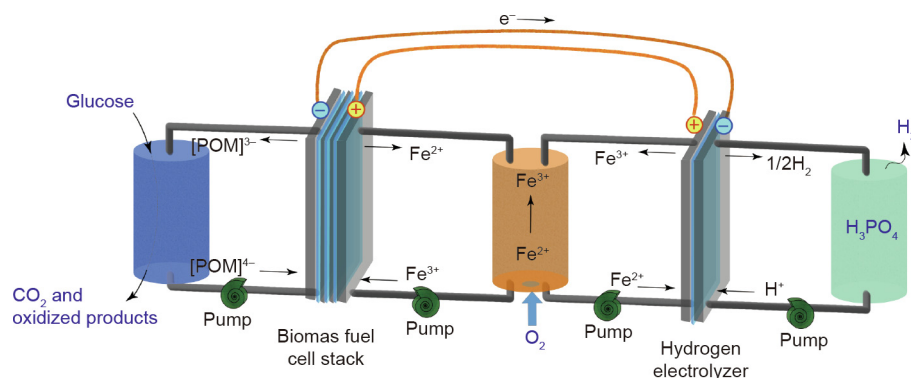
Fig. 5. A schematic illustration of the integration of reactors (stored glucose-POM solution and H_3PO_4 solution on the far left and right side, respectively), LFFCs (a biomass fuel cell stack), PEMEC (the hydrogen electrolyzer), and a "sharedcell" (the tank storing Fe^{2+}/Fe^{3+} solution in the middle).

was found that the use of polymeric biomass, such as cellulose, starch, and hemicellulose, can result in higher power density than the use of small-molecule alcohols and acids. In fact, most natural polymeric biomass comprises polyhydroxyl compounds, and hydroxyl groups play an important role in the photo-redox reaction of POM and alcohols [30,81,82]. To understand the effect of hydroxyl groups on photo-redox activity, Wu et al. [83] investigated the performance of an LFFC fueled with a series of model biomass compounds with hydroxyl numbers from one to six. The power output of an LFFC is strongly affected by the content of the hydroxyl groups in the biomass molecular structure. The experimental results demonstrated that the presence of more hydroxyl groups accelerated the photo-electrochemical reaction between POM and the biomass, resulting in a greater degree of POM reduction, and thereby leading to a higher power output. Therefore, biomass compounds with a polyhydroxyl molecular structure, such as starch, hemicellulose, cellulose, and even switchgrass and wood powders, are ideal fuels for LFFCs. Liu et al. [32] studied the degradation mechanism of biomass by POM using glucose as a model biomass. In fact, solar radiation on the POM degradation of biomass sugar is the result of two effects: heating and photocatalysis. Reduced POMs can increase the temperature of the reaction system because of strong visible and near-infrared light adsorption, and thus significantly enhance the thermal oxidation of glucose. The efficiency of an LFFC operating with glucose as a fuel through photocatalytic oxidation and working at a voltage of 0.4 V is 36.7%, which means that the consumption of 1 kg glucose will generate 1.43 kW·h of electricity.

3.4. Flow fuel cells using non-biomass-based materials: Sludge and coal

In addition to conventional biomass, unconventional biomass fuels are also used as fuel for LFFCs, including sludge, low-quality coal and grease, and more. Sewage sludge is a hazardous waste produced in the domestic and industrial wastewater treatment process, which contains proteins, lipids, humic acids, polysaccharides, and hazardous organic and inorganic pollutants. Sludge treatment, which is an expensive practice, accounts for over 50% of the total cost of water treatment [84]. At present, there are different technical routes to dispose of sewage sludge, in the attempt to achieve energy reuse while reducing environmental impact. Sludge can be converted into biogas, liquid fuels, or gaseous fuels in the anaerobic digestion process. The two main technical challenges are slow methanogenesis and an inhibition issue caused by accumulated volatile fatty acids in the anaerobic digestion of sludge [85,86]. Sludge can also be burned directly or co-combusted with coal in coal-fired power plants, resulting in the potential issues of fly ash and toxic chemical emission [87,88]. Electricity generation from sewage sludge through MFCs is an important route for municipal domestic waste treatment and renewable energy development [89–91]. However, no practical applications have been reported so far due to the lower power density of MFCs. Zhang et al. [79] investigated the performance of sludge-based LFFCs. Most of the organic matter in the sludge could be degraded after reacting for 24 h at 100 °C. The power density of the cell could reach as high as 50 mW·cm^{-2}, which is 100 times

Table 1
Comparison of different biomass-fueled LFFCs.

Fuels	Anode electrolyte	Cathode or cathode electrolyte	Oxidants	Biomass reaction conditions	Discharging conditions	Power density (mW·cm^{-2})	Ref.
Cellulose	PMo$_{12}$ with Cu^{2+}–Fe^{3+}	Pt/C	O$_2$	Solar-induced	Room temperature	0.65	[30]
Lignin	PMo$_{12}$	Pt/C	O$_2$	Solar-induced	Room temperature	0.55	
Switchgrass	PMo$_{12}$	Pt/C	O$_2$	Solar-induced	Room temperature	0.62	
Poplar powder	PMo$_{12}$	Pt/C	O$_2$	Solar-induced	Room temperature	0.65	
Starch	PMo$_{12}$	Pt/C	O$_2$	Solar-induced	Room temperature	0.32	
Starch	PMo$_{12}$	Pt/C	O$_2$	Heated to 95 °C	Room temperature	0.45	
Starch	H$_3$PW$_{11}$MoO$_{40}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	O$_2$	100 °C for 4 h	80 °C	34	[31]
Cellulose	H$_3$PW$_{11}$MoO$_{40}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	O$_2$	100 °C for 4 h	80 °C	22	
Switchgrass	H$_3$PW$_{11}$MoO$_{40}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	O$_2$	100 °C for 4 h	80 °C	43	
Bush Allamanda	H$_3$PW$_{11}$MoO$_{40}$	H$_{12}$P$_3$Mo$_{18}$V7O$_{85}$	O$_2$	100 °C for 4 h	80 °C	51	
Glucose	H$_3$PW$_{11}$MoO$_{40}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	O$_2$	100 °C for 90 min	80 °C	45	
Glucose	H$_3$PW$_{11}$MoO$_{40}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	O$_2$	Solar-induced for 8 h	80 °C	9	
Lignin	PMo$_{12}$	Pt/C	O$_2$	Heating	80 °C	0.96	[10]
Lignin	PMo$_{12}$	PMo$_{12}$	O$_2$	Heating	80 °C	5.0	
Lignin	PMo$_{12}$	Fe^{3+}/Fe^{2+}	Air	Heating	80 °C	10.8	
Lignin	H$_3$PMo$_{11}$VO$_{40}$	Fe^{3+}/Fe^{2+}	Air	Heating	80 °C	12.4	
Wheat straw	PMo$_{12}$	Fe^{3+}/Fe^{2+}	Air	Heating 95 °C for 45 min	70 °C	11	[78]
Glucose	Fe^{3+}/Fe^{2+} and PW$_{12}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	Air	Heating 95 °C for 2 h	Room temperature	2.59	[73]
Starch	Fe^{3+}/Fe^{2+} and PW$_{12}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	Air	Heating 95 °C for 2 h	Room temperature	1.57	
Cellulose	Fe^{3+}/Fe^{2+} and PW$_{12}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	Air	Heating 95 °C for 2 h	Room temperature	0.72	
Wheat straw	Fe^{3+}/Fe^{2+}	VO$_2^+$/VO^{2+}–HNO$_3$-O$_2$	O$_2$	Heating 100 °C for 20 h	80 °C	100	[74]
Glucose	Fe^{3+}/Fe^{2+}	VO$_2^+$/VO^{2+}–HNO$_3$-O$_2$	O$_2$	Heating 100 °C for 4 h	80 °C	125.7	[75]
Bagasse	Fe^{3+}/Fe^{2+}	VO$_2^+$/VO^{2+}–HNO$_3$-O$_2$	O$_2$	Heating 100 °C for 5 h	Room temperature	45.1	
Orange peel	Fe^{3+}/Fe^{2+}	VO$_2^+$/VO^{2+}–HNO$_3$-O$_2$	O$_2$	Heating 100 °C for 5 h	Room temperature	36.9	
Corn stalks	Fe^{3+}/Fe^{2+}	VO$_2^+$/VO^{2+}–HNO$_3$-O$_2$	O$_2$	Heating 100 °C for 5 h	Room temperature	30.8	
Lignin	Nickel foam Methyl violet/ZnCl$_2$	Pt/C	Air	Shaking and ultrasound	Room temperature	0.3	[76]
Sawdust 85% H$_3$PO$_4$	Pt/C	Pt/C	Air	Heating	250 °C	21	[77]
Pulp 85% H$_3$PO$_4$	Pt/C	Pt/C	Air	Heating	250 °C	26	
Sewage sludge	PMo$_{12}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	O$_2$	Heating 150 °C for 2 h	80 °C	50	[79]
Wheat straw	PMo$_{12}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	O$_2$	Heating 150 °C for 2 h	80 °C	80	[70]
Wine residue	PMo$_{12}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	O$_2$	Heating 150 °C for 2 h	80 °C	97	
Coal	PMo$_{12}$	H$_{12}$P$_3$Mo$_{18}$V$_7$O$_{85}$	O$_2$	Heating 200 °C for 5 h	80 °C	120	[80]

higher than that of sludge-based MFCs reported in the literature. Thus, the LFFC could be a promising method for sludge utilization. The accumulation of soluble inorganics in sludge-based LFFCs requires further study.

Low-rank coal (such as lignite) usually has a low combustion heat and low commercial value. Technology for the effective utilization of low-rank coals with significantly reduced pollution is highly desired. Weibel et al. [92] tried to convert coal into electrical energy using a redox electric pair (Fe^{3+}/Fe^{2+}) as the electrolyte. However, their results were not encouraging because of the very low conversion efficiency. Nunoura et al. [93] developed a high-temperature (operating at 250 °C) aqueous alkaline biocarbon-based fuel cell. However, the performance was not promising and the apparatus was rather complicated. Zhang et al. [80] used an LFFC to generate electricity from low-rank coals without complicated pretreatment. The coal particles could be gradually oxidized by POM at 100–200 °C. The power density of the lignite-based fuel cell was as high as 120 mW·cm^{-2}, which is the highest power density that has been obtained through LFFC technology thus far. The experimental results showed that some of the chemical substances in low-quality coal can be converted into electricity; however, it was difficult to achieve energy conversion for a large number of aromatic groups through low-temperature LFFC.

Besides sludge and low-rank coal, other types of organic matter (e.g., vegetable oils and animal fats) have been used to test the degradation effects of LFFCs [94]. The results show that the current LFFC treatment of oils and fats is basically impossible. The degradation treatment effect of oil and fat substances is limited. There are two possible reasons: First, the molecular bonds of the oils and fats are relatively strong, and it is difficult to cleave the bonds. Second, oil is not very soluble in water, which increases the difficulty of contact between the catalyst and organic matter in the fuel cells of a water system. Liu et al. [95] developed a system combining anaerobic fermentation and an LFFC in which the fermentation products were used as fuel in the second step. This combined food waste system showed a relatively high electrical efficiency of 34% and a short treatment time. Chemicals such as waste and lignite are more complex than polyhydroxy polymer biomass. More efficient pretreatment methods are required for waste and lignite LFFCs, while new catalysts could also help to improve fuel cell performance.

3.5. Advantages and challenges

The biomass-based LFFC is a novel strategy for renewable energy development that shows very promising results. Compared with conventional fuel cell technologies, the direct biomass LFFC has many advantages.

First of all, with this groundbreaking fuel cell technology, biomass such as grass, wood, algae, combustible agricultural waste, and even sewage sludge can be directly converted into electricity at a low temperature. Second, biomass-based LFFCs use liquid POM as a biomass degradation catalyst instead of noble-metal-based electrocatalysts. Biomass functions as a fuel and does not require pre-purification or treatment, since the POM catalyst is extremely stable and has a low sensitivity to most organic and inorganic contaminants. Third, a high power output has been demonstrated by LFFCs. Last but not least, the LFFC is an environmentally friendly technology. Theoretically, only CO_2 and H_2O are produced through biomass oxidation. It is expected that biomass-based LFFCs can be a low-cost and suitable alternative for both small power units and large power plants for sustainable energy production from biomass.

Challenges still remain for LFFCs in terms of both scientific research and commercialization:

(1) High-efficiency catalysts are needed. Candidate catalysts should possess strong oxidizing ability that can oxidize various organic substrates and cleave C–C bonds at low temperatures.

(2) The performance of the LFFC still needs improvement. Experimental results have demonstrated that it is difficult to convert 100% of biomass into CO_2 and that the oxidation reaction rate is relatively slow. The kinetics of the electrode reactions must be investigated in order to maximize the power output.

(3) The separation of inorganic and organic residues from the catalyst is also a challenge for the commercial use of LFFCs.

(4) The lifetime of an LFFC should be considered. POM corrodes graphite electrode plates and membranes and decreases the lifetime of stacks.

(5) The structural configuration of the cells and stacks must be well designed in order to reduce internal resistance.

One of the challenges of the biomass-based LFFC is to completely oxidize biomass in order to improve the total energy performance and minimize waste residuals. Biomass has a very complicated chemistry, as it may contain lignin, cellulose, hemicellulose, fatty resins, proteins, and many other organics. As a result, it is usually very difficult to completely oxidize raw biomass in solution at a low temperature. However, a high degree of the oxidation will not only improve the biomass usage but also significantly reduce the cost of waste residual treatment. There are several methods to improve the oxidation of biomass in the anode cell. First, a higher temperature can significantly increase the oxidation of biomass in anode solution. It has been reported that lignin can be completely oxidized by POM at a high temperature [96]. The use of chemicals with a high electric potential, such as vanadium-containing POMs, is another option. A more effective option is to use a co-catalyst such as Pt/C particles to significantly improve the degree of reaction, which will improve the total conversion of biomass to CO_2. The use of solar energy or light instead of heat should also improve the oxidation reaction rate and degree. All of these options present interesting topics for future study.

4. Low-temperature electrolysis of biomass to hydrogen

As discussed earlier, biomass is an excellent source for hydrogen production. Traditional methods for biomass conversion include biomass reforming and microbial approaches. The former produces syngas but not pure hydrogen at high temperatures, while the latter is a very slow process at a low temperature. Traditional water electrolysis can produce pure hydrogen but carries a high energy cost. The recently reported biomass electrolysis method with redox pair mediation can significantly reduce the energy input for hydrogen production. In this section, we review new developments and future challenges in biomass electrolysis for hydrogen production.

4.1. Lignocellulose and lignin as resources

Lignin, which accounts for 15%–30% by weight of lignocellulosic biomass, is the second most abundant biomass component in nature, after cellulose [97]. Unlike carbohydrates, lignins are chemically cross-linked phenolic biopolymers. Because of its rigid structure, it is difficult to utilize lignin in most biorefinery processes, and it is generally considered to be a waste in, for example, the paper-making industry. The full utilization of lignin would not only help in renewable energy development but could also eliminate the environmental issues associated with the lignin waste. Lignin valorization by the depolymerization of lignin into value-added chemicals or fuels has attracted great interest for the biorefinery industry. Lignin has a high hydrogen content and is a renewable source for the sustainable production of hydrogen, which is

one of the cleanest fuels. However, the current technologies, which include the chemical degradation of lignin and the microbial fermentation method, face challenges in producing hydrogen.

Recently, a novel PEM electrolysis approach using biomass as a sacrificial agent was reported [66]. In this electrolysis, hydrogen gas was produced with a low electrical energy consumption because biomass supplied part of the energy for water splitting. The traditional noble metal catalyst at the anode was replaced with aqueous POM solution for biomass degradation and oxidation. The consumed electric energy was reported to be only about 16.7% of the energy consumption of water electrolysis. These exciting results provide a way to electrochemically degrade lignocellulosic biomass and produce hydrogen at the same time (Fig. 6 [31]). In addition to using POM as the charge mediator, Fe^{3+} ion has been used as a biomass degradation catalyst and charge carrier in biomass fuel cells and electrolysis [98,99]. The standard electrode potential of the Fe^{3+}/Fe^{2+} ion pair is 0.77 V versus the normal hydrogen electrode (NHE). It was reported that the mechanism involved phenolic units of lignin being oxidized and degraded through Fe^{3+} oxidation [100,101]. At the same time, the reduced Fe^{2+} ion that formed was regenerated to Fe^{3+} during the PEM electrolysis or fuel cell discharging.

The charge carrier, POM or the Fe^{3+}/Fe^{2+} ion pair is very important in lignin degradation and in electron transfer from the biomass to the anode electrode. The critical role of PMo_{12} and Fe^{3+}/Fe^{2+} ion pairs in this process has been verified by control experiments using phosphoric acid (H_3PO_4) as an electrolyte to substitute for PMo_{12} or Fe^{3+} on the anode side [98]. The results showed that no significant electrolytic current was detected in the control experiments, even when a high potential of 1.2 V was applied. These results indicate a large over potential for the direct anodic oxidation of lignin without Fe^{3+}/Fe^{2+} or a POM catalyst. Therefore,

lignocellulosic biomass alone cannot be directly applied as feedstock to generate hydrogen in a PEM electrolyzer; rather, it should be accompanied by a charge carrier.

Research on $FeCl_3$-catalyzed biomass electrolysis reported electrolytic current densities of 0.34–0.37 $A \cdot cm^{-2}$ for an applied cell potential of 1.2 V. When using three different types of lignin—Kraft lignin (KL), alkaline lignin (AL), and sulfonated lignin (SL)—as the feedstock at the anode, the electrolytic I–V curves were almost the same, suggesting that the electrolysis performances were not significantly affected by the source of lignin. In fact, the important factor controlling the electrolysis performance was found to be the concentration of Fe^{2+}, which formed in the biomass oxidation with Fe^{3+}. This is because Fe^{2+} ions, rather than lignin molecules, are actually electrically oxidized at the anode. As a similar case, the degree of reduction of PMo_{12} in the PMo_{12}-mediated system is the key factor determining the electrolytic performance because the PMo_{12} anion transfers electrons from the lignin to the electrode.

The oxidation of lignin is a critical issue in low-temperature electrolytic hydrogen evolution. The catalyst, PMo_{12} or Fe^{2+}, is recycled by the anode under the electric field to gradually depolymerize and oxidize the lignin. Research showed that after three oxidation cycles with a total reaction time of 18 h at 100 °C, 17.8% and 22.4% of the lignin was dissolved in the electrolyte solution by PMo_{12} and $FeCl_3$, respectively [98]. Lignin degradation can be improved by increasing the oxidation cycles and the reaction temperature. It was reported that 14.0% of solid lignin was degraded into small molecules at a reaction temperature of 100 °C for 18 h. However, the lignin degradation increased significantly to 26.6% if the oxidation was conducted at 190 °C for 1 h. The production of CO_2 at the anode side was verified by gas emission analysis, indicating lignin oxidation. This was probably caused
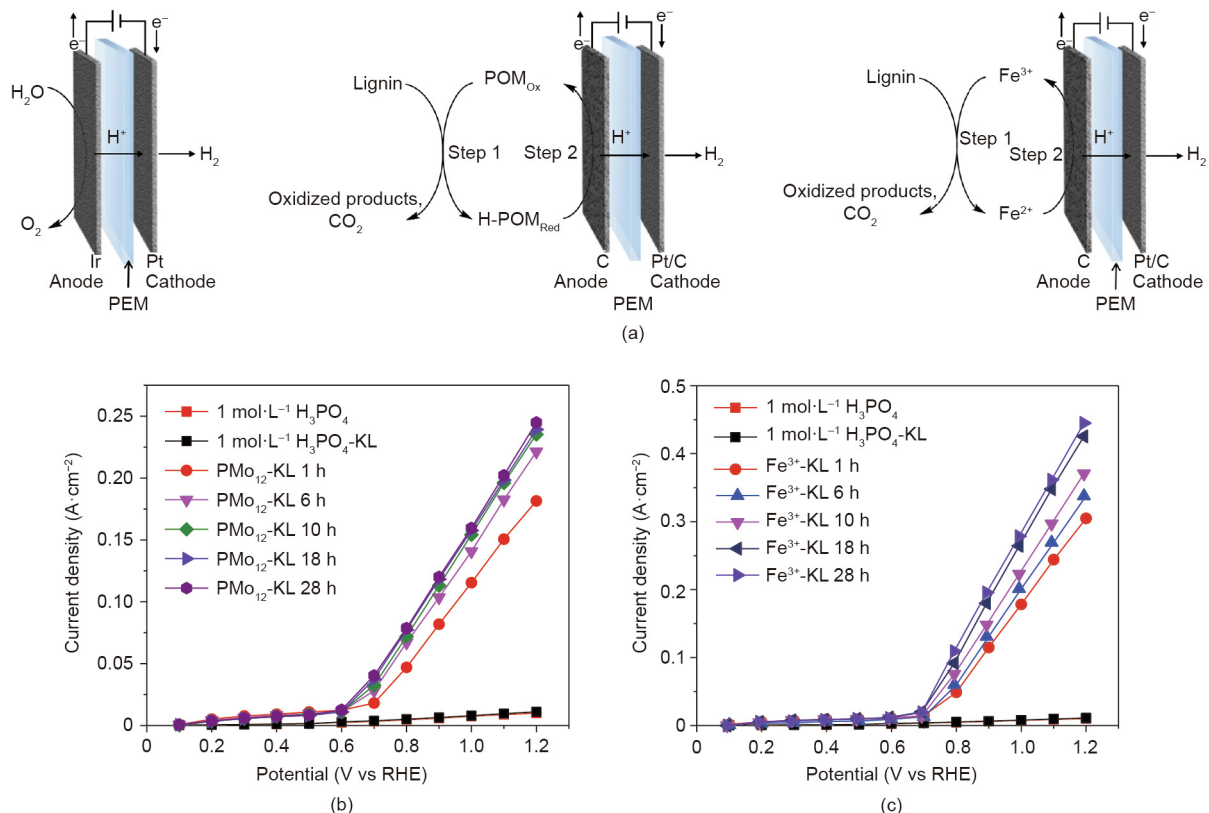

Fig. 6. (a) POM-mediated (middle) and Fe^{3+}-mediated (right) PEM electrochemical reforming for hydrogen production from lignin. (b, c) Polarization curves using Fe^{3+}, PMo_{12}, and H_3PO_4 as the electrolyte and Kraft lignin (KL) as the feedstock. RHE: reversible hydrogen electrode.

by cleavage of the methoxy group ($-O-CH_3$), C–O bond, and even some C–C bonds in the biomass during the oxidation. Total organic carbon (TOC) analysis of the aqueous phase after lignin oxidation showed that the electrolyte solution contained $0.77-0.90$ g·L^{-1} organic materials, indicating dissolution of the lignin. The organic compounds in the aqueous phase after lignin oxidation were analyzed by gas chromatography–mass spectrometry (GC–MS). Vanillin, phenol, 1,2-dimethoxybenzene, guaiacol, 3,4-dimethoxybenzaldhyde, and some complex compounds were found in the PMo_{12}-reacted electrolyte solution. When $FeCl_3$ was used as a catalyst, the products that were identified in the solution included phthalic anhydride, 4-methylbenzaldehyde, vanillin, benzoic acid, and other chlorine-substituted chemicals. Further heteronuclear single quantum coherence nuclear magnetic resonance (HSQC NMR) analysis showed that after POM oxidation, only a very small amount of β–β′ linkage (in the structure of resinol) was detected, indicating that most of the ether linkages (β–5 and β–O–4) in the lignin molecules were broken. For the $FeCl_3$-oxidized lignin solution, no ether linkages were observed at all. Therefore, the ether bonds in the lignin structure can be effectively broken by both PMo_{12} and $FeCl_3$ catalyst.

4.2. Advantages and challenges

This novel POM- or $FeCl_3$-mediated PEM electrolyzer has several advantages compared with traditional electrolysis:

(1) The lignin feedstock can be directly oxidized to small molecules by POM or $FeCl_3$ under mild conditions (< 100 °C) at the anode side. Although microbes can consume biomass-derived substrate in a microbial electrolyzer to produce hydrogen, they are vulnerable to reaction conditions (e.g., pH, temperature, and concentration). In addition, the level of oxidation of biomass by microbes is too low to achieve large-scale hydrogen production. A POM or $FeCl_3$ mediator can oxidize biomass with a quick reaction rate and under broader reaction conditions, such as a temperature of 50–120 °C and a pH of 0.5–6.

(2) The noble metal catalyst (e.g., Pt or Ir) in traditional designs can be replaced by POM and $FeCl_3$ at the anode electrode. The traditional noble metal catalyst used in a PEM electrolyzer can oxidize small molecular alcohols at a low temperature for hydrogen evolution, but it is inactive for polymeric biomass. Even for water electrolysis, the anode should be coated with a noble metal catalyst (e.g., Ir) to decrease the overpotential for oxygen evolution. For an electrolyte-pair-mediated PEM electrolyzer, the mediator (POM or $FeCl_3$) functions to deliver electrons to the anode electrode for hydrogen evolution. Therefore, a noble metal catalyst is not necessary at the anode side, which can significantly reduce the cost of the electrolysis device.

(3) Energy consumption is greatly reduced because the anodic oxygen evolution reaction is replaced by biomass oxidation with POM or Fe^{3+} ions. Table 2 shows a comparison of different electrolyzers for hydrogen evolution from biomass, and shows the

energy-saving advantages of electrolyte-pair-mediated PEM electrolysis for hydrogen evolution [66,99].

(4) POM and $FeCl_3$ are chemically and thermally stable, and are completely regenerated during the electrolysis. The POM catalyst is tolerant to most organic and inorganic contaminants because POMs are robust and self-healing under severe conditions [102]. Borrás-Almenar et al. [103] indicated that for a reaction mixture containing the substrate and a POM catalyst, hundreds of thousands of turnovers are possible. $FeCl_3$ is also very stable in acidic reaction solutions. Both POM and $FeCl_3$ are recycled in the biomass oxidation and anodic regeneration process.

(5) Both POM and $FeCl_3$ are low-cost chemicals. Compared with the noble metals that are widely used in traditional electrolysis and fuel cells, or microbes with a limited lifetime, POM and $FeCl_3$ are low cost and recyclable for electrolytic hydrogen production.

5. Concluding remarks

Low-temperature electrochemical conversion of biomass to electricity and hydrogen is a promising route for sustainable energy development. This review compared common technologies and low-temperature concepts for biomass-to-electricity and biomass-to-hydrogen conversion, and introduced the recent reported electrolyte-pair-mediated (e.g., POM and $FeCl_3$) PEM electrolyzer or fuel cell. The energy and environmental benefits of the electrolyte-pair-mediated approach are obvious; however, challenges still need to be overcome in future research.

(1) Developing more powerful catalysts that can completely convert biomass to CO_2 is one of the challenges that remains. Biomass functions as a fuel in electricity or hydrogen production. High biomass utilization is critical for energy conversion in the low-temperature electrochemical process. However, in current research on the use of POM and $FeCl_3$ as catalysts, it was reported to be difficult to completely oxidize the biomass (i.e., 100% oxidation) to CO_2. Even though biomass can theoretically be oxidized to CO_2, this process requires a long time. To remedy this issue, one approach involves developing new catalysts that can powerfully oxidize biomass and function as charge carriers to transfer electrons simultaneously. A broader scale of catalyst candidate, including metal ions, metal complexes, organic mediators, and enzymes, could be researched in future development. Alternatively, co-catalysts could be developed for the current POM or Fe^{3+} system. Research has verified that POM- and Fe^{3+}-mediated systems work very well for biomass conversion. If a co-catalyst is developed that can synergetically catalyze biomass oxidation, the biomass energy utilization can be further improved.

(2) The power density of the biomass-based fuel cell has a large margin for improvement. The current POM- or Fe^{3+}-mediated biomass flow fuel cell can achieve a similar power output as the alcohol fuel cell. Performance improvement could be enhanced in many aspects, such as fuel cell design (including heat and water management), parameter optimization (including flow rate,

Table 2
A comparison of different electrolyzers for hydrogen evolution from biomass.

Electrolyzer	Fuel	Electrolyte	Temperature (°C)	Current density (mA·cm^{-2})	Applied potential (V)	Power consumption (kW·h per Nm^3 H$_2$)
Photo-electrochemical cell	Alcohols and saccharides	KOH or H_2SO_4	Ambient	0.05–2.55	0–1.23	—
PEM alcohol electrolyzer	Methanol, ethanol, glycerol	Water, KOH, or H_2SO_4	60–80 °C	100	0.45–0.8	1.08–1.91
				200	0.50–1.2	1.20–2.87
				500	0.60–2.0	1.44–4.79
POM-mediated cell	Alcohols, starch, cellulose, lignin, wood powder	Aqueous POM	Ambient to 80 °C	100	0.15–0.7	0.36–1.67
				200	0.28–0.8	0.67–1.91
				500	0.60–1.2	1.44–2.87
Fe^{3+}-mediated cell	Glucose, lignin, raw biomass	$FeCl_3$ solution	Ambient to 100 °C	100	0.70–0.8	1.75–1.84
				200	0.88–1.0	2.28–2.32

temperature, and electrolyte concentration), and process integration with biorefining or biomass upgrading.

(3) The fundamentals of the electrolyte-pair-mediated process in the biomass flow fuel cell or hydrogen evolution have not yet been fully understood, including the POM charge and discharge characteristics, electrode overpotentials, and regeneration of POMs in both the cathode and anode cells. It is clear that this knowledge is critically important to further improve the performance of the fuel cell. To further study the electrochemical process, *in situ* electrochemical technology, such as *in situ* electrochemical impedance spectroscopy (EIS) and *in situ* overpotential measurement, could be introduced into the discharge process. The difficulty of *in situ* measurement is that the configuration of the fuel cell or electrolyzer device must be modified to install a reference electrode for *in situ* monitoring.

(4) Another issue is chemical separation. Raw biomass contains a small amount of inorganic salts (0.5%–10%), and these inorganic salts will accumulate in the electrolyte solution as biomass oxidation proceeds. Although the salts will not affect the mediator POM and Fe^{3+} performance during discharge, they will gradually accumulate and must be removed from the reaction system.

Compliance with ethics guidelines

Wei Liu, Congmin Liu, Parikshit Gogo, and Yulin Deng declare that they have no conflict of interest or financial conflicts to disclose.

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